



International Congress on Organic Chemistry

dedicated to the 150-th anniversary of
the Butlerov's Theory of Chemical Structure of
Organic Compounds

Book of Abstracts

Ministry of Education and Science of the Russian Federation
Russian Academy of Sciences (RAS)
Government of the Republic of Tatarstan
Kazan (Volga region) Federal University
Kazan Scientific Center of RAS
A.E. Arbuzov Institute of Organic and Physical Chemistry
Academy of Sciences of the Republic of Tatarstan
D.I. Mendeleev Russian Chemical Society

September 18-23, 2011
KAZAN, RUSSIA



ORGANIZERS



Ministry of Education and Science
of the Russian Federation



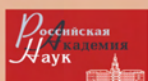
Russian Academy of Sciences (RAS)



Government of the Republic of Tatarstan



Kazan (Volga region) Federal University



Kazan Scientific Center of RAS



A.E. Arbuzov Institute of Organic
and Physical Chemistry



Academy of Sciences of
the Republic of Tatarstan



D.I. Mendeleev Russian Chemical Society

Ministry of Education and Science of the Russian Federation
Russian Academy of Sciences (RAS)
Government of the Republic of Tatarstan
Kazan (Volga region) Federal University
Kazan Scientific Center of RAS
A.E. Arbuzov Institute of Organic and Physical Chemistry
Academy of Sciences of the Republic of Tatarstan
D.I. Mendeleev Russian Chemical Society

International Congress on Organic Chemistry
dedicated to the 150-th anniversary of the Butlerov's Theory of Chemical Structure
of Organic Compounds

Book of Abstracts

September 18-23, 2011

COMMITTEES

ORGANIZING COMMITTEE

Chairmen of the Organizing Committee

- S.M. Aldoshin - Vice-president of the Russian Academy of Science (RAS),
academician of RAS
I.Sh. Khalikov - Prime-minister of the Republic of Tatarstan

Vice-Chairmen

- I.R. Gafurov - Rector of the Kazan (Volga region) Federal University
A.M. Mazgarov - President of the Tatarstan Academy of Sciences
O.G. Sinyashin - Chairman of the Kazan Scientific Center of the Russian
Academy of Sciences

General Scientific Secretary Scientific Secretary

V.I. Galkin
I.S. Antipin

Members of the Committee:

G.A. Abakumov	V.I. Minkin	S.N. Khadzhiev
E.E. Antipenko	B.F. Myasoedov	A.I. Konovalov
I.P. Beletskaya	O.M. Nefedov	V.V. Lunin
Y.N. Bubnov	D.K. Nourgaliev	I.R. Metshin
V.N. Charushin	V.A. Tartakovsky	P.D. Sarkisov
O.N. Chupakhin	G.A. Tolstikov	R.S. Yarullin
M.P. Egorov	B.A. Trofimov	M.S. Yunusov
I.L. Eremenko	R.Z. Sagdeev	N.S. Zefirov
A.Kh. Gilmutdinov	M.Kh. Salakhov	

INTERNATIONAL ADVISORY COMMITTEE

R. Breslow (USA)	M.M. Mikolajczyk (Poland)
E.E. Cameron (USA)	R. Noyori (Japan)
E. Hey-Hawkins (Germany)	L.K. Sydnes (Norway)
R.E. Hoffman (Israel)	N.P. Tarasova (Russia)
A.G. Gabibov (Russia)	R. Ungaro (Italy)
J.-M. Lehn (France)	

PROGRAM COMMITTEE

Chairman of the Program Committee

Vice-Chairmen
Scientific Secretary

O.G. Sinyashin

M.P. Egorov, V.N. Charushin

V.F. Mironov

Members of the Committee:

S.O. Bachurin

I.P. Beletskaya

A.A. Bredikhin

V.K. Cherkasov

O.N. Chupakhin

V.E. Kataev

A.I. Konovalov

A.V. Kuchin

V.Y. Kukushkin

V.A. Mamedov

V.I. Minkin

A.M. Muzafarov

I.A. Novakov

V.I. Ovcharenko

V.L. Rusinov

V.A. Tartakovsky

A.G. Tolstikov

LOCAL ORGANIZING COMMITTEE

Chairman of the Local Organizing Committee

Vice-Chairman

I.R. Gafurov

D.K. Nourgaliev

Members of the Committee:

I.S. Antipin

R.A. Cherkasov

G.A. Chmutova

G.A. Evtyugin

V.I. Galkin

I.V. Galkina

V.V. Gorbachuk

L.S. Safiullin

I.I. Stoikov

B.N. Solomonov

N.A. Ulakhovich

R.I. Zhdanov

M.A. Ziganshin

Heads of the Working Groups:

V.A. Burilov

I.A. Chelnokova

F.V. Devyatov

N.I. Ivanova

F.Kh. Karataeva

M.A. Kazymova

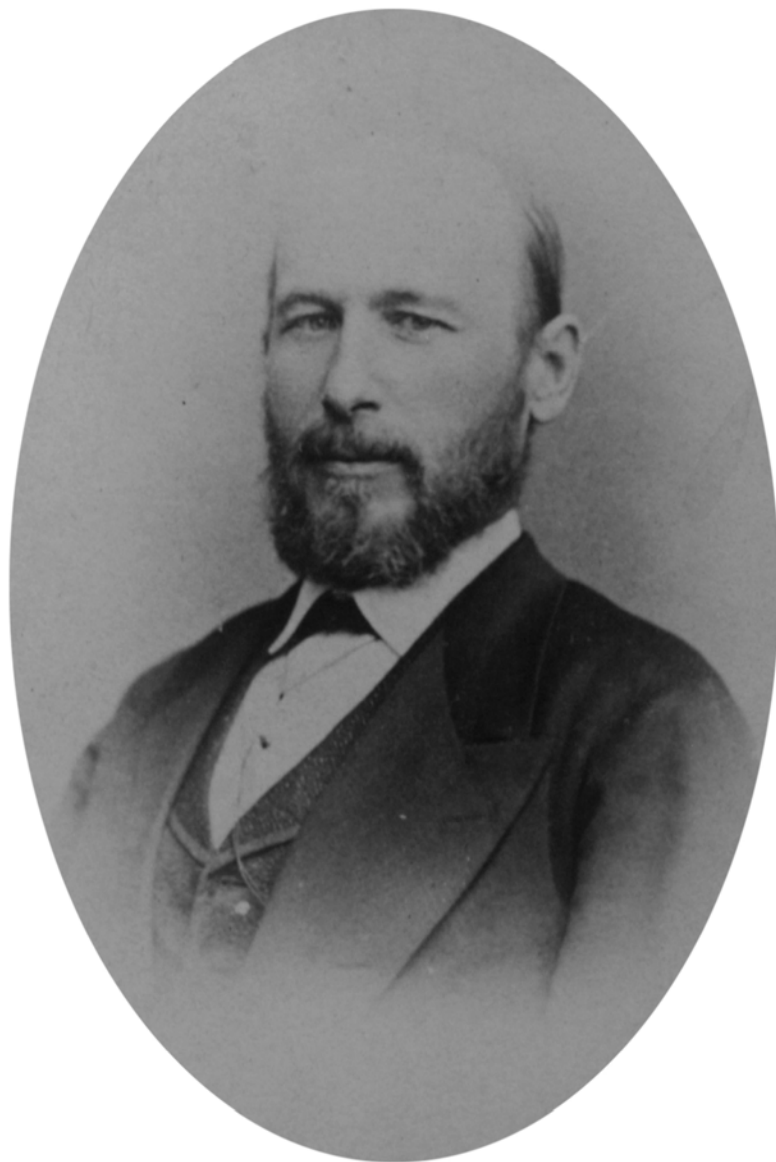
T.D. Keshner

A.A. Krylov

A.R. Kurbangalieva

T.I. Madzhidov

L.M. Mukhtarova



A.M. Butlerov

Photo from the collection of Rare Books and Manuscripts Department of Kazan
Federal University Library.

Dear participants!

It is my genuine pleasure to greet you at this International Congress of Organic Chemistry devoted to the 150th anniversary of the creation of the theory of organic substances by Alexander Butlerov which is taking place in hospitable Tatarstan, in the thousand-year-old city of Kazan.

Kazan is deservedly called by historians “the cradle of Russia’s organic chemistry” as it was here, in Kazan University founded in 1804, that the Kazan school of chemistry, one of the largest in the world, was born, thanks to the works by outstanding chemists Karl Klaus, Nicolay Zinin, Butlerov and Markovnikov. The true pinnacle of accomplishments of the Kazan school of chemistry was creation of the theory of the structure of organic compounds which gave the beginning to the new era of chemistry development.



Rustam N. Minnikhanov

President of the Republic of Tatarstan

For more than two hundred years, knowledge and experience have been carefully passed down from the teacher to the student, thus training ever new generations of organic chemists. Alexander and Boris Arbuzov, Alexander Razumov, Gilm Kamai and Arkady Pudovik do not complete the list of the names that brought fame to the school in the XX century.

The development of organic chemistry in Kazan has never stood apart from production process and reformations in the social area. Tatarstan today is a republic of grand chemistry. Such companies as “Nizhnekamskneftechim”, “Kazanorgsynthes” and “Nizhnekamskshina” provide the foundation and determine the development dynamics of the petrochemical industry in the Russian Federation.

New long-term directions are opening up with the construction of “TANEKO” – Oil Refining and Petrochemical Complex – integrated chemical complex for production of ammonia, methanol and carbamide. One of the largest chemical and petrochemical clusters in Russia is being formed in Tatarstan where the most modern scientific methods are applied.

I am confident that this authoritative forum bringing together the best Russian and foreign scholars in the field of organic chemistry will contribute to the development of science and technology. I am hopeful that this contact with the past and the present of the Kazan school of chemistry will be a lasting impression for the participants of this Congress.

I cordially wish you new ideas, fruitful research results, creative accomplishments, happiness and good health.

*President of Tatarstan Republic
Rustam Minnikhanov*



Oleg G. Sinyashin

*Chairmen of the Kazan Scientific Center of
Russian Academy of Sciences*



Ilshat R. Gafurov

*Rector of Kazan (Volga region) Federal
University*

Dear colleagues and friends!

On behalf of Kazan Federal University, Kazan Scientific Center of Russian Academy of Sciences and ourselves, we cordially welcome the participants of International Congress on Organic Chemistry, dedicated to the 150th anniversary Butlerov's theory of the chemical structure of organic compounds! Butlerov's name is inscribed in golden letters not only in the history of chemistry but science in general due to his creation of the Theory of Chemical Structure of Organic Compounds. The role of this theory in organic chemistry can be compared with the role of Mendeleev's periodic system in inorganic chemistry. It gave a powerful impetus to the development of organic synthesis industry opening the way for the wide introduction of chemistry achievements in everyday life.

Butlerov was one of those who initiated Kazan Chemical School making a significant contribution into its development. This fact reflected in firmly fixed Mendeleev's definition of "Butlerov's direction" among Kazan scholars. Butlerov played a remarkable role in the development of the Academy of Sciences by promoting the reputation of advanced Russian science in the global research community. Through the efforts of Butlerov's predecessors and successors – K. Klaus, N. Zinin, V. Markovnikov, A. Zaitsev, F. Flavitsky, E. Wagner, A. Arbuzov and other prominent scientists - Kazan Chemical School has earned a worldwide recognition. Born in the walls of Kazan University, it has been expanding research horizons for a century and a half. An academic branch of Kazan School of Organic Chemists emerged in the victorious 1945. There was also established A. Arbuzov Institute of Organic and Physical Chemistry, which became one of the largest diversified chemical centers in the Volga Region developing Butlerov's traditions in active cooperation with Butlerov Institute of Chemistry at Kazan University.

Today, when one of the oldest universities in the country acts as a Federal University, creative cooperation, the consolidation of strengths and means of KFU and Kazan Scientific Center of Russian Academy of Sciences, as well as of other universities and research institutes and the largest chemical companies in our region should be emphasized. This is an important condition for the formation of the knowledge-based economy. And Butlerov's saying that "science is the best source of social forces, so the paths of knowledge and development always coincide with each other" sounds ever-living nowadays.

We are sure that one of the most notable events of 2011 - International Congress on Organic Chemistry, which was proclaimed the Year of Chemistry by the UN, will be a significant step towards addressing the current theoretical and practical challenges facing chemical sciences. We wish all participants of this authoritative scientific forum new creative achievements, good health, well-being and inexhaustible vitality!

*Ilshat R. Gafurov
Oleg G. Sinyashin*

A Word about Butlerov



Alexander I. Konovalov
*The Leader of present-day Kazan
Chemical School*

A.M. Butlerov – is one of the most prominent scientists of Russia of the second half of the XIX century.

The scientific homeland of A.M. Butlerov is Kazan and Kazan University. That is the place where he absorbed the basics of the chemical science under the supervision of famous scientists. Among them are N.N. Zinin, who was the first to synthesize aniline which led to the foundation of aniline dye industry in the world, and K.K. Klaus, who discovered ruthenium (Russian) which plays an important role in the catalytic processes nowadays. Moreover this is the place where he became the Great Master of chemistry, creating the theory of chemical structure of organic compounds 150 years ago. This theory became the guiding

light in “the wild forest, full of wonderful things” - organic chemistry. He also conducted famous “butlerov” syntheses on the basis and in support of his theory in Kazan. And Kazan is the place where he discovered the reactions which were later named after him. That is the place where he laid the foundation of worldwide famous Kazan Butlerov school of chemists – organics, directing his first students to the scientific way: V.V. Markovnikov and A.M. Zaitsev, who later became themselves the pride of the Russian science.

The personality of A.M. Butlerov acquired a special coloring during his period of life and work in Saint Petersburg. Due to his talent, pedagogical pledge and spirit A.M. Butlerov became not only the head of his chemical school, but also the leader of Russian chemists. His numerous students and followers who grew up under the influence of Butlerov’s ideas, surpassed the development of chemistry in Russia for decades ahead.

While celebrating the 150-th anniversary of the theory of chemical structure of organic compounds we honour A.M. Butlerov as a great scientist, great teacher and a great person.

Alexander I. Konovalov

TITLES OF SESSIONS

The Congress topics

1. Theoretical Organic Chemistry: Bonding, Structure and Reactivity
2. “Chiral” Organic Chemistry
3. Advanced Methods of Organic Synthesis
4. Catalysis in Organic Synthesis
5. Supramolecular Organic Chemistry: VI International Symposium “Design and Synthesis of Supramolecular Architectures”
6. Bioorganic and Medicinal Chemistry
7. Organometallics in Organic Synthesis
8. Symposium “Modern trends in functionalization of C-H bonds in arenes and heteroarenes”

CONGRESS SCHEDULE

September 18, 2011

Time	
09.00 – 18.00	Registration
15.00 – 18.00	Social Events
18.30 – 19.00	Flowers-laying to Butlerov's monument
19.00	Welcome-party

September 19, 2011

Time	
09.00 – 10.00	Congress opening ceremony
10.00 – 10.50	Key-note lecture <i>A. Konovalov (Russia)</i> K1
10.50 – 11.40	Key-note lecture <i>A. Suzuki (Japan)</i> K2
11.40 – 12.10	Coffee-break

Time		Sessions				
		Theoretical Organic Chemistry	Advanced Methods of Organic Synthesis	Organometallics in Organic Synthesis	Bioorganic & Medicinal Chemistry	Supramolecular Chemistry
12.10 – 12.40	oral	<i>V. Palyulin (Russia)</i> O1	<i>D. Bonifazi (Belgium)</i> O13	<i>D. Yakhvarov (Russia)</i> O27	<i>P. Metz (Germany)</i> O44	<i>Y. Gorbunova (Russia)</i> O61
12.40 – 13.10	oral	<i>M. Olivucci (Italy)</i> O2	<i>A. Terentyev (Russia)</i> O14	<i>C. Allen (USA)</i> O28	<i>E. Milaeva (Russia)</i> O45	<i>E. Karpichev (Ukraine)</i> O62
13.10 – 14.30	Lunch					
14.30 – 15.20	Key-note lecture		<i>N. De Kimpe (Belgium)</i> K3			
15.20 – 15.40	Coffee-break					
15.40 – 16.20	plenary	<i>E. Babaev (Russia)</i> PL1	<i>D. Bruce (UK)</i> PL5	<i>V. Mironov (Russia)</i> PL11	<i>Ch. McKenna (USA)</i> PL18	<i>A. Rusanov (Russia)</i> PL25
16.20 – 16.50	oral	<i>V. Nenajdenko (Russia)</i> O3	<i>I. Balova (Russia)</i> O15	<i>F. Suzenet (France)</i> O29	<i>K. Kudryavtsev (Russia)</i> O46	<i>V. Gorbachuk (Russia)</i> O63
16.50 – 17.20	oral	<i>S. Katsyuba (Russia)</i> O4	<i>M. Kuznetsov (Russia)</i> O16	<i>I. Fedyushkin (Russia)</i> O30	<i>A. Garabadzhiu (Russia)</i> O47	<i>G. Kostin (Russia)</i> O64
17.20 – 17.50	oral	<i>D. Kazakov (Russia)</i> O5	<i>V. Kuropatov (Russia)</i> O17	<i>A. Prokhorov (Russia)</i> O31	<i>Y. Voloshin (Russia)</i> O48	<i>S. Selektor (Russia)</i> O65
17.50 – 18.20	oral	<i>N. Gritsan (Russia)</i> O6	<i>V. Sokolov (Russia)</i> O18	<i>K. Zaitsev (Russia)</i> O32	<i>A. Fedorov (Russia)</i> O49	<i>E. Ushakov (Russia)</i> O66
18.20 – 18.50	oral	<i>T. Madzhidov (Russia)</i> O7	<i>A. Kurbangalieva (Russia)</i> O19	<i>I. Ramazanov (Russia)</i> O33	<i>I. Galkina (Russia)</i> O50	<i>A. Yakimansky (Russia)</i> O67

September 20, 2011

Time		
09.30 – 10.20	Key-note lecture	<i>I. Beletskaya (Russia)</i> K4
10.20 – 10.50	Coffee-break	

Time		Sessions				
		Theoretical Organic Chemistry	Advanced Methods of Organic Synthesis	Organometallics in Organic Synthesis	Bioorganic & Medicinal Chemistry	Supramolecular Chemistry
10.50 – 11.30	plenary	<i>M. Antipin (Rissia)</i> PL2	<i>R. Larock (USA)</i> PL6	<i>M. Hissler (France)</i> PL12	<i>N. Zefirov (Russia)</i> PL19	<i>B. König (Germany)</i> PL26
11.30 – 12.10	plenary	<i>J. Miller (USA)</i> PL3	<i>S. Tsuboi (Japan)</i> PL7	<i>M. Mikolajczyk (Poland)</i> PL13	<i>P. Masson (France)</i> PL20	<i>I. Antipin (Russia)</i> PL27
12.10 – 12.40	oral	<i>A. Vasilyev (Russia)</i> O8	<i>V. Mamedov (Russia)</i> O20	<i>V. Milyukov (Russia)</i> O34	<i>V. Semenov (Russia)</i> O51	<i>A. Mirochnik (Russia)</i> O68
12.40 – 13.10	oral	<i>M. Balakina (Russia)</i> O9	<i>A. Saikia (India)</i> O21	<i>P. Onysko (Ukraine)</i> O35	<i>N. Nifantiev (Russia)</i> O52	<i>S. Chvalun (Russia)</i> O69
13.10 – 14.40	Lunch					
14.40 – 15.30	Key-note lecture		<i>S. Florio (Italy)</i> K5			
15.30 – 15.50	Coffee-break					
15.50 – 16.30	plenary	<i>S. Vasilevsky (Russia)</i> PL4	<i>J. Thomas (UK)</i> PL8	<i>V. Kukushkin (Russia)</i> PL14	<i>H. Knöelker (Germany)</i> PL21	<i>S. Gromov (Russia)</i> PL28
16.30 – 17.00	oral	<i>M. Kadirov (Russia)</i> O10	<i>G. Roeschenthaler (Germany)</i> O22	<i>T. Kawashima (Japan)</i> O36	<i>T. Inokuchi (Japan)</i> O53	<i>O. Kataeva (Russia)</i> O70
17.00 – 17.30	oral	<i>A. Khlebnikov (Russia)</i> O11	<i>A. Shutalev (Russia)</i> O23	<i>I. Odinets (Russia)</i> O37	<i>M. Nawrozkij (Russia)</i> O54	<i>E. Mikhalitsyna (Russia)</i> O71
17.30 – 18.00	oral	<i>Y. Vereshchagina (Russia)</i> O12	<i>C. Correia (Brazil)</i> O24	<i>L. Parfenova (Russia)</i> O38	<i>T. Gorshkova (Russia)</i> O55	<i>A. Chibisov (Russia)</i> O72
18.00 – 19.00	Poster session I					

September 21, 2011

Time		
09.30 – 10.20	Key-note lecture	<i>R. Hoffmann (Germany)</i> K6
10.20 – 10.50	Coffee-break	

Time		Sessions				
		S _N ^H SYMPOSIUM	Advanced Methods of Organic Synthesis	Organometallics in Organic Synthesis	Bioorganic & Medicinal Chemistry	Supramolecular Chemistry
10.50 – 11.30	plenary	<i>M. Makosza (Poland)</i> PL34	<i>V. Ananikov (Russia)</i> PL9	<i>O. Kulinkovich (Estonia)</i> PL15	<i>J. Wood (USA)</i> PL22	<i>V. Fedin (Russia)</i> PL29
11.30 – 12.10	plenary	<i>G. Rusinov (Russia)</i> PL35	<i>L. Tietze (Germany)</i> PL10	<i>E. Hey-Hawkins (Germany)</i> PL16	<i>S. Bachurin (Russia)</i> PL23	<i>O. Fedorova (Russia)</i> PL30
12.10 – 12.40	oral	<i>A. Gulevskaya (Russia)</i> O80	<i>L. Fedenok (Russia)</i> O25	<i>A. Dilman (Russia)</i> O39	<i>B. Fedorov (Russia)</i> O56	<i>S. Vatsadze (Russia)</i> O73
12.40 – 13.10	oral	<i>V. Shteingarts (Russia)</i> O81	<i>Yu. Shklyaev (Russia)</i> O26	<i>V. Saloutin (Russia)</i> O40	<i>K. Lammertsma (Netherlands)</i> O57	<i>M. Shcherbina (Russia)</i> O74
13.10 – 14.40	Lunch					
14.40 – 15.30	Key-note lecture		<i>V. Minkin (Russia)</i> K7			
15.30 – 15.50	Coffee-break					
		S _N ^H SYMPOSIUM	Catalysis in Organic Synthesis	Organometallics in Organic Synthesis	Bioorganic & Medicinal Chemistry	Supramolecular Chemistry
15.50 – 16.30	plenary	<i>V. Gevorgyan (USA)</i> PL36	<i>B. Maes (Belgium)</i> PL39	<i>V. Kukhar (Ukraine)</i> PL17	<i>R. Romeo (Italy)</i> PL24	<i>G. Evtyugin (Russia)</i> PL31
16.30 – 17.00	oral	<i>L. Belen’kii (Russia)</i> O82	<i>I. Gridnev (Japan)</i> O91	<i>A. Muzafarov (Russia)</i> O41	<i>A. Nikolaev (Russia)</i> O58	<i>V. Livshits (Russia)</i> O75
17.00 – 17.30	oral	<i>V. Galkin (Russia)</i> O83	<i>K. Marichev (Ukraine)</i> O92	<i>K. Gavrilov (Russia)</i> O42	<i>L. Baltina (Russia)</i> O59	<i>R. Amirov (Russia)</i> O76
17.30 – 18.00	oral	<i>A. Pestov (Russia)</i> O84	<i>M. Novikov (Russia)</i> O93	<i>A. Görgülü (Turkey)</i> O43	<i>A. Gabibov (Russia)</i> O60	<i>A. Ziganshina (Russia)</i> O77
19.00	Banquet					

September 22, 2011

Time		
09.30 – 10.20	Key-note lecture	<i>V. Charushin (Russia)</i> K8
10.20 – 10.50	Coffee-break	

Time		Sessions			
		S _N ^H SYMPOSIUM	Catalysis in Organic Synthesis	“Chiral” Organic Chemistry	Supramolecular Chemistry
10.50 – 11.30	plenary	<i>A. Kotov (Russia)</i> PL37	<i>T. Collins (USA)</i> PL40	<i>K. Mori (Japan)</i> PL42	<i>N. Melnikova (Russia)</i> PL32
11.30 – 12.10	plenary	<i>V. Petrosyan (Russia)</i> PL38	<i>V. Dyakonov (Russia)</i> PL41	<i>Y. Shi (USA)</i> PL43	<i>A. Mustafina (Russia)</i> PL33
12.10 – 12.40	oral	<i>I. Utepova (Russia)</i> O85	<i>N. Rostovskii (Russia)</i> O94	<i>A. Trifonov (Russia)</i> O100	<i>A. Oshchepkov (Russia)</i> O78
12.40 – 13.10	oral	<i>Lyakhovnenko (Russia)</i> O86	<i>Ju. Ivanova (Russia)</i> O95	<i>E. Korshin (Israel)</i> O101	<i>V. Semionova (Russia)</i> O79
13.10 – 14.40	Lunch				
14.40 – 15.30	Key-note lecture		<i>P. Schreiner (Germany)</i> K9		
15.30 – 15.50	Coffee-break				
		S _N ^H SYMPOSIUM	Catalysis in Organic Synthesis	“Chiral” Organic Chemistry	
15.50 – 16.30	oral	<i>A. Matern (Russia)</i> O87	<i>A. Kornev (Russia)</i> O96	<i>A. Bredikhin (Russia)</i> O102	
16.30 – 17.00	oral	<i>A. Aksenov (Russia)</i> O88	<i>A. Sukhorukov (Russia)</i> O97	<i>S. Zlotin (Russia)</i> O103	
17.00 – 17.30	oral	<i>A. Sheremetev (Russia)</i> O89	<i>V. Kiselev (Russia)</i> O98	<i>V. Krasnov (Russia)</i> O104	
17.30 – 18.00	oral	<i>A. Starosotnikov (Russia)</i> O90	<i>V. Akhmetova (Russia)</i> O99	<i>A. Karasik (Russia)</i> O105	
18.00-19.00	Poster session II				

September 23, 2011

Time		
09.30 – 10.20	Key-note lecture	<i>G. Blackburn (UK)</i> K10
10.20 – 11.10	Key-note lecture	<i>M. Egorov (Russia)</i> K11
11.10 – 11.30	oral	<i>I. Eremenko (Russia)</i> KO12
11.30 – 12.00	oral	<i>Ch. McKenna (USA)</i> KO13
12.00 – 12.30	Congress closing ceremony	
14.30	Social Events	

BUTLEROV CONGRESS SCIENTIFIC PROGRAMME

Key-Note Lectures			
Date	Time		
19 Spt	10.00 – 10.50	K1	Alexander I. Konovalov (Russia) 150 years of the Butlerov theory of chemical structure
	10.50 – 11.40	K2	Akira Suzuki (Japan) Cross-coupling reactions of organoboron compounds
	14.30 – 15.20	K3	Norbert De Kimpe (Belgium) Ring transformations of functionalized β -lactams towards azaheterocycles
20 Spt	09.30 – 10.20	K4	Irina P. Beletskaya (Russia) Transition metal catalysis, application to fine organic synthesis, success and problems
	14.40 – 15.30	K5	Saverio Florio (Italy) New horizons in the chemistry of small ring heterocycles: dynamics and complexation phenomena at work
21 Spt	09.30 – 10.20	K6	Reinhard W. Hoffmann (Germany) Streamlining organic synthesis for the 21st century
	14.40 – 15.30	K7	Vladimir I. Minkin (Russia) Modern trends in the evolution of the theory of chemical structure. From A.M. Butlerov to the present time
22 Spt	09.30 – 10.20	K8	Valeriy N. Charushin and Oleg N. Chupakhin (Russia) New approaches to modification of C-H bonds in arenes by action of nucleophilic reagents
	14.40 – 15.30	K9	Peter R. Schreiner (Germany) Revisiting Butlerov's sugar hypothesis on its 150th birthday
23 Spt	09.30 – 10.20	K10	George M. Blackburn (UK) Why and how did nature select phosphorus for its dominant roles in biology?"
	10.20 – 11.10	K11	Mikhail P. Egorov and Oleg M. Nefedov (Russia) Cycloaddition reactions in the chemistry of heavy carbene analogs
Short Comments			
23 Spt	11.10 – 11.30	KO12	Igor L. Eremenko (Russia) The organic ligands as a tool for the directed synthesis metalcontaining molecules with predetermined physical properties
	11.30 – 12.00	KO13	Charles E. McKenna (USA) Alexander Mikhailovich Butlerov: An Appreciation

Theoretical Organic Chemistry: Bonding, Structure and Reactivity

Plenary Lectures			
Date	Time		
19 Spt	15.40 – 16.20	PL1	E.V. Babaev (Russia) Topological paradoxes of the structural theory
20 Spt	10.50 – 11.30	PL2	M.Yu. Antipin (Russia) The "valence stick" in organic molecules: From Butlerov to modern understanding the nature of chemical bond
	11.30 – 12.10	PL3	J.S. Miller (USA) Extraordinarily long 2.9 Å and multicenter C-C bonds - What is a chemical bond?
	15.50 – 16.30	PL4	S.F. Vasilevskiy (Russia) Unexpected cleavage of acetylenic moiety in α -ketoacetylenes under influence of 1,2-diaminoethane: New route to 2-substituted imidazolines
Oral Reports			
19 Spt	12.10 – 12.40	O1	V.A. Palyulin (Russia) Quantitative structure-property relationships: Recent approaches
	12.40 – 13.10	O2	M. Olivucci (Italy) From computational photobiology to the development of biomimetic molecular devices
	16.20 – 16.50	O3	V.G. Nenajdenko (Russia) Sulflower and other chemical flowers
	16.50 – 17.20	O4	S.A. Katsyuba (Russia) Interionic interactions and their impact on structure and properties of some imidazolium- and phosphonium-based ionic liquids
	17.20 – 17.50	O5	D.V. Kazakov (Russia) Chemiluminescence from organic reactions. Fundamentals and applied aspects
	17.50 – 18.20	O6	N.P. Gritsan (Russia) Reactivity of thiophenolate toward chalcogenadiazoles
	18.20 – 18.50	O7	T.I. Madzhidov (Russia) The peculiarities of the electronic structure of organoselenium compounds and its complexes with different acceptors
20 Spt	12.10 – 12.40	O8	A.V. Vasilyev (Russia) New pathways of organic synthesis based on superelectrophilic activation of acetylene compounds
	12.40 – 13.10	O9	M.Yu. Balakina (Russia) Molecular design of polymer materials with quadratic nonlinear optical activity: Structure-property relationship for epoxy-based oligomers with dendritic multichromophore fragments
	16.30 – 17.00	O10	M.K. Kadirov (Russia) Active radical intermediates in fuel cell in situ and radical products of perfluorinated membranes side-chain degradation

	17.00 – 17.30	O11	A.F. Khlebnikov (Russia) Fused aziridines: Convenient source of azomethine ylides for creating polyheterocycles
	17.30 – 18.00	O12	Ya.A. Vereshchagina (Russia) Polarity and structure of polyfunctional nitroethenes

Advanced Methods of Organic Synthesis

Plenary Lectures			
Date	Time		
19 Spt	15.40 – 16.20	PL5	D.W. Bruce (UK) The preparation of functional N-heterocycles and their application in material's chemistry
20 Spt	10.50 – 11.30	PL6	R.C. Larock (USA) Novel syntheses of carbocycles and heterocycles via iodine, palladium and aryne chemistry
	11.30 – 12.10	PL7	S. Tsuboi (Japan) Some serendipities in my research life
	15.50 – 16.30	PL8	J. Thomas (UK) Approaches to the synthesis of some biologically active compounds
21 Spt	10.50 – 11.30	PL9	V.P. Ananikov (Russia) The nature of the catalyst in transition-metal-catalyzed carbon-heteroatom and carbon-carbon bonds formation reaction
	11.30 – 12.10	PL10	L.F. Tietze (Germany) Multiple Pd-catalyzed transformations for the synthesis of natural products, drugs and materials
Oral Reports			
19 Spt	12.10 – 12.40	O13	D. Bonifazi (Belgium) Doped π -conjugated organic emitters: Synthesis, properties and supramolecular organization
	12.40 – 13.10	O14	A.O. Terentyev (Russia) Synthesis of cyclic peroxides
	16.20 – 16.50	O15	I.A. Balova (Russia) Cyclization of functionalized (buta-1,3-diynyl)arenes in the synthesis of endiynes fused to heterocycles
	16.50 – 17.20	O16	M.A. Kuznetsov (Russia) Synthesis, intra- and intermolecular transformations of N-aminoaziridine derivatives
	17.20 – 17.50	O17	V.A. Kuropatov (Russia) Chemistry of sterically hindered <i>o</i> -quinones. Functionalization with annelated dithiol, thiazole, imidazole and tetrathiafulvalene moieties
	17.50 – 18.20	O18	V.V. Sokolov (Russia) Synthesis of sultams by cycloalkylation of α -substituted methanesulfonamides

	18.20 – 18.50	O19	A.R. Kurbangalieva (Russia) 3,4-Dichloro-2(5 <i>H</i>)-furanones: Useful synthons for the preparation of a variety of O-, N- and S-heterocycles
20 Spt	12.10 – 12.40	O20	V.A. Mamedov (Russia) A novel rearrangement of quinoxalin-2(1 <i>H</i>)-ones for the synthesis of 2-heteroaryl-benzimidazoles
	12.40 – 13.10	O21	A.K. Saikia (India) Novel synthesis of oxygen heterocycles via Prins and oxonium-ene cyclization
	16.30 – 17.00	O22	G.-V. Roeschenthaler (Germany) Fluorine, an element for (almost) all events. Recent advances in fluoroorganic chemistry
	17.00 – 17.30	O23	A.D. Shutalev (Russia) Recent advances in the synthesis of tetrahydro- and dihydro-1 <i>H</i> -1,3-diazepin-2-ones
	17.30 – 18.00	O24	C.R.D. Correia (Brazil) Regio- and stereoselective Heck arylation of cinnamates and allylamine derivatives using arenediazonium salts
21 Spt	12.10 – 12.40	O25	L.G. Fedenok (Russia) Mechanism and synthetic capabilities of the vic-(alkynyl)arenediazonium salts cyclization reaction
	12.40 – 13.10	O26	Yu.V. Shklyayev (Russia) Synthesis of the partially hydrogenated nitrogen-containing heterocycles: How does Ritter-type heterocyclization proceed?

Organometallics in Organic Synthesis

Plenary Lectures			
Date	Time		
19 Spt	15.40 – 16.20	PL11	V.F. Mironov (Russia) Reaction of 2,2,2-trihalo-benzo-1,3,2-dioxaphospholes with terminal acetylenes: Easy <i>ipso</i> -substitution of oxygen by carbon and P–C bond formation
20 Spt	10.50 – 11.30	PL12	M. Hissler (France) Organophosphorus and organometallic chemistry for the design of organic conjugated systems
	11.30 – 12.10	PL13	M. Mikolajczyk (Poland) Phosphonate-based strategy for synthesis of cyclopentenone and cyclopentanone natural and bioactive products
	15.50 – 16.30	PL14	V.Yu. Kukushkin (Russia) Aminocarbenes: "X.O" of organometallic chemistry
21 Spt	10.50 – 11.30	PL15	O.G. Kulinkovich (Estonia) Progress in synthetic applications of alkoxytitanacyclopropane reagents

	11.30 – 12.10	PL16	E. Hey-Hawkins (Germany) Imitation and modification of bioactive lead structures via integration of boron clusters
	15.50 – 16.30	PL17	V.P. Kukhar (Ukraine) Amino-phosphonates and bis-phosphonates. New synthetic advances
Oral Reports			
19 Spt	12.10 – 12.40	O27	D.G. Yakhvarov (Russia) Synthetic electrochemistry – recent discoveries and perspectives
	12.40 – 13.10	O28	C. Allen (USA) Organic chemistry on an inorganic platform: Approaches to organic-inorganic hybrid polymeric materials
	16.20 – 16.50	O29	F. Suzenet (France) Desulfurizing palladium-catalyzed cross-coupling reaction: A Useful tool in heterocyclic chemistry
	16.50 – 17.20	O30	I.L. Fedushkin (Russia) Addition of alkynes to gallium bis-amido complex: Imitation of transition metal-based catalytic systems
	17.20 – 17.50	O31	A.M. Prokhorov (Russia) Heteroaromatic derivatives of carborane by C-H bond functionalisation in azines
	17.50 – 18.20	O32	K.V. Zaitsev (Russia) Using functionalized aluminum complexes as a new approach to ring-opening polymerization
	18.20 – 18.50	O33	I.R. Ramazanov (Russia) Organoaluminums in cyclopropane synthesis
20 Spt	12.10 – 12.40	O34	V.A. Miluykov (Russia) The 1,2-diphosphacyclopentadienide-anions in organic and organometallic synthesis
	12.40 – 13.10	O35	P.P. Onysko (Ukraine) Biomimetic transamination in phosphorylated imines
	16.30 – 17.00	O36	T. Kawashima (Japan) Umpolung of a hydrogen atom of water utilizing hexacoordinated dihydrophosphates and its application to one-pot deuteride reduction of carbonyl compounds
	17.00 – 17.30	O37	I.L. Odinet (Russia) Phosphorylation of dienone pharmacophore for targeted design of highly effective and fluorescent cytostatics
	17.30 – 18.00	O38	L.V. Parfenova (Russia) Zirconium complex catalysis in alkene hydro-, carbo- and cycloaluminations: From mechanism to chemo- and enantioselectivity control
21 Spt	12.10 – 12.40	O39	A.D. Dilman (Russia) Nucleophilic trifluoromethylation of C=N and C=C bonds
	12.40 – 13.10	O40	V.I. Saloutin (Russia) Fluorinated 2-ethoxymethylidene-3-oxo esters for design of heterocycles and ligands

	16.30 – 17.00	O41	A.M. Muzafarov Molecular hybrid nanoobjects as perspective platform for drug delivery systems
	17.00 – 17.30	O42	K.N. Gavrilov (Russia) P*-chiral phosphite-type ligands as an efficient stereoselectors for the transition metal-catalyzed asymmetric reactions
	17.30 – 18.00	O43	A.O. Görgülü (Turkey) Synthesis and characterization of oxime-phosphazenes

Bioorganic and Medicinal Chemistry

Plenary Lectures			
Date	Time		
19 Spt	15.40 – 16.20	PL18	C.E. McKenna (USA) The organophosphorus chemistry of nucleotides: New advances in synthesis, stereochemistry and design of bioactive molecules
20 Spt	10.50 – 11.30	PL19	N.S. Zefirov (Russia) Design of multivalent drugs
	11.30 – 12.10	PL20	P. Masson (France) Reactions of human cholinesterases with cresyl saligenin phosphate: A Trojan horse poisoning by tri- <i>o</i> -cresyl phosphate
	15.50 – 16.30	PL21	H.-J. Knöelker (Germany) Design and synthesis of membrane-anchored bace inhibitors as potential drugs for the treatment of Alzheimer's disease
21 Spt	10.50 – 11.30	PL22	J.L. Wood (USA) Synthetic studies of oxindole-containing natural products
	11.30 – 12.10	PL23	S.O. Bachurin (Russia) Focused design of medicinal agents for the disorders of nervous system
	15.50 – 16.30	PL24	R. Romeo (Italy) Phosphonated N,O-nucleosides: Synthesis and biological evaluation
Oral Reports			
19 Spt	12.10 – 12.40	O44	P.R. Metz (Germany) Recent advances in the total synthesis of bioactive natural products
	12.40 – 13.10	O45	E.R. Milaeva (Russia) Novel strategy in bioorganometallic chemistry for the design of protectors against oxidative stress
	16.20 – 16.50	O46	K.V. Kudryavtsev (Russia) Application of 5-arylpyrrolidine-2-carboxylic acid scaffold for design of biologically active compounds
	16.50 – 17.20	O47	A.V. Garabadzhiu (Russia) DNA - "recognizing" ligands. Design and results

	17.20 – 17.50	O48	Y.Z. Voloshin (Russia) Organic reactions of the metal-centered quasi-aromatic cages and their potential for the design of the topological drugs
	17.50 – 18.20	O49	A.Yu. Fedorov (Russia) Synthesis and biological evaluation of new coumarin- and colchicine-type tubulin assembly inhibitors
	18.20 – 18.50	O50	I.V. Galkina (Russia) Target synthesis of biologically active compounds in the series of functionalized quaternary phosphonium salts
20 Spt	12.10 – 12.40	O51	V.V. Semenov (Russia) Plant polyalkoxybenzene modification - the approach to high effective analogs of natural antimitotic drugs
	12.40 – 13.10	O52	N.E. Nifantiev (Russia) Fucoidans – a platform for new drugs discovery
	16.30 – 17.00	O53	T. Inokuchi (Japan) Synthesis of indolequinolines for anti-infective and anticancer agents
	17.00 – 17.30	O54	M.B. Nawrozkij (Russia) 6-Benzylpyrimidin-4(3 <i>H</i>)-ones. Non-nucleoside HIV reverse transcriptase inhibitors: Chemical synthesis and structure-activity relationships
	17.30 – 18.00	O55	T. Gorshkova (Russia) Supramolecular structure of plant cell wall polysaccharides: Novel players
21 Spt	12.10 – 12.40	O56	B.S. Fedorov (Russia) New anticancer compounds encapsulated with supramolecular thixotropic hydro gel showing fractal structure based on cysteine, and silver ions and nanoparticles
	12.40 – 13.10	O57	K. Lammertsma (Netherlands) Phosphorus as enabling vehicle – new developments and applications
	16.30 – 17.00	O58	A.E. Nikolaev (Russia) Synthesis and antimicrobial activity of amphiphilic macrocycles and their acyclic counterparts
	17.00 – 17.30	O59	L.A. Baltina (Russia) New skeletal and oxidative transformations of licorice root triterpenic acids
	17.30 – 18.00	O60	A.G. Gabibov (Russia) Mechanisms of antibody-mediated cleavage of phosphoorganic pesticides

Supramolecular Organic Chemistry: VI International Symposium

"Design and Synthesis of Supramolecular Architectures"

Plenary Lectures			
Date	Time		
19 Spt	15.40 – 16.20	PL25	A.I. Rusanov (Russia) Supramolecular chirality of colloidal surfactants
20 Spt	10.50 – 11.30	PL26	B. König (Germany) Luminescent chemosensors and chemical photocatalysts from self-assembly of amphiphilic receptors and dyes
	11.30 – 12.10	PL27	I.S. Antipin (Russia) Calix[4]arenes based supramolecular systems: From molecular design to nanotechnological applications
	15.50 – 16.30	PL28	S.P. Gromov (Russia) Design of light-sensitive molecular devices and machines based on unsaturated and macrocyclic compounds
21 Spt	10.50 – 11.30	PL29	V.P. Fedin (Russia) Synthesis, structure and functional properties of microporous zinc carboxylates
	11.30 – 12.10	PL30	O.A. Fedorova (Russia) Supramolecular devices based on photoresponsive assemblies of cucurbit[7]uril and crown-ether derived styryl and (bis)styryl dyes
	15.50 – 16.30	PL31	G.A. Evtugyn (Russia) Multifunctional macrocyclic receptors in electroanalysis. Broadening electrochemical horizons
22 Spt	10.50 – 11.30	PL32	N.B. Melnikova (Russia) Langmuir films of fullerene and calixarene derivatives as a biomimetic models. Physicochemical characteristics and biological potentialities
	11.30 – 12.10	PL33	A.R. Mustafina (Russia) Stimuli responsive colloids from luminescent nanoparticles
Oral Reports			
19 Spt	12.10 – 12.40	O61	Yu.G. Gorbunova (Russia) Design and synthesis of supramolecular architectures based on novel phosphorus-containing porphyrins
	12.40 – 13.10	O62	E.A. Karpichev (Ukraine) Design of nanoreactors by controllable self-organization of dimeric amphiphilic compounds
	16.20 – 16.50	O63	V.V. Gorbachuk (Russia) Molecular recognition in formation and decomposition of clathrates with solid supramolecular hosts
	16.50 – 17.20	O64	G.A. Kostin (Russia) Complexation of Pd with thiacalix[4]arenes during extraction from nitric acid solutions

	17.20 – 17.50	O65	S.L. Selektor (Russia) Control of structure formation as a way of the modulating the photophysical and receptor characteristics of high-ordered ultrathin films based on conjugated organic compounds
	17.50 – 18.20	O66	E.N. Ushakov (Russia) Crown ether-based optical molecular sensors and photocontrolled ionophores
	18.20 – 18.50	O67	A.V. Yakimansky (Russia) Supramolecular graft-copolymer architectures on the platform of polyimide macroinitiators of ATRP
20 Spt	12.10 – 12.40	O68	A.G. Mirochnik (Russia) Supramolecular architecture and control of photo-stimulated processes in polyfunctional materials
	12.40 – 13.10	O69	S.N. Chvalun (Russia) Self-assembling supramolecular structures formed by tapered dendrons of various nature
	16.30 – 17.00	O70	O.N. Kataeva (Russia) Metal assisted self-assembly of phosphorus derivatives of ferrocen
	17.00 – 17.30	O71	E.A. Mikhailsyna (Russia) Synthesis and characterization of new supramolecular structures based on aza-crowned-porphyrins
	17.30 – 18.00	O72	A.K. Chibisov (Russia) J-aggregates of cyanine dyes as supramolecular system
21 Spt	12.10 – 12.40	O73	S.Z. Vatsadze (Russia) Novel ligands and methods for modification of coordination polymers
	12.40 – 13.10	O74	M.A. Shcherbina (Russia) Hollow six-stranded helical columns of a helicene
	16.30 – 17.00	O75	V.A. Livshits (Russia) Supramolecular cyclodextrin complexes in solution, solid phase and on the silica/water and silica/gas interfaces. ESR and fluorescence study
	17.00 – 17.30	O76	R.R. Amirov (Russia) NMR-paramagnetic probing of supramolecular interactions
	17.30 – 18.00	O77	A.Y. Ziganshina (Russia) Calix[4]resorcinols as building blocks for molecular devices
22 Spt	12.10 – 12.40	O78	A.S. Oshchepkov (Russia) Synthesis and sensor properties of naphthalimide derivatives containing diaza-18-crown-6 ether moiety
	12.40 – 13.10	O79	V.V. Semionova (Russia) Photochemistry of supramolecular complex of stilbene with a metalloorganic frame

Symposium "Modern trends in functionalization of C-H bonds in arenes and heteroarenes"

Plenary Lectures			
Date	Time		
21 Spt	10.50 – 11.30	PL34	M. Makosza (Poland) Nucleophilic substitution of hydrogen in electron-deficient arenes. Missing part of the aromatic substitution puzzle
	11.30 – 12.10	PL35	G.L. Rusinov (Russia) Direct nucleophilic functionalization of the C-H bond in azines
	15.50 – 16.30	PL36	V. Gevorgyan (USA) New advances in selected transition metal-catalyzed transformations
22 Spt	10.50 – 11.30	PL37	A.D. Kotov (Russia) Functionalization of C-, N-, O-containing heteroaromatic systems
	11.30 – 12.10	PL38	V.A. Petrosyan (Russia) Anodic and chemical aromatic substitution
Oral Reports			
21 Spt	12.10 – 12.40	O80	A.V. Gulevskaya (Russia) C-N bond formation via the nucleophilic aromatic substitution of hydrogen: Oxidative alkylamination and arylamination of nitroarenes
	12.40 – 13.10	O81	V.D. Shteingarts (Russia) Reductive activation of arencarbonitriles for the formation of carbon-carbon bond
	16.30 – 17.00	O82	L.I. Belen'kii (Russia) Positional selectivity in electrophilic substitution in p-excessive heteroaromatics
	17.00 – 17.30	O83	V.I. Galkin (Russia) Stable crystalline σ -complexes of 4,6-dinitrobenzofuroxan and amines
	17.30 – 18.00	O84	A.V. Pestov (Russia) Synthesis of chelating polymer sorbents by using the S_N^H methodology
22 Spt	12.10 – 12.40	O85	I.A. Utepova (Russia) The methodology of nucleophilic substitution of hydrogen (S_N^H) in the synthesis of nitroxide radicals
	12.40 – 13.10	O86	A.S. Lyakhovnenko (Russia) Sodium azide in polyphosphoric acid - a new reagent for direct electrophilic amination of aromatic compounds and annulation methods of pyrrole, pyrimidine and pyridine rings developed on its basis
	16.00 – 16.30	O87	A.I. Matern (Russia) The role of electron transfer in S_N^H reactions in azines

	16.30 – 17.00	O88	A.V. Aksenov (Russia) Nitroalkanes in polyphosphoric acid – a new reagents for acetamidation and carboxyamidation of aromatic compounds and synthetic methods developed on its basis
	17.00 – 17.30	O89	A.B. Sheremetev (Russia) Development of flexible strategies towards dihetaryamine constructions. Synthesis of compounds when furazan and S-tetrazine rings bridged through the NH-spacer
	17.30 – 18.00	O90	A.M. Starosotnikov (Russia) Nitroarenes as a basis for the synthesis of benzo-fused N-heterocycles

Catalysis in Organic Synthesis

Plenary Lectures			
Date	Time		
21 Spt	15.50 – 16.30	PL39	B.U.W. Maes (Belgium) Functionalization of heterocycles via transition metal-catalyzed reactions: Halide effects and direct C-H functionalizations
22 Spt	10.50 – 11.30	PL40	T.J. Collins (USA) TAML activators: Effective small molecule peroxidase mimics for constructing and deconstructing organic compounds
	11.30 – 12.10	PL41	V.A. Dyakonov (Russia) New strategy in design and construction of small, medium and macrocycles
Oral Reports			
21 Spt	16.30 – 17.00	O91	I.D. Gridnev (Japan) Trial and error mechanism of enantioselection in asymmetric hydrogenation
	17.00 – 17.30	O92	K.A. Marichev (Ukraine) Stable carbenes in catalysis of transesterification
	17.30 – 18.00	O93	M.S. Novikov (Russia) Rhodium carbenoid-azirine coupling as a novel route to 4-6-membered heterocycles
22 Spt	12.10 – 12.40	O94	N.V. Rostovskii (Russia) Reactions of azirines with cyclic and acyclic diazo keto esters: Two types of catalysis
	12.40 – 13.10	O95	J.V. Ivanova (Russia) The study of intermediates of Pd-catalyzed reactions by ESI-MS and NMR methods
	16.00 – 16.30	O96	A.N. Kornev (Russia) Heterocyclic systems containing N-N-P chain: From unique rearrangements in metal coordination sphere to the aromatic molecules of fundamentally new type

	16.30 – 17.00	O97	A.Yu. Sukhorukov (Russia) Six-membered cyclic oxime ethers in stereoselective and asymmetric synthesis
	17.00 – 17.30	O98	V.D.Kiselev (Russia) High pressure effect on the rate and equilibrium of common and catalyzed cycloaddition reactions in solution
	17.30 – 18.00	O99	V.R. Akhmetova (Russia) Regiodirected synthesis and stereochemistry of novel 1,3,4-thiadiazolidines and 1,5,3-dithiazepinanes

“Chiral” Organic Chemistry

Plenary Lectures			
Date	Time		
22 Spt	10.50 – 11.30	PL42	K. Mori (Japan) Significance of chirality in chemical communications
	11.30 – 12.10	PL43	Y. Shi (USA) Organocatalytic and metallocatalytic oxidation of olefins
Oral Reports			
22 Spt	12.10 – 12.40	O100	A.A. Trifonov (Russia) Enantioselective intramolecular alkenes hydroamination catalyzed by rare-earth complexes supported by chiral binaphthylamido ligands
	12.40 – 13.10	O101	E.E. Korshin (Israel) Stereoselective cascade-type homolytic intramolecular C-alkenylation versus reductive bridged heterocyclization in 4-hydroxyproline derivatives
	16.00 – 16.30	O102	A.A. Bredikhin (Russia) Chirality in action: Beyond the chiral drugs
	16.30 – 17.00	O103	S.G. Zlotin (Russia) Tandem of organocatalysis and ionic liquids: Novel opportunities for asymmetric organic synthesis
	17.00 – 17.30	O104	V.P. Krasnov (Russia) Acylation kinetic resolution of racemic amines with profens and amino acids derivatives
	17.30 – 18.00	O105	A.A. Karasik (Russia) Phosphorus based macrocyclic ligands: Synthesis and applications

Abstracts

Key-note lectures



The performance leader in:

- Magnetic Resonance
NMR, EPR, MRI
- X-ray and Elemental Analysis XRF,
XRD, EDS, OES, CS/ONH
- Life Sciences Mass Spectrometry
FTMS, MALDI, ICP-MS, GC-MS, LC-MS
- Molecular Spectroscopy
IR, NIR, Raman
- Microanalysis
AFM, SPM
- Superconductor wire products

www.bruker.com , www.bruker.ru

Bruker: Innovation with Integrity

150 YEARS OF THE BUTLEROV THEORY OF CHEMICAL STRUCTURE

A.I. Kononov

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
kononov@knc.ru

Basic fundamental propositions of A.Butlerov's theory of chemical structure as well as its subsequent development and application to different phenomena of organic chemistry are in the focus of attention.

Main conceptual views of A.Butlerov on the nature of chemical compounds and their transformations are discussed.

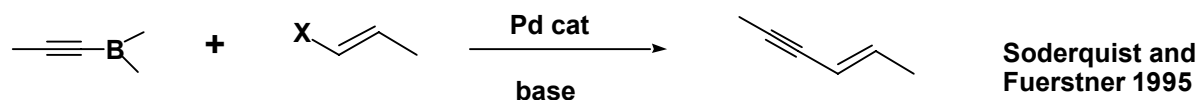
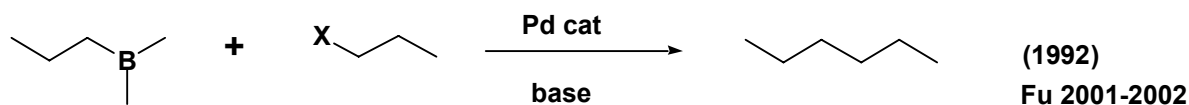
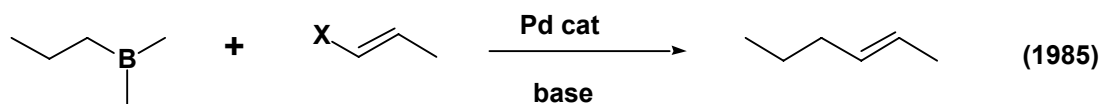
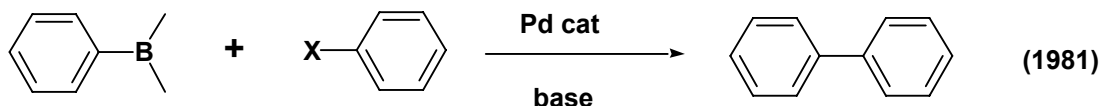
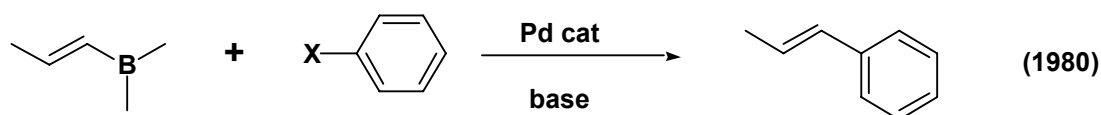
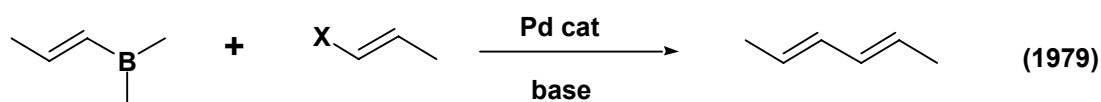
The role of A.Butlerov as the head of Kazan school of chemistry in the development of organic chemistry in Russia in the second half of XIX century is shown.

CROSS-COUPLING REACTIONS OF ORGANOBORON COMPOUNDS

A. Suzuki

Hokkaido University, Sapporo, Japan
asuzuki@eng.hokudai.ac.jp

The palladium-catalyzed cross-coupling reaction between different types of organoboron compounds and various organic halides or triflates in the presence of base provides a powerful and general methodology for the formation of carbon-carbon bonds. The (sp²)C-B compounds (such as aryl- and 1-alkenylboron derivatives) and (sp³)C-B compounds (alkylboron compounds) readily cross-couple with organic electrophiles to give coupled products selectively in high yields. Recently, the (sp)C-B compounds (1-alkynylboron derivatives) have been also observed to react with organic electrophiles to produce expected cross-coupled products. The overview of such coupling reactions is discussed to understand the whole.



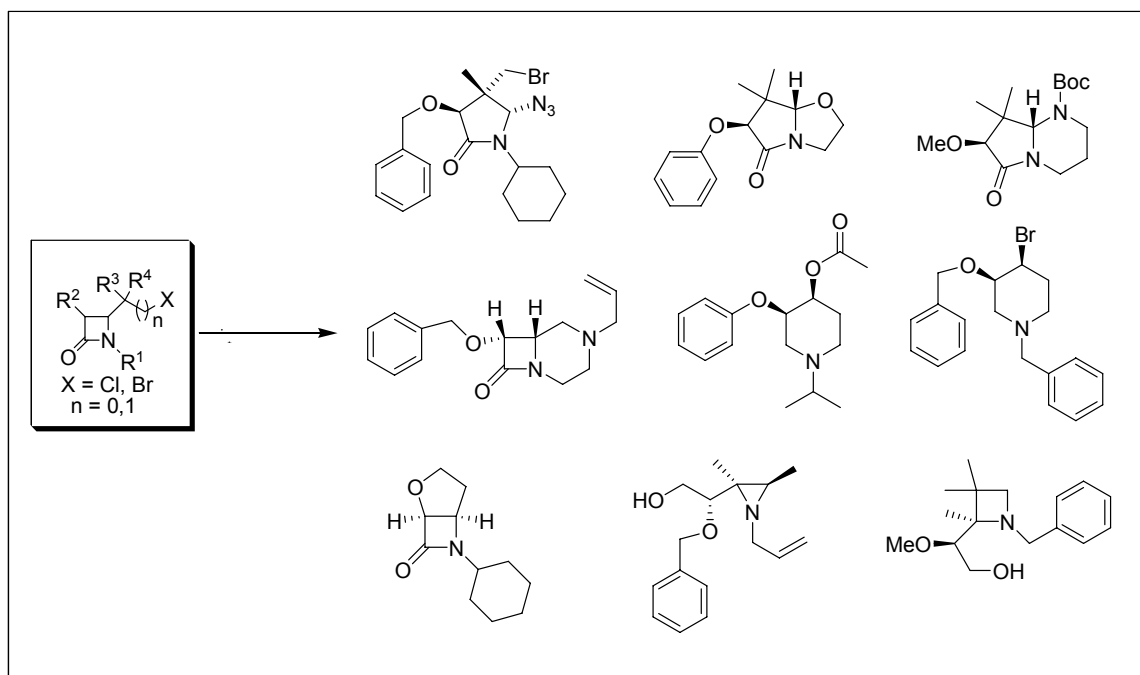
Additionally, current topics of the coupling reaction will be presented briefly.

S. Dekeukeleire
K. Mollet
E. Leemans
M. Dhooghe
N. De Kimpe

RING TRANSFORMATIONS OF FUNCTIONALIZED β -LACTAMS TOWARDS AZAHETEROCYCLES

Department of Sustainable Organic Chemistry and Technology,
Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium
norbert.dekimpe@UGent.be

β -Lactams, substituted with halogens in the side chain at the 4-position, have almost not been studied. The synthetic potential of these specifically halogenated β -lactams will be highlighted by the synthesis of functionalized aziridines, azetidines, pyrrolidines, piperidines, γ -lactams, bicyclic β -lactams and oxolanes. These halogenated azetidinones are suitable for ring transformations via iminium intermediates to afford a whole variety of functionalized γ -lactams, carrying halogens, alkoxy, hydroxy and nitrogen functionalities. The intermediate charged species were intercepted by intramolecular trapping with internal nucleophiles to generate novel bicyclic γ -lactams. This peculiar type of rearrangement was investigated and supported by molecular modeling. The title functionalized β -lactams were suitable substrates for the synthesis of bicyclic β -lactams of the rare 2-oxa-6-azabicyclo[3.2.0]heptan-7-one type, which are known for their antimycotic activities.



A ring expansion of halogenated β -lactams towards functionalized piperidines concerned the first example of the transient generation of 1-azoniabicyclo[2.2.0]hexanes which stereospecifically underwent ring opening to the final azaheterocycles. All rearrangements of these halogenated β -lactams have a broad scope in terms of substitution pattern. These ring expansions allowed the design of suitable, flexible and versatile building blocks for a large variety of azaheterocyclic compounds.

**TRANSITION METAL CATALYSIS, APPLICATION
TO FINE ORGANIC SYNTHESIS, SUCCESS AND
PROBLEMS**

I.P. Beletskaya

Moscow State University, Department of Organic Chemistry, Moscow,
Russia

beletska@org.chem.msu.ru

Various transition metal catalyzed reactions (particularly Pd- and Cu-catalyzed) leading to formation of C-C and C-Heteroatom bonds will be considered. We will mainly focus on the nature of the catalyst, problems of stability, recycle ability and leaching.

NEW HORIZONS IN THE CHEMISTRY OF SMALL RING HETEROCYCLES: DYNAMICS AND COMPLEXATION PHENOMENA AT WORK

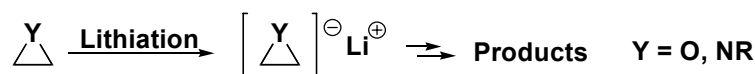
S. Florio

 Universita di Bari, Dipartimento Farmaco-Chimico, Bari, Italy
 florio@farmchim.uniba.it

Making heterocycles by metallation-electrophile trapping of simpler and promptly available parent substances has become a useful synthetic strategy. Emerging points of such a methodology, however, are concerned with the regiochemistry of such a metallation and the stereochemistry of the trapping step.



Lithiation of epoxides and aziridines has been extensively studied over the last ten to fifteen years. Contributions from a number of research groups worldwide have demonstrated that $\square$ -lithiation, leading to oxiranyl- and aziridinylolithiums and their very rich chemistry, may compete with $\square$ -lithiation, ending up with the formation of allylic alcohols or amines, and *ortho* and *lateral* lithiation in the case of aryl derivatives, depending on the structural features of the starting heterocycle other than on the experimental conditions.^{1,2}



The present lecture will focus on the lithiation of epoxides and aziridines to demonstrate that the regio and the stereoselectivity of the metallation reaction depend upon various factors including the solvent coordinating ability, temperature, reaction time, carbons and nitrogen ring substitution as well as upon dynamics and complexation phenomena.³ Studies of Multinuclear and Multidimensional Magnetic Resonance Spectroscopy and Dynamic NMR have been used to shed light on the structural features of such reactive intermediates, on their reaction mechanisms and to plan stereoselective syntheses of functionalized epoxides and aziridines and substances derived by their synthetic elaboration.⁴

References:

1. Aziridines and Epoxides in Organic Synthesis, Yudin, A. K.(Ed), Wiley&VCH, **2006**, 172-179. Oxiranyl and Aziridinyl Anions as Reactive Intermediates in Synthetic Organic Chemistry, Tetrahedron Symposia in Print, Florio, S. (Ed.), **2003**, 9683. Hodgson, D. M.; Bray, C. D.; Humphreys, P. G. Synlett **2006**, 1-22.
2. Capriati, V.; Florio, S.; Salomone, A. "Oxiranyllithiums as chiral Synthons for Asymmetric Synthesis" Chapt. 4 in "Stereochemical Aspects of Organolithium Compounds", Ed. Gawley, R. E. Vol. 26 in "Topics in Stereochemistry" Ed. Siegel, J. S., Verlag Helvetica Acta, Zurich, **2010**, pp 135-164.
3. Florio, S.; Luisi, R. "Aziridinyl Anions: Generation, Reactivity and Use in Modern Synthetic Chemistry" *Chem. Rev.* **2010**, 110, 5128
4. Capriati, V.; Florio, S.; Luisi, R.; Musio, B. *Org. Lett.* **2005**, 7, 3749; Luisi, R.; Capriati, V. Di Cunto, P.; Florio, S.; Mansueto, R. *Org. Lett.* **2007**, 9, 3295; Luisi, R.; Giovine, A.; Florio, S. *Chem. Eur. J.* **2010**, 16, 2683; Dammacco, M.; Degennaro, L.; Florio, S.; Luisi, R.; Musio, B.; Altomare, A. *J. Org. Chem.* **2009**, 74, 6319; de Ceglie, M. C.; Musio, B. Affortunato, F.; Moliterni, A.; Altomare, A.; Florio, S.; Luisi, R. *Chem. Eur. J.* **2011**, 17, 286.

**STREAMLINING ORGANIC SYNTHESIS FOR THE
21ST CENTURY**

R.W. Hoffmann

The Philipps-Universität, Fachbereich Chemie, Marburg, Germany
rwhe@chemie.uni-marburg.de

In the multistep synthesis of fine chemicals and of pharmaceuticals every step generates a substantial amount of undesired coproducts and waste. Hence, streamlining of multistep syntheses is a key factor in rendering synthesis sustainable. Streamlining means to avoid non-essential steps in synthesis. The possibilities and strategies to attain this goal will be illustrated with examples from multistep natural products synthesis. The potential of biomimetic synthesis, of chemoselective methods, of permutation of steps, and of cascade reactions will be discussed in this context.

**MODERN TRENDS IN THE EVOLUTION OF THE
THEORY OF CHEMICAL STRUCTURE.
FROM A.M. BUTLEROV TO THE PRESENT TIME**

V.I. Minkin

Institute of Physical & Organic Chemistry, Southern Federal
University, Rostov on Don, Russia
minkin@ipoc.sfedu.ru

At the turn of 19th and 20th centuries the classical theory of chemical structure based on the concepts of tetravalency of a carbon atom, its capacity to form chain and cyclic compounds and the fundamental prediction made by A. M. Butlerov on that only one rational formula is possible for each compound gained development in two principal directions. The first one was concerned with recognition of the role of spatial molecular structure (J. H. van't Hoff), whereas another one relates to the concept of electron pairs (G. Lewis) and establishment of the electronic nature of chemical bonds as corroborated by the advent of quantum mechanics.

In the report, main stages of the development of the electronic theory of chemical structure are considered along with characterization of discovered novel types of chemical bonds (multicenter, secondary and mechanical, charge-shift bonds) and evolution is analyzed of the conceptual arsenal of modern chemistry including such notions as valency, coordination, aromaticity, oxidation numbers, isomerism, electromerism and other. Special attention is given to non-classical organic and organometallic compounds with non-standard coordination and geometries. The peculiar structural organization of these compounds falls outside the scope of the classical theory of chemical structure and requires introduction of new notions of hypervalency and hypercoordination, dynamical molecular structure and other. Quantum chemistry, in general, and orbital analysis, in particular, serve as the main and the most efficient theoretical tools for the analysis of such type compounds and the topological theory of distribution of electronic density (QTAIM) provides for gaining deepest insight into the nature of bonding.

A good number of principal notions of the theoretical structural chemistry, e.g. valency, aromaticity, oxidation number, including the central notion of chemical bond cannot be physically unambiguously determined, but it is these and other similar notions which compose the working language of modern theoretical chemistry, a branch of science rested on the basis of the classical theory of chemical structure.

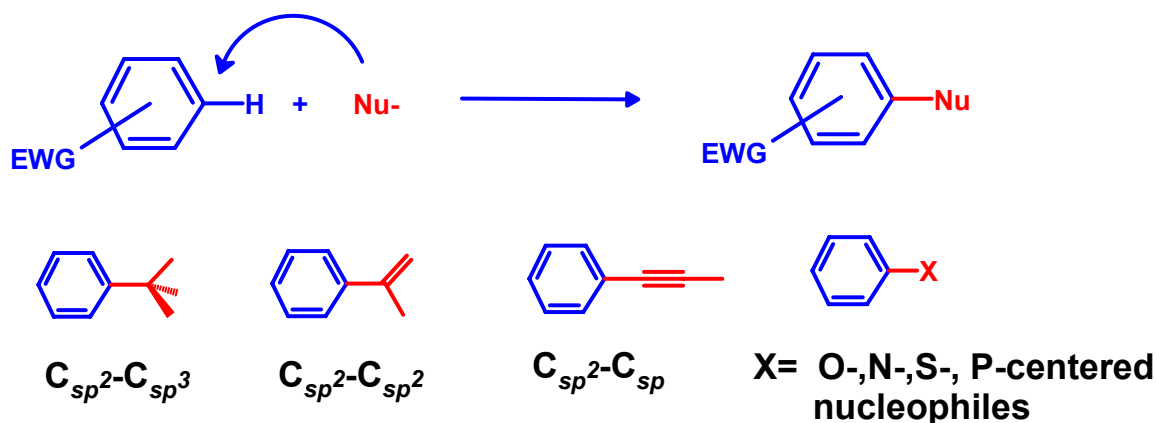
NEW APPROACHES TO MODIFICATION OF C-H BONDS IN ARENES BY ACTION OF NUCLEOPHILIC REAGENTS

V.N. Charushin
O.N. Chupakhin

I.Ya. Postovsky Institute of Organic Synthesis, Yekaterinburg, Russia
charushin@ios.uran.ru

Aromatic compounds are vulnerable for all kind of substitution reactions, initiated by either electrophilic or nucleophilic reagents. In particular, electrophilic aromatic substitution of hydrogen is a well-developed synthetic procedure, in which the cationic nature of intermediate σ^H -adducts facilitates elimination of a proton from the $C(sp^3)$ -H bond, thus enabling the system to restore the lost aromaticity.

Modification of C-H bonds in arenes can also be achieved through the nucleophilic displacement of hydrogen (S_N^H) in π -deficient aromatic compounds. As for reagents for the S_N^H reactions are concerned, they involve a great deal of C-, O-, N-, P- and S-centered nucleophiles, halogenides, peroxides, etc., thus enabling one to perform nucleophilic alkylation, alkenylation, alkynylation, amino- and hydroxyarylation, hetarylation, amination, hydroxylation, alkoxylation, cyanation, halogenation, as well as carboranylation, ferrocenylation and other types of reactions.



Indeed, the data accumulated in the literature during the last two decades demonstrate a common character of the S_N^H reactions, as a fundamental property of aromatic compounds.¹⁻⁴ The S_N^H reactions undoubtedly belong to the key chemical processes, which provide a good complimentary basis for all kind of cross-couplings and other types of nucleophilic displacement reactions.

References:

1. O.N. Chupakhin, V.N. Charushin, H. C. van der Plas. Nucleophilic Aromatic Substitution of Hydrogen. New York: Academic Press, 1994, 368 pp.
2. M. Makosza. Nucleophilic substitution of hydrogen in electron-deficient arenes, a general process of great practical value. *Chem. Soc. Rev.*, 2010, vol. 39, p. 2855-2868.
3. V.N. Charushin, O.N. Chupakhin. S_N^H Methodology and New Approaches to Condensed Heterocyclic Systems, *Pure and Applied Chemistry*, 2004, vol. 76, No. 9, p. 1621-1631.
4. V.N. Charushin, O.N. Chupakhin. Nucleophilic aromatic substitution of hydrogen and related reactions. *Mendeleev Communications*, 2007, vol. 17, p. 249-254.

The work was financially supported by the State Program for Supporting of Leading Scientific Schools of the Russian Federation (grant NSh-65261.2010.3).

REVISITING BUTLEROV'S SUGAR HYPOTHESIS ON ITS 150TH BIRTHDAY

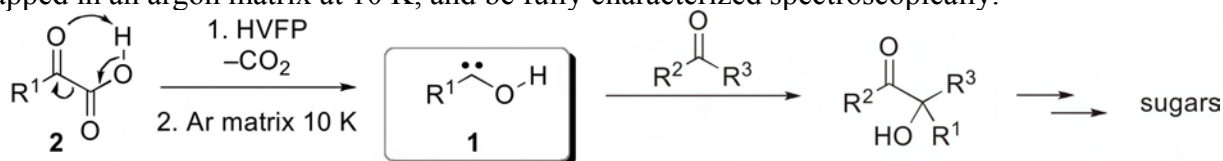
P.R. Schreiner

Justus-Liebig University, Institute of Organic Chemistry, Giessen, Germany
prs@org.chemie.uni-giessen.de

The formose (*formaldehyde gives aldose*) reaction, discovered by A. Butlerov in 1861, describes the formation of simple sugars through the oligomerization of formaldehyde in water in the presence of $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$.^[1] Yet, the initial condensation of two formaldehyde molecules, despite numerous proposals is a mechanistic riddle to date.^[2] This has been recognized early on by Breslow who states that “*the active form of formaldehyde or some other ill-defined species is unknown.*”^[3] Hydroxycarbenes ($\text{R}-\text{C}-\text{OH}$, **1**, cf. Scheme) were suggested as these key species but they had not been prepared until 2008, when we were able to synthesize this new class of compounds through broadly applicable CO_2 extrusion from α -keto carboxylic acids.^[4]

Apart from their potential involvement in the chemistry of life,^[5] hydroxycarbenes are prototypical donor-substituted carbenes that play a fundamental role in the class of synthetically valuable heterosubstituted carbenes as reagents and metal ligands. All attempts to prepare free hydroxycarbenes through, e.g., thermal decomposition of Fischer carbenes have failed.^[6] The parent hydroxycarbene, **1a** ($\text{R}^1=\text{H}$) also plays an important role in deciphering the organic chemistry of small organic molecules in prebiotic earth and extraterrestrial environments because **1a** is also *implied* in the thermal decomposition of glyoxylic acid (**2a**, $\text{R}^1=\text{H}$) that also gives rise to formic acid, CO , CO_2 , H_2 , and H_2O .^[4a]

In the present talk we show that hydroxycarbenes **1** can be generated in a general fashion ($\text{R}^1=\text{OH}$, CH_3 , OCH_3 , Ar) thermally through high-vacuum flash pyrolysis (HVFP), subsequently be trapped in an argon matrix at 10 K, and be fully characterized spectroscopically.



The lecture will present firm experimental as well as high-level computational evidence for the first successful preparations of carbenes of type **1**, and will present their reactions that largely depend on the nature of the substituent R. For instance, while **1a** ($\text{R}^1=\text{H}$) disappears within only 2 h through *H-tunneling* under a very high barrier (ca. 30 kcal mol⁻¹), **1b** ($\text{R}^1=\text{OH}$) survives under matrix isolation conditions for at least several days.^[7] Some of the structural as well as energetic details for the formation of sugars through the *formose* reaction will also be revealed, specifically, the reaction of **1** with simple carbonyls to give α -hydroxy carbonyl derivatives, and eventually polyols (sugars).

References:

- [1] A. C. R. Butlerov, *Acad. Sci.* 1861, 53, 145-147.
- [2] A. N. Simonov, O. P. Pestunova, L. G. Matvienko, V. N. Parmon, *Kinetics and Catalysis* 2007, 48, 245-254.
- [3] R. Breslow, *Tetrahedron Lett.* 1959, 1, 22-26.
- [4] a) P.R. Schreiner, H. P. Reisenauer, F.C. Pickard, A.C. Simmonett, W.D. Allen, E. Mátyus, A.G. Császár, *Nature* 2008, 453, 906-910; b) D. Gerbig, H.P. Reisenauer, C.-H. Wu, D. Ley, W.D. Allen, P.R. Schreiner, *J. Am. Chem. Soc.* 2010, 132, 7273-7275; c) D. Gerbig, D. Ley, H.P. Reisenauer, P.R. Schreiner, *Beilstein J. Org. Chem.* 2010, 6, in press.
- [5] A.F. Jalbout, L. Abrell, L. Adamowicz, R. Polt, A. J. Apponi, L.M. Ziurys, *Astrobiology* 2007, 7, 433-442.
- [6] M.A. Sierra, *Chem. Rev.* 2000, 100, 3591-3637.
- [7] P.R. Schreiner, H.P. Reisenauer, *Angew. Chem. Int. Ed.* 2008, 47, 7071-7074.

**“WHY AND HOW DID NATURE SELECT
PHOSPHORUS FOR ITS DOMINANT ROLES IN
BIOLOGY?”**

G.M. Blackburn

Krebs Institute, Department of Molecular Biology, Sheffield
University, UK
g.m.blackburn@sheffield.ac.uk

Life is pervaded by phosphorus – as esters and anhydrides of phosphoric acid. These fulfil vital roles in the structure of biopolymers, vitamins and cofactors, membranes, storage of energy, signalling, and many further roles. It is remarkable that the activities of 60% of all human proteins are modulated because of phosphorylation by kinases and dephosphorylation by phosphatases. Indeed, the regulation of such control by inhibitors of such enzymes is a major, current target for biotechnology and medicine. The sequence of the human genome shows that we each have some 500 kinases in our enzyme repertoire! And yet, transfer of the phosphoryl group is one of the most difficult of all life-supporting reactions. The effective acceleration of phosphate ester hydrolysis by monoesterases has been estimated as close to 10^{21} . Therefore such biological catalysis has become the subject of intensive mechanistic and structural investigation at the present time.

So, the first question I have to address is: “Was there an alternative to phosphorus in the evolution of primitive biology?”. Recent claims to have converted bacteria to grow on arsenate instead of phosphate are wide of the mark. A survey of the properties of the mono- and di-esters of oxyacids of various elements readily establishes that there is *no* alternative candidate. Phosphorus is unique: Unique on Earth and therefore Unique in the Universe.

The second question to be addressed follows: “How was it possible for catalysis of such enormous efficiency to have evolved from primordial beginnings?”. My work in this field began in Cambridge in 1964 where I used highly radioactive ^{32}P -phosphate to label an antibiotic for studies in Francis Crick’s laboratory using ribosomes. Today, the protein structural work of 3 Nobel Laureates has revealed just how that experiment worked in atomic detail. I next moved into enzyme studies, first using organic synthesis to make stable analogues of biological phosphates, and then enzymes to evaluate their success – or otherwise! My present work on biological catalysis calls for high resolution ^{19}F NMR in Sheffield to analyse the trifluoromagnesate (MgF_3^-) and tetrafluoroaluminate (AlF_4^-) complexes of phosphoglucomutase, phosphoserine phosphatase, phosphoglycerate kinase and other phosphate transfer enzymes coupled with protein crystallography in Grenoble. It has identified mechanisms for enzyme catalysed phosphoryl transfer at atomic resolution. Our results reveal subtle features of the recognition and very tight binding of these enzymes to the transition states of the reactions they catalyze. I shall argue that the “rules” of catalysis of phosphoryl transfer that emerge are amazingly simple.

On the primitive Earth, Evolution was confronted by a solvable task to use phosphorus!

**CYCLOADDITION REACTIONS IN THE CHEMISTRY
OF HEAVY CARBENE ANALOGS**

M.P. Egorov
O.M. Nefedov

N.D. Zelinsky Institute of Organic Chemistry of Russian Academy of
Sciences, Moscow, Russia

High reactive carbene analogs of Group 14 elements are the key intermediates of the reactions of organosilicon, organogermanium, and organotin compounds including industrial important. Physico-chemical methods are widely used now to study structure, reactivity, and reaction mechanisms of carbene analogs.

Here we report on the kinetics and reaction mechanisms of short-lived silylenes, germylenes, and stannylenes with alkenes, 1,3-dienes, 1,3,5-trienes, alkynes, and aromatics studied by laser flash photolysis in the gas phase, matrix isolation as well as DFT and ab initio quantum chemical calculations. The main trends in reactivity and mechanisms of cycloaddition reactions of carbene analogs will be discussed.

This work was supported in part by the RFBR (project No. 09-03-00475), the President of the Russian Federation (Presidential program for support of leading research schools, Grant NSh-8242.2010.3), and the Russian Academy of Sciences (Program OX-01).

**THE ORGANIC LIGANDS AS A TOOL FOR THE
DIRECTED SYNTHESIS POLYNUCLEAR METAL
CONTAINING MOLECULES WITH SPECIFIC
PHYSICAL PROPERTIES**

I.L. Eremenko
A.A. Sidorov

N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian
Academy of Sciences, Moscow, Russia
sidorov@igic.ras.ru

Formation of complex polynuclear complexes with the same or different metal atoms requires a different approach. If, in case of molecular structures in which the location of the metal centers, their electronic structure and packing in the crystal determines the physical properties of molecular materials (eg, magnetic, optical, catalytic), it is not always a simple self-assembly of such systems from simple components allow one to solve the problem of obtaining materials with desired characteristics. Here the correct choice of organic ligand-blocks often determines the outcome. Therefore, the organic component of the complex may be crucial in predicting how the synthetic methods and the final structure. It should also add that even the usual characteristics of a substance as its solubility in organic solvents, which is essential for certain future manufacturing operations, volatility, hydrolysis resistance and other can be given in the selection of the organic units in the assembly of polynuclear metal structures

The report examines examples of the use of various organic ligand-blocks in the chemical assembly of polynuclear metal architectures. Shows how to generate coordination magnetically active polymers, fluorescent clusters, polynuclear molecular precursors for various kinds of inorganic materials in the form of nanoscale films and crystals.

This study was supported by the Russian Foundation for Basic Research, the Council on Grants of the President of the Russian Federation, the State Department of Science and Innovation Policy, the Ministry of Education and Science of the Russian Federation, the Russian Academy of Sciences.

**ALEKSANDR MIKHAILOVICH BUTLEROV: AN
APPRECIATION**

C.E. McKenna

University of Southern California, Department of Chemistry,
Los Angeles, California, USA
mckenna@usc.edu

With the enormous and ever accelerating acquisition of chemical knowledge over the past century and one decade into this one, that the work of a particular chemist carried out some 150 years ago could continue to impact modern research and teaching in organic chemistry is extraordinary. A perspective on A.M. Butlerov's links and relevance to contemporary chemical science will be presented.

Section 1.

Theoretical Organic Chemistry: Bonding, Structure and Reactivity

Химикам



Оборудование

- автоматические титраторы, pH-метры
- весы, анализаторы влагосодержания
- вытяжные шкафы
- дигесторы, в т.ч. СВЧ
- дилутер-диспенсер: разведение 1:50'000 за шаг, точность 1%
- дистилляторы, бидистилляторы
- мешалки верхнеприводные до 100 л
- мешалки магнитные, плитки нагревательные
- поляриметры, рефрактометры, плотномеры
- реакторы химические, в т.ч. многоступенчатые
- роторные гомогенизаторы/диспергаторы: для объемов от 1 мл
- роторные испарители от 50 мл до 20 л; насосы вакуумные
- системы очистки воды до 1го типа
- спектрофотометр 190 – 119 нм (УФ, ИК, видимый диапазон)
- сушильные шкафы, в т.ч. вакуумные
- термостаты жидкостные: от -100 до 200 °C
- шейкеры, центрифуги



Расходные материалы

- расходка для ТСХ и ВЭЖХ
- горелки
- кюветы
- перчатки
- фильтры
- стекло Pyrex
- шприцы и степперы Hamilton

Реактивы

- ацетонитрил для ВЭЖХ и синтеза
- гидраналы
- растворители для ВЭЖХ
- реактивы для синтеза
- красители, индикаторы
- соли, буферные растворы
- волюметрические растворы, ГСО



Aldrich•Binder•Haake•Hamilton•Hanna•Heidolph•Hellma•Huber•IKA•J.T. Baker•Jenway•Macherey Nagel
Merck •Mettler Toledo•Miele•Millipore•Panreac•Pyrex•Riedel de Haen•Sigma•Supelco•Vacuubrand•Whatman

Диазм | www.dia-m.ru
Офис в Москве: ул. Космонавта Волкова, 10. Тел.: (495) 745-0508 | факс: (495) 745-0509 | e-mail: info@dia-m.ru
Офис в Новосибирске: пр. Ак. Лаврентьева, 6/1 | Тел/факс: (383) 328-0048 | e-mail: nsk@dia-m.ru
Офис в Казани: Оренбургский тракт 20, оф. 217 | Тел/факс: (843) 277-6040 | e-mail: kazan@dia-m.ru

TOPOLOGICAL PARADOXES OF THE STRUCTURAL THEORY

E.V. Babaev

Moscow State University, Chemistry Department, Moscow, Russia
babaev@org.chem.msu.ru

The classical structural theory is still the “daily language” in synthetic chemistry. Its’ essence follows from the language of graph theory: for any set of **K** molecules, having in total **V** atoms and **E** bonds (obtained by arranging **2E** valence electrons into **E** pairs, i.e. into $(2c, 2e)$ -bonds) one can construct certain molecular graph with **V** vertices, **E** edges, and **K** components. This lead to simple balance *eqn (1)* for any molecule with localized bonds:

$$V - E = K - C \quad (1).$$

Here **C** – is the “cyclicity” (number of independent cycles of size ≥ 3) in molecular graph. Shifting from graphs to 2D space-fill molecular models, the value **C** is equal to number of handles (“holes”) in the 2D surface of molecule. The *eqn (1)* can be easily expanded for multiple bonds (“2-mebered” cycles) and even to lone pairs (loops, a sort of “1-membered” cycle) without loss of generality.

As was early shown by author [1-3], switch from graphs to *hypergraphs* (and from 2D surfaces to *pseudo-manifolds*) change *eqn (1)* to fundamentally new balance *eqn (2)*:

$$2(V - E) = 2(K - C) + M - L \quad (2).$$

Here **M** is index of multi-centered bonding, and **L** – the number of free radical centers. (E.g. **L**=1 for atom H, **M**=0 for molecule H_2 , **M**=1 for cation-radical H_2^+ , **M**=2 for cations H_3^+ , CH_5^+ or allyl).

Importantly, the left part of *eqn (2)* correspond to *particles* (atoms **V** and electrons **2E**), whereas right part of *eqn (2)* is their *topology*. Evidently, in any reaction the number of particles (ΔV and ΔE) is unchanged (material balance). Consequently, their overall topology is also unchanged, *eqn (3)*:

$$2(\Delta K - \Delta C) + \Delta M - \Delta L = 0 \quad (3).$$

Actually, *eqn (3)* is a new “Topology Conservation Law” for chemistry. Paradoxical consequence of *eqn (3)* is that our common chemical entities – cycles **C**, components **K**, free radical centers **L** and multi-centered bonds **M** – can not (dis)appear traceless, but only interchange to one another.

References:

- [1]. Babaev E.V. Intuitive Chemical Topology Concepts. / In: Chemical Topology: Introduction and Fundamentals. Eds. Bonchev D., Rouvray R., 1999, Gordon & Breach Publ., Reading, pp.167-264.
- [2]. Babaev E.V. The invariance of molecular topology in chemical reactions. / In: Graph theoretical approaches to chemical reactivity. Eds. Bonchev D., Mekenyan O. (Seria: Understanding Chemical Reactivity, Vol.9). Kluwer Academic Publ., Dordrecht-Boston-London, 1994, pp. 209-220.
- [3]. <http://www.chem.msu.ru/eng/misc/babaev/match/>

**THE "VALENCE STICK" IN ORGANIC MOLECULES:
FROM BUTLEROV TO MODERN UNDERSTANDING
THE NATURE OF CHEMICAL BOND**

M.Yu. Antipin

Institute of Organoelement Compounds, Russian Academy of
Sciences, Moscow, Russia
m_antipin@yahoo.com

Professor A. Butlerov was the first Russian chemist who understood in a full mere the meaning of the "valence stick" in organic compounds as an indication of some specific chemical interactions between atoms forming a molecule. From that time many other more and more sophisticated theories of the chemical structure were developed that explained successfully the spatial and electronic structure of myriads of molecules of interest in terms of chemical bonds (interactions) between atoms. Nowadays, modern very complicated quantum chemical molecular calculations and corresponding high accuracy experimental data are actively used in studies of chemical bonding. Amongst such calculations the Bader's "Quantum Theory of Atoms in Molecules" (QTAIM) is often applied for many organic, organoelement and other compounds.

The QTAIM is based on analysis the topology of the full electron density distribution (EDD) function of the molecular system, and allows one to describe different characteristics of the chemical bonds in terms of observable (in contrast to the molecular orbital calculations) EDD characteristics. In particular, one of the most important topological features of the chemical bond is the so called "bond path" (*bp*) – the line (not necessary the straight one) of the maximum electron density in its 3-dimentional relief between two interacting atoms. The second criteria of a bond is presence of the "bond critical point" (*bcp*) on the *bp*-line. The gradient of the EDD function vanishes in the *bcp*. If both the *bp* and *bcp* between two atoms exist – we have a chemical bond between them according to QTAIM. So, the "valence stick" in this theory attains more physically rigid meaning (as *bp*), and it might not be a straight line but may be curved like "bent bonds" in cyclopropanes, strained cage molecules and some other compounds.

It is also essential that EDD function and its topology may be reconstructed also from the high-resolution single crystal X-ray diffraction data that gives an attractive opportunity to compare directly the theory and experiment during chemical bond analysis. Results of similar analysis of chemical bonding will be demonstrated for a several series of organic and organoelement compounds for which non-typical chemical bonds were observed.

**EXTRAORDINARILY LONG 2.9 Å AND
MULTICENTER C-C BONDS - WHAT IS A
CHEMICAL BOND?**

J.S. Miller

University of Utah, Department of Chemistry, Salt Lake City, USA
jsmiller@chem.utah.edu

Carbon-carbon (CC) bonding is a key essence of organic and biochemistry. The length of a CC bond, *i.e.* 1.54 Å found in the diamond allotrope of carbon, is among the essential information learned by all organic chemistry students. This is the length of a single bond (σ) between sp^3 -hybridized carbons and is the longest of all common CC bonds. Our studies of the $[TCNE]_2^{2-}$ (TCNE = tetracyanoethylene) dimers reveal that 2.90 ± 0.05 Å 2 electron/4 center ($2e^-/4c$) CC bonds are present. Structural, spectroscopic, magnetic and computational data supporting this multicenter formulation will be presented. These unusual bonds lead to unusual physical properties that will be discussed, as will what is a bond? Furthermore, examples of long, multicenter C-C bonds existing for other dianions, *e.g.*, $[cyanil]_2^{2-}$, as well as dications, *e.g.*, $[TTF]_2^{2+}$ (TTF= tetrathiafulvalene), and homo-, *e.g.*, $[tri-t-butylphenalenyl]_2$, and heterodimers *e.g.*, $[TTF \cdots TCNE]$, will be described.

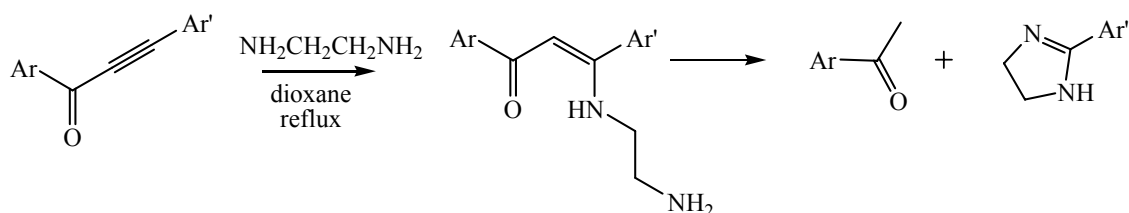
UNEXPECTED CLEAVAGE OF ACETYLENIC
MOIETY IN ALPHA-KETOACETYLENES UNDER
INFLUENCE OF 1,2-DIAMINOETHANE: NEW
ROUTE TO 2-SUBSTITUTED IMIDAZOLINES

S.F. Vasilevskiy¹
M.P. Davydova¹
G.A. Tolstikov²

1 - Institute of Chemical Kinetics and Combustion of the Russian
Academy of Sciences, Novosibirsk, Russia
2 - Novosibirsk Institute of Organic Chemistry of the Russian
Academy of Sciences, Novosibirsk, Russia
vasilev@kinetics.nsc.ru

Although acetylenes are well-recognized as convenient building blocks for many useful transformations for organic synthesis, medicinal chemistry, and materials science, their synthetic potential is far from full utilization of unique reactivity of triple bonds.

For preparing of heterocyclic compounds we used perspective synthetic methodology - reactions of polyfunctional reagents ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, NH_2NH_2 , NH_2OH , $\text{NH}_2\text{-C(=NH)-NH}_2$ etc.) with α -ketoacetylenes [1,2]. Such methodology allow us to prepare some pyrazole, isoxazole, pyrimidine derivatives (these modifications will be presented). But more remarkable transformation we found analyzing of reaction of activated acetylenes with 1,2-diaminoethane



This work presents example of cleavage of $\text{C}\equiv\text{C}$ moiety in α -ketoacetylenes by interaction with 1,2-diaminoethane in boiling dioxane with the formation of corresponding methylaryl ketones (40-50%) and 2R-substituted 4,5-dihydro-1H-imidazoles (40-45%).

We observed and isolated intermediates of above mention reaction – product of addition of 1,2-diaminoethane to triple bond - 3-(2-aminoethylamino)-3-(Ar)-1-(Ar')-prop-2-en-1-ones (10-15%).

This reaction can be considered as a cleavage of $\text{C}\equiv\text{C}$ moiety via disproportionation. Mechanism of these transformations will be discussed.

References:

1. Vasilevsky, S. F., Davydova, M. P., Tolstikov, G. A., *Chem. Heterocycl. Compd.*, **2008**, 44, 1257-1261 (Engl. Transl.)
2. Davydova, M. P., Vasilevsky, S. F., Tolstikov, G. A., *Russ. Chem. Bull., Int. Ed.*, **2011**, 1, 1-2

This work was supported by the Interdisciplinary Grant No.93 of SB of the Russian Academy of Sciences (2009–2011), Grant RFBR No.10-03-00257-a (2010–2012), Grant 5.9.3. of the Russian Academy of Sciences (2009–2011) and the Chemical Service Centre of SB RAS.

**QUANTITATIVE STRUCTURE-PROPERTY
RELATIONSHIPS: RECENT APPROACHES**

V.A. Palyulin
N.S. Zefirov

Moscow State University, Department of Chemistry, Moscow, Russia
vap@org.chem.msu.su

QSAR/QSPR (quantitative structure-activity/property relationships) approaches can be considered as universal techniques for modeling and prediction of numerous properties of chemical compounds and materials. These approaches are based on the correlations of property values with the parameters (descriptors) of chemical structures. The structure-property relationships are evaluated using various statistical methods, artificial neural networks, etc. The developed structure-property model can be used for the prediction of properties of new chemical compounds for which these properties were never studied or even the compounds themselves were never synthesized. A large number of physico-chemical properties were modeled for various organic compounds basing on their structural formulas. Some properties of materials can be predicted as dependent on the structure of small molecules used as additives (e.g. antioxidants). Good results were obtained for the prediction of diffusion coefficients of small molecules in polymers.

Prediction of biological activity for organic compounds is one of the most challenging problems. For that purpose we proposed Molecular Field Topology Analysis (MFTA) which involves the construction of a molecular supergraph (a simple graph such that the molecular graphs of all training set structures can be represented as its subgraphs). A uniform descriptor set is obtained by superimposing each training set structure onto the molecular supergraph. For each supergraph vertex the values of atomic charge, van der Waals radius and other local parameters for the respective atom in a particular structure are assigned. For unoccupied vertices the neutral descriptor values are used. The analysis of the impact of local descriptors on the activity for supergraph positions is highly helpful in the design of new active structures. The developed structural generators in conjunction with MFTA significantly increase the efficiency of the design of active structures.

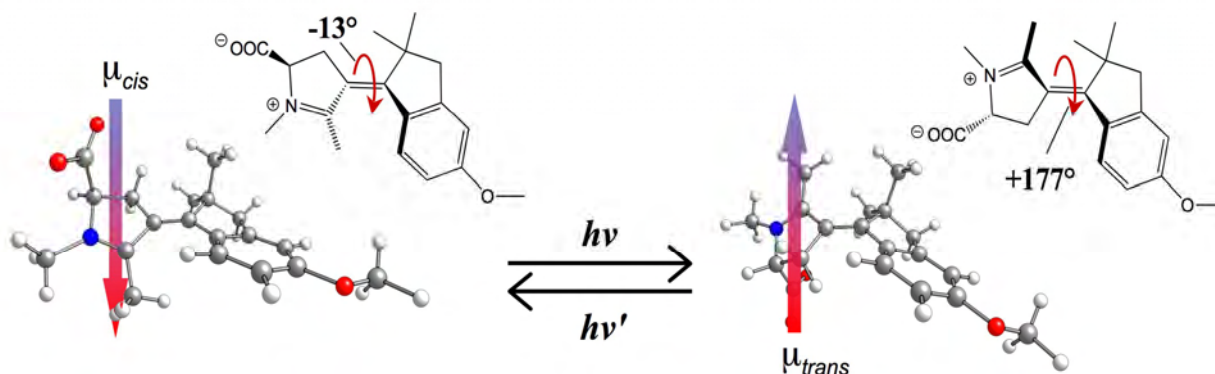
FROM COMPUTATIONAL PHOTOBIOLOGY TO THE DEVELOPMENT OF BIOMIMETIC MOLECULAR DEVICES

M. Olivucci

University of Siena, Department of Chemistry, Siena, Italy
olivucci@unisi.it

During the last few years we have started to explore the possibility of designing and synthesizing molecules that could mimic the photoisomerization of the visual pigment Rhodopsin and, in particular its low-temperature photochromism [1]. When embedded in the opsin cavity the Rhodopsin chromophore (i.e. the protonated Schiff base of retinal) displays an ultrafast and stereoselective photoisomerization with high quantum yield. In order to design a chromophore displaying a similar efficiency in common solvents we have been looking at diverse alkylated Schiff bases featuring a single isomerizable double bond.

In this lecture we show that the indanylidene-pyrroline (NAIP) framework [2-4] provides a computationally and synthetically viable prototype for the development of systems that reproduce the excited state electronic structure and photoisomerization dynamics of Rhodopsin in methanol or water. We will also show that, on the basis of these studies we have been able to achieve systems that, in perspective, can be used as electrostatic switches. In fact, we have been able to design an unprecedented “dipole” switch capable of inverting, reversibly, its ca. 15 D dipole moment upon double bond photoisomerization [5].



References:

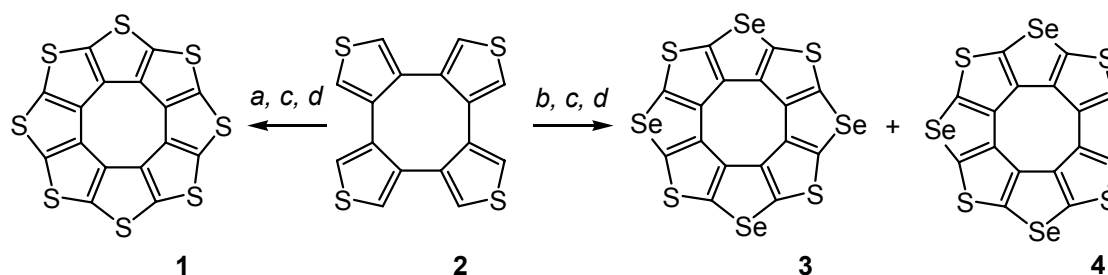
- [1] Shapiro I., Ryazantsev M. N., Frutos L.-M., Ferré N., Lindh R. & Olivucci M. (2011) *J Am Chem Soc* 133:3354-3364.
- [2] Lumento F., Zanirato, V., Fusi, S., Busi, E., Latterini, L., Elisei, F., Sinicropi, A., Andruniów, T., Ferré, N., Basosi, R. & Olivucci, M. (2007) *Angew Chem Int Ed Engl* 46:414-420.
- [3] Sinicropi A., Martin, E., Ryasantsev, M., Helbing, J., Briand, J., Sharma, D., Léonard, J., Haacke, S., Cannizzo, A., Chergui, M., Zanirato, V., Fusi, S., Santoro, F., Basosi, R., Ferré, N. & Olivucci, M. (2008) *Proc. Nat. Acad. Sci. USA* 105:17642-17647.
- [4] Briand J., Bräm, O., Réhault, J., Léonard, J., Cannizzo, A., Chergui, M., Zanirato, V., Olivucci, M., Helbing, J. & Haacke, S. (2010) *Phys Chem Chem Phys* 12:3178 - 3187.
- [5] Melloni A., Rossi Paccani, R., Donati, D., Zanirato, V., Sinicropi, A., Parisi, M. L., Martin, E., Ryazantsev, M., Ding, W. J., Frutos, L. M., Basosi, R., Fusi, S., Latterini, L., Ferré, N. & Olivucci, M. (2010) *J Am Chem Soc* 132:9310-9319.

SULFLOWER AND OTHER CHEMICAL FLOWERS

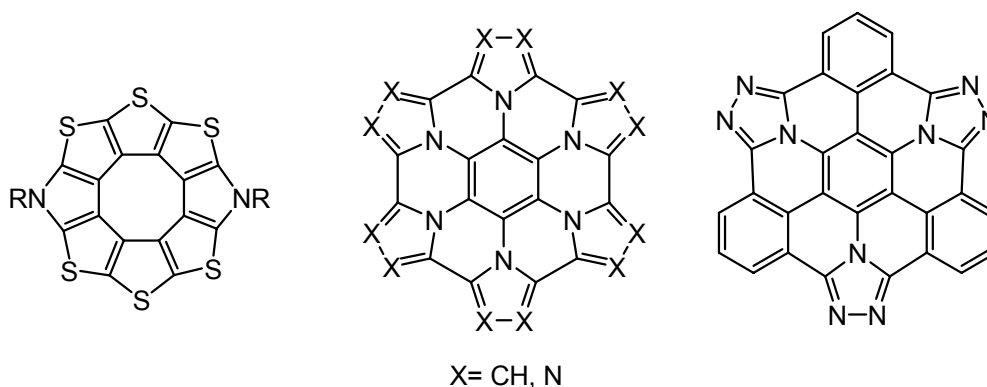
V.G. Nenajdenko

Moscow State University, Department of Chemistry, Moscow, Russia
nen@acylium.chem.msu.ru

Recently we have described synthesis of the first fully heterocyclic circulene Sulflower **1**, which is a new type of heterocyclic molecules. The properties of Sulflower were comprehensively studied, including fabrication of field-effect transistors. Reaction of initial tetrathiophene **2** with selenium under standard and variously modified conditions leads to formation of target sulfur-selenium circulene **3** and "dehydrohelicene" **4**. The synthesis of others heterocyclic circulenes is now in progress.



- a) 16 eq. LDA + 16 eq. sulfur, Et₂O
 b) 16 eq. LDA + 16 eq. selenium, Et₂O
 c) HCl
 d) vacuum sublimation



**INTERIONIC INTERACTIONS AND THEIR IMPACT
ON STRUCTURE AND PROPERTIES OF SOME
IMIDAZOLIUM- AND PHOSPHONIUM-BASED IONIC
LIQUIDS**

S.A. Katsyuba¹
E.E. Zvereva¹
T.P. Gryaznova¹
P.J. Dyson²
V.V. Ermolaev¹
V.A. Miluykov¹
O.G. Sinyashin¹

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan
Scientific Centre of the Russian Academy of Sciences, Department of
Physical Chemistry, Kazan, Russia

2 - Ecole Polytechnique Federale de Lausanne (EPFL), Institut des
Sciences et Ingenierie Chimiques, Lausanne, Switzerland
katsyuba@iopc.ru

Density functional theory combined with X-ray crystallography, IR and NMR spectroscopy has been used to study interionic interactions and structure of several imidazolium- and phosphonium-based ionic liquids (ILs).

Multiple short contacts between the counterions are typical for the both kinds of ILs in crystals, melts and solutions. Various modes of ion pairing and their spectral manifestations have been found; the CH-groups of the imidazolium ring form hydrogen bonds with the halides and such weakly-coordinating anions as BF_4^- , PF_6^- , Tf_2N^- , while only halides are able to pronounced H-bonding with the CH-groups of tetraalkylphosphonium cations. This fundamental difference between the halides and the perfluoro anions causes essential differences in structure of the corresponding ILs. Namely, ILs based on the weakly-coordinating anions can be regarded as consisting of the ion pairs, while both the imidazolium and the phosphonium halides represent a network of the counterions bonded by strongly anti-cooperative hydrogen bonds.

It is demonstrated that neither the energy of ion pairing nor specific capability to hydrogen bond formation of various ILs explain the differences in their melting points. However the analysis of potential energy surfaces of ion pairs within the framework of a simple anharmonic oscillator model allows rationalization and prediction of melting points ($T_{\text{m.p.}}$) and heat capacities (C_p) of ILs. Possible influence of the cation conformation on C_p and $T_{\text{m.p.}}$ of the ILs is discussed in the context of this theoretical model.

Financial support of Switzerland-Russia S&T Cooperation Program is gratefully acknowledged

**CHEMILUMINESCENCE FROM ORGANIC
REACTIONS. FUNDAMENTALS AND APPLIED
ASPECTS**

D.V. Kazakov

Institute of Organic Chemistry, Ufa Scientific Center of the RAS, Ufa,
Russia
dkazakov@anrb.ru

The process of transforming chemical energy into light emission has been an attractive topic of intensive research over the years, in view of its fundamental mechanistic significance and the diversity of practical applications. Bio- and chemiluminescence (CL), the emission of light in biochemical and chemical reaction, is widely used in technology, biology and medicine. On the other hand, the in-depth knowledge of CL systems paves the way for understanding the otherwise difficult to explore “dark” processes associated with such reactions.

In this report, important role of CL in organic chemistry is discussed. Brightly emitting organic peroxides-based biological systems are illustrated. Relation between fundamental significance of CL phenomenon and its practical applications in medicine and biochemistry is demonstrated by the reactions of cyclic peroxides 1,2-dioxetanes, a kind of energy storage system. Special attention is given to our recent results obtained in the field of chemistry and chemiluminescence of high-energy organic peroxides:

- A new type of chemiexcitation for liquid-phase organic reactions is reported (oxygen-transfer chemiluminescence) which is realized during oxidation of saturated hydrocarbons by dioxiranes.¹ A novel mechanisms of light generation in the reactions of peroxides with luminescent lanthanide complexes are described.

- A key role of singlet oxygen, oxidant and important intermediate of chemical and biochemical processes, in freshly discovered light emitting peroxide reactions is demonstrated.^{2,3}

- A new promising direction of research is introduced: chemistry and chemiluminescence of pharmacologically valuable organic peroxides – 1,2,4,5-tetroxanes and 1,2,4-trioxolanes. Achievements and applied perspectives of the area are discussed.⁴

References:

1. Kazakov D.V., Barzilova A.B., Kazakov V.P., *Chem. Commun.*, 2001, 191.
2. Adam W., Kazakov D.V., Kazakov V.P., *Chem. Rev.*, 2005, **105**, 3371.
3. Kazakov D.V., Kazakov V.P., Maistrenko G.Ya., Mal'zev D.V., Schmidt R., *J. Phys. Chem. A*, 2007, **111**, 4267.
4. Kazakov D.V., Kazakova O. B., Ishmuratov G.Yu., Terent'ev A.O., Nikishin G.I., Tolstikov G.A. *Dokl. Ak. Nauk*, 2011, **436**, 774.

This work was supported by RFFI, project 09-03-00831a.

REACTIVITY OF THIOPHENOLATE TOWARD CHALCOGENADIAZOLES

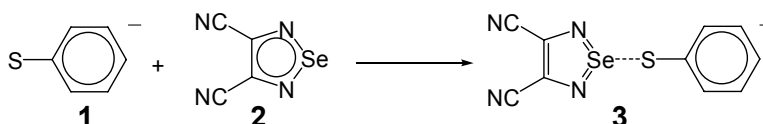
N.P. Gritsan¹
E.A. Suturina¹
A.V. Zibarev²

1 - Institute of Chemical Kinetics and Combustion

2 - Novosibirsk Institute of Organic Chemistry

gritsan@kinetics.nsc.ru

Recently, we discovered that reaction of **1** with 3,4-dicyano-1,2,5-selenadiazole (**2**) gives the product of hypercoordination at the Se center (**3**) isolated in the form of the salt [K(18-crown-6)][**3**] (**4**). The latter type of reactivity has never been observed previously. The X-ray structure of **4** revealed that the Se-S distance in **3** (2.722 Å) is *ca.* 0.5 Å longer than the sum of the covalent radii, but *ca.* 1 Å shorter than the sum of VdW radii of Se and S.



To estimate the scope of this new reaction, thermodynamics and kinetics of the interaction between **1** and various 1,2,5-chalcogenadiazoles (chalcogen: S, Se, Te) were theoretically investigated at the DFT level using B3LYP, M06-2X and B97-D functionals. The general character of the discussed hypercoordination in the case of heavier chalcogens has been predicted. According to the QTAIM and NBO analysis, the Se-S bond in **3** is a donor-acceptor one. Its formation leads to transfer of ~40% of negative charge from **1** onto the heterocycle.

For various **1** / chalcogenadiazole reaction systems, thermodynamics and kinetics of electron transfer reaction were also theoretically studied to rationalize interchalcogen hypercoordination vs. reduction to π -RA dichotomy.

References:

1. I.Yu. Bagryanskaya, Yu.V. Gatilov et al. *Eur. J. Inorg. Chem.* **2007**, 4751

The authors are grateful to the RFBR (project 10-03-00735) and the Russian Ministry of Education and Science (project. 14.740.11.0716) for financial support.

THE PECULIARITIES OF THE ELECTRONIC STRUCTURE OF ORGANOSELENIUM COMPOUNDS AND ITS COMPLEXES WITH DIFFERENT ACCEPTORS

T.I. Madzhidov¹
G.A. Chmutova¹
A. Martin Pendas²

1 - Kazan Federal University, Chemical Institute of A.M. Butlerov,
Kazan, Russia

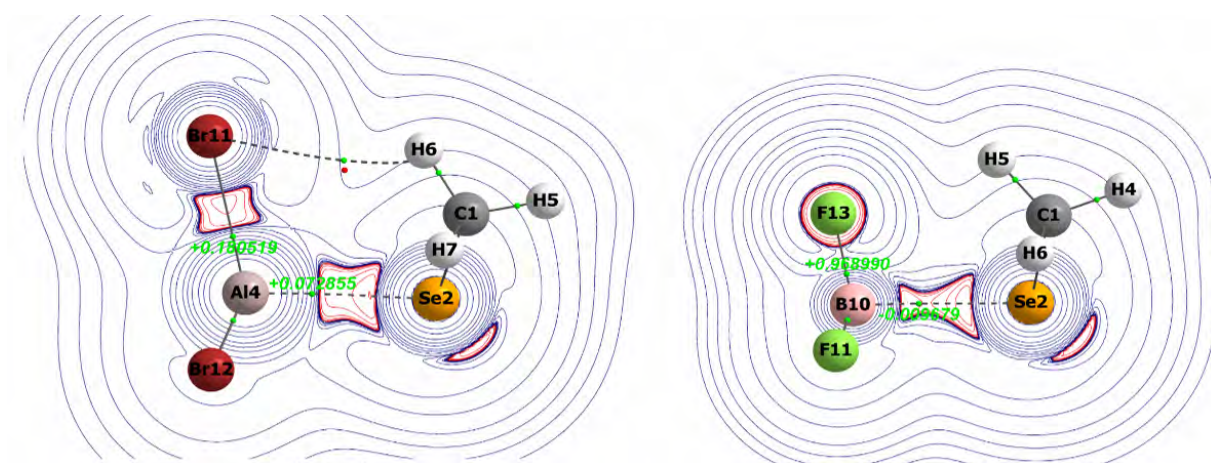
2 - University of Oviedo, Department of Physical and Analytical
Chemistry, Oviedo, Spain
 tmadzhidov@gmail.com

The study of the electronic density distribution in organoselenium compounds and its complexes with modern quantum-chemical approaches (Quantum Theory of Atoms in Molecules, Interacting Quantum Atom) revealed specifics of selenium atom as electron donor.

Classic electrostatic term of the interaction is much less important in complex stabilization than sharing of the electrons (covalent contribution). From the other hand electrostatic contribution along with orbital interactions determine the mutual orientation of the components in the complex. This allows explaining the experimental geometry of the complexes.

Se...X interaction was found to be primarily of repulsive nature due to positive charge of the selenium atom; however the whole intermolecular interaction is attractive. The greatest negative energy of the electrostatic interaction refers to attraction of selenium to negatively charged atom that is directly bound to electron acceptor centre. The major stabilizing contribution is the exchange-correlation one.

The charge concentration points corresponding to the lone pair of selenium atom, that are determined as the laplacian of the charge density minima, manage the direction of attack of the electron acceptor. It was shown that the changes in properties of the lone pair of selenium are essentially dependent on the electron acceptor type.



One can expect similar effects in the complexes involving the heavy donor atoms with diffuse electronic shells (tellurium, arsenic, antimony and so on).

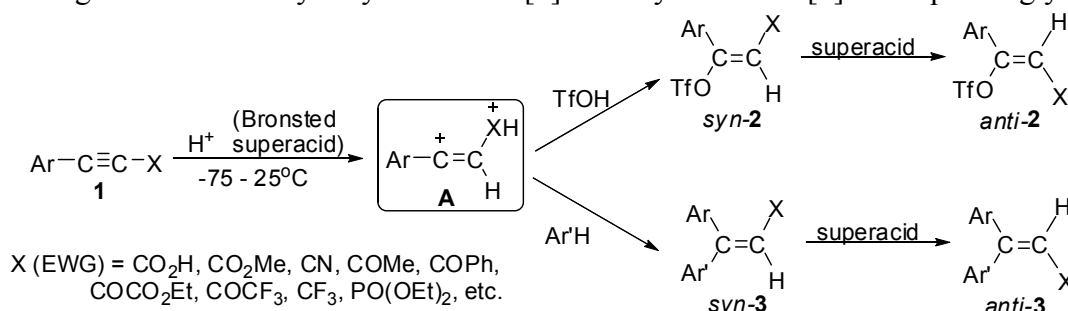
The authors are grateful to Russian Federal Program "Scientific and scientific-pedagogical personnel of innovative Russia" (№ P1349, 11th of June of 2010) for financial support.

NEW PATHWAYS OF ORGANIC SYNTHESIS BASED ON SUPERELECTROPHILIC ACTIVATION OF ACETYLENE COMPOUNDS

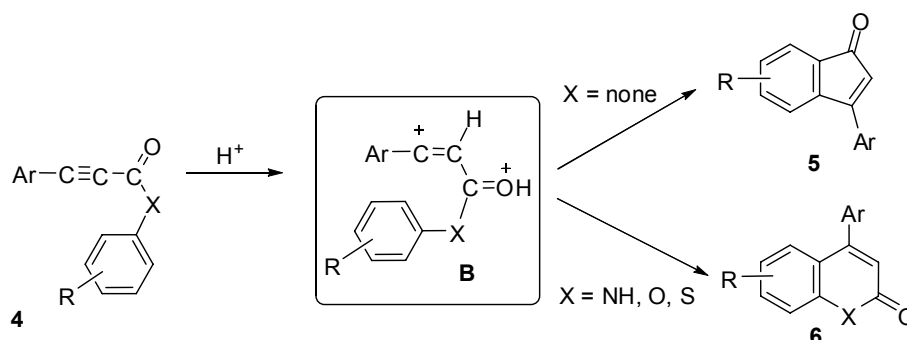
Saint-Petersburg State Forest Technical Academy, Saint-Petersburg,
Russia
aleksvasil@mail.ru

A.V. Vasilyev

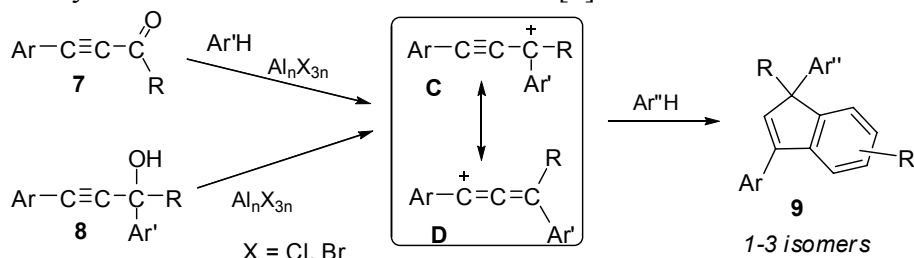
Protonation of acetylene compounds **1** with electron withdrawing groups in Bronsted superacids (HSO_3F , $\text{CF}_3\text{SO}_3\text{H}$, $\text{HSO}_3\text{F-SbF}_5$, $\text{CF}_3\text{SO}_3\text{H-SbF}_5$, HF-SbF_5) leads to superelectrophilic dication **A** (see review [1]). The species **A** may react with molecules of superacid $\text{CF}_3\text{SO}_3\text{H}$ or arenes forming stereoselectively vinyl triflates **2** [2] or diarylalkenes **3** [1] correspondingly.



Intramolecular cyclization of dications **B**, formed from substrata **4** under the action of Bronsted superacids or strong Lewis acids AlX_3 ($\text{X} = \text{Cl}, \text{Br}$), gives various carbo- **5** [3] and heterocycles **6**.



In the presence of AlX_3 ($\text{X} = \text{Cl}, \text{Br}$) acetylene compounds **7**, **8** form mesomeric cations $\text{C} \leftrightarrow \text{D}$, which finally lead to isomeric indene structures **9** [4].



References:

1. Vasilyev A.V. Russ. J. Org. Chem. 2009. V.45. N 1. P.1-17.
2. Vasilyev A.V., Walspurger S., Chassaing S., Pale P., Sommer J. Eur. J. Org. Chem. 2007. N. 34. P.5740-5748.
3. Vasilyev A.V., Walspurger S., Haouas M., Sommer J., Pale P., Rudenko A.P. Org. and Biomol. Chem. 2004, N. 2, P. 3483-3489.
4. Shchukin A.O., Vasilyev A.V., Grinenko E.V. Russ. J. Org. Chem. 2010. V.46. N 1. P.82-97.

**MOLECULAR DESIGN OF POLYMER MATERIALS
WITH QUADRATIC NONLINEAR OPTICAL
ACTIVITY: STRUCTURE-PROPERTY
RELATIONSHIP FOR EPOXY-BASED OLIGOMERS
WITH DENDRITIC MULTICHROMOPHORE
FRAGMENTS**

**M.Yu. Balakina
O.D. Fominykh**

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
mbalakina@yandex.ru

The use of theoretical modeling for the development of organic polymer materials with quadratic nonlinear optical (NLO) activity is helpful for the optimization of electric characteristics of the material and planning the synthesis of oligomers containing dipole chromophores, which are the molecular sources of the effect. The application of dendritic multichromophore fragments attached to the polymer bearing chain provides the promising way of synthesis of NLO polymers, where the undesirable dipole-dipole interaction of chromophores resulting in decrease of the NLO response is minimized.

Here by the Conformational Search we studied the structure of epoxy-based oligomers with a number of units from two to six, every unit containing bidendron with azo-chromophores in each branch. The flexibility of the bearing chain was studied by Molecular Dynamics. Molecular polarizabilities of the studied systems are calculated quantum-chemically at the TDHF//AM1 level.

The analysis of characteristic conformations of dendritic fragment revealed the structural factors responsible for its NLO activity: mutual orientation of both the chromophore groups, and the spacer and dendritic fragment; the length of chromophore-core tether groups. Cross-linking of chromophore containing dendritic branches results in realization of structures with small angles between the chromophore groups, and fixes the chromophores orientation order thus providing relaxation stability of NLO response. Conformational search revealed the stacking-like arrangement of chromophore groups in the oligomers of various lengths, their existence being due to the van der Waals interactions as determined by the *Atoms in Molecules* approach.

Financial support of Russian Foundation for Basic Research is appreciated (Project № 09-03-00696-a).

**ACTIVE RADICAL INTERMEDIATES IN FUEL CELL
IN SITU AND RADICAL PRODUCTS OF
PERFLUORINATED MEMBRANES SIDE-CHAIN
DEGRADATION**

M.K. Kadirov¹
Sh. Schlick²

1 - The Institute of Organic and Physical Chemistry, Kazan Scientific
Center of Russian Academy of Sciences, Kazan, Russia

2 - Department of Chemistry and Biochemistry, University of Detroit
Mercy, Detroit
kamaka59@gmail.com

With application of tiny H₂/O₂ fuel cell (FC) with Nafion/Pt membrane-electrode assembly (MEA), designed for research by ESR of the paramagnetic particles formed during its work in a presence of spin traps, a spin-adducts of hydrogen, methanol and ethanol electrocatalytic oxidation have been registered. By a variation of oxidation conditions, in particular FC potential, it was possible to receive an interesting results concerning direct electrooxidation of fuel. The work of ESR FC *in situ* was supervised by measuring of diagnostic curves: potential - current density, power density - current density and efficiency - power density.

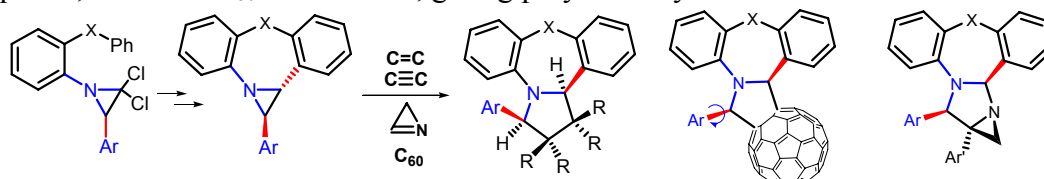
Radical intermediates obtained by 77 K UV irradiation of Nafion 117 containing Fe(II), Fe(III) and Cu(II) impurities and following annealing at higher temperatures have been studied by ESR. The mechanism of chemical transformations of Nafion/H₂O in the above mentioned conditions of processing has been proposed. These transformations occur due to the Nafion side chain which is responsible for the hydrophilic properties of the ionomer. The reason for such changes is because of the active OH and OH₂ radicals which are formed in water pools inside Nafion during UV-irradiation at 77 K. Fluorine alkyl radicals have been observed in absence of air. These changes are not due to main fluorinecarbon chain, because it is hydrophobic and the access of active radical products of the water photolysis is impossible.

FUSED AZIRIDINES: CONVENIENT SOURCE OF AZOMETHINE YLIDES FOR CREATING POLYHETEROCYCLES

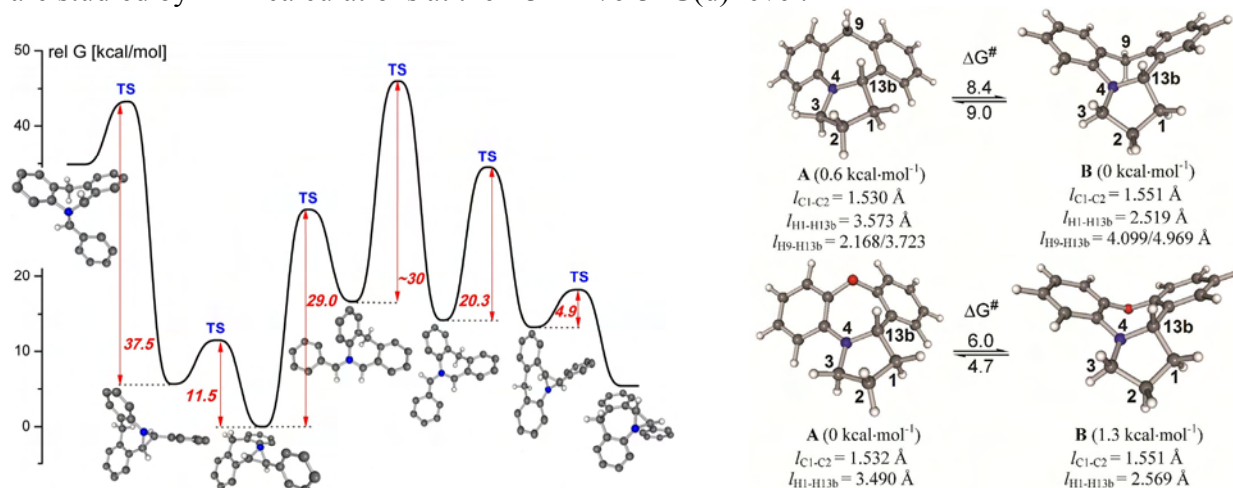
A.F. Khlebnikov
M.S. Novikov
P.P. Petrovskii
A.S. Konev
M.V. Golovkina

Saint-Petersburg State University, Department of Chemistry,
 St. Petersburg, Russia
 alexander.khlebnikov@pobox.spbu.ru

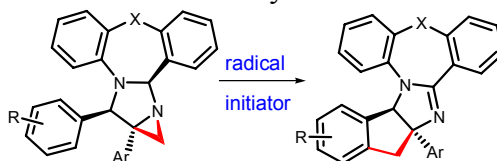
An effective approach to azirino-fused heterocycles is developed based on domino and successive reactions. The fused aziridines are excellent precursors of azomethine ylides, especially in solvent free conditions, which undergo a stereoselective 1,3-dipolar cycloaddition to C=C, C≡C dipolarophiles, fullerene C₆₀ and azirines, giving polyheterocycles.¹



Details of the cycloaddition reactions and the conformational behavior of the cycloadducts are studied by DFT calculations at the B3LYP/6-31G(d) level.



Some novel further transformations of the cycloadducts are discussed.



References:

- [1] (a) Khlebnikov, A. F.; Novikov, M. S.; Petrovskii, P. P.; Magull, J.; Ringe, A. *Org. Lett.* **2009**, *11*, 979. (b) Khlebnikov, A. F.; Novikov, M. S.; Petrovskii, P. P.; Konev, A. S.; Yufit, D. S.; Selivanov, S. I.; Frauendorf, H. *J. Org. Chem.* **2010**, *75*, 5211. (c) Khlebnikov, A. F.; Novikov, M. S.; Golovkina, M. V.; Petrovskii, P. P.; Konev, A. S.; Yufit, D. S.; Stoeckli-Evans, H. *Org. Biomol. Chem.* **2011**, *9*, 3886. (d) Khlebnikov, A. F.; Novikov, M. S.; Petrovskii, P. P.; Stoeckli-Evans, H. *J. Org. Chem.* **2011**, accepted manuscript.

We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (project 11-03-00186), Council for Grants of the President of Russian Federation (grant no. MK-3112.2010.3), and Federal Grant-in-Aid Program «Human Capital for Science and Education in Innovative Russia» (Governmental Contract no. 16.740.11.0442).

POLARITY AND STRUCTURE OF POLYFUNCTIONAL NITROETHENES

Ya.A. Vereshchagina¹
E.A. Ishmaeva¹
D.V. Chachkov²
V.M. Berestovitskaya³

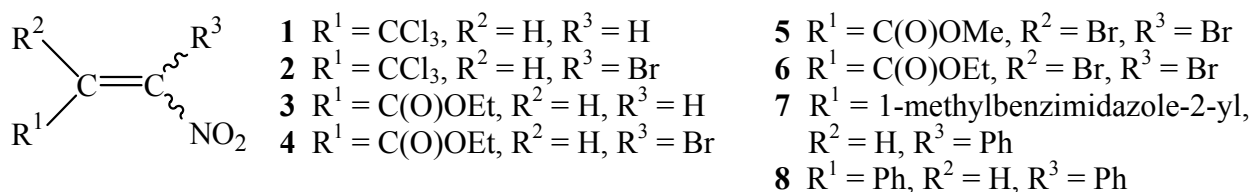
1 - Kazan (Volga Region) Federal University, Butlerov Institute of Chemistry, Kazan, Russia

2 - Kazan Branch of Joint Supercomputer Center of Russian Academy of Sciences, Kazan, Russia

3 - Herten Russian State Pedagogical University, Saint-Petersburg, Russia
 yavereshchagina@yahoo.com

Polyfunctional nitroethenes are convenient compounds for a study of general theoretical problems of organic chemistry as well as for synthesis of biologically active substances.

We have determined polarities of nitroethenes **1-8** in benzene solution, and have studied spatial structures of **1-8** by the methods of dipole moments, NMR and IR spectroscopy, X-ray analysis and quantum chemical calculations (DFT B3LYP/6-31G*).



It was established that the nitro and ester (or trichloromethyl) groups are *trans*-arranged in the molecules of **1-4**, i.e. nitroalkenes have *E*-configuration, their bromo-containing analogues have *Z*-configuration, and *s-cis*-orientation of the C=C and C=O double bonds is preferred for nitroacrylates **3**, **4**. The polarities of **1**, **2** in CH₂Cl₂ and C₆H₆ solutions were calculated using B3LYP/6-31G* method within the limits of SCIPCM model. Detailed interpretation of the experimental Fourier-transform IR spectra of **1-4** was carried out on the basis of the computation of their vibration spectra. Alkyl 2,3-dibromo-3-nitroacrylates **5**, **6** have untrivial *Z*-configuration in solution. It was found that 2-(1-methylbenzimidazole-2-yl)-1-nitro-1-phenylethene **7** has *Z*-configuration in crystal, and the energetically advantageous *E*-isomer of **7** (theoretical data) exists in solution; 1,2-diphenyl-1-nitroethene **8** has *E*-form. For all compounds, the computational results are in a good agreement with the experimental data obtained.

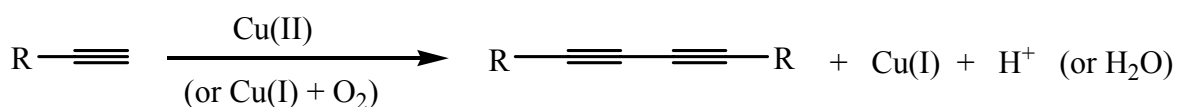
This research was supported by the Russian Foundation for Basic Research (grant No. 10-03-00098-a).

**FEATURE OF THE MECHANISM OF OXIDATIVE
DEHYDRODIMERIZATION OF PROPYNOL**

**L.G. Fedenok
M.S. Shvartsberg**

Institute of Chemical Kinetics and Combustion, Siberian Branch of the
Russian Academy of Sciences, Novosibirsk, Russia
fedenok@kinetics.nsc.ru

Oxidative dehydrodimerization (oxidative coupling) of terminal acetylenes is an important modern method for preparing highly unsaturated dimeric, polymeric, and macrocyclic structures.¹



The detailed study of the oxidative coupling kinetics of a series of various acetylenes in a buffer solution (amine, HOAc in pyridine) shows the reaction to be second orders with respect to reagents, zero order with respect to Cu(I), and inverse second order with respect to acetic acid.^{2,3} It has been established that the reactivity of acetylenes increases with increasing their acidity. From the data obtained the reaction mechanism is proposed whose final stage involves synchronous oxidation of two acetylide anions with the simultaneous formation of the C-C bond. Propynol oxidation under the same conditions obeys quite different kinetic rules.^{4,5} Thus, e.g., for the $[\text{Cu(I)}]/[\text{Cu(II)}] \geq 5$, the reaction has zero order with respect to Cu(II) and the first one respect with to Cu(I). In addition, we have revealed the surprising thing that the reaction rate increases with increasing [HOAc] at constant $[\text{OAc}^-]$.⁵ This fact served a basis for interpreting the ‘anomalous’ kinetics of the oxidative coupling of propynol. We assume that the presence of hydroxyl group in a molecule results in two consequences. On the one hand, the dissociation of its proton decreases the ethynyl hydrogen mobility, but the acid, present in solution, shifts dissociation equilibrium to the left. On the other hand, the sterically free hydroxyl group participates in the complexation with copper ions to facilitate the dimer complex formation on the final stage of the synchronous transfer of electrons. The scheme proposed is in fair agreement with experimental data.⁵

References:

- [1] Siems, P.; Livingston, R.C.; Diederich, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 2632-2657.
- [2] Fedenok, L.G.; Berdnikov, V.M.; Shvartsberg, M.S. *J. Org. Chem. USSR.* **1973**, *9*, 1806-1809.
- [3] Fedenok, L.G.; Berdnikov, V.M.; Shvartsberg, M.S. *J. Org. Chem. USSR.* **1974**, *10*, 934-936.
- [4] Clifford, A.A.; Waters, W.A. *J. Chem. Soc.* **1963**, 3056-3062.
- [5] Fedenok, L.G.; Berdnikov, V.M.; Shvartsberg, M.S. *J. Org. Chem. USSR.* **1978**, *14*, 1334-1337.
- [6] Fedenok, L.G.; Shvartsberg M.S. *Tetrahedron Lett.* **2003**, doi: 52, 10.1016/j.tetlet.2011.05.065.

RAMAN SPECTROSCOPY OF PHOSPHORUS-CONTAINING DENDRIMERS BUILT FROM THIOPHOSPHORYL CORE

V.L. Furer¹
A.E. Vandyukov²
J.-P. Majoral³
A.M. Caminade³
V.I. Kovalenko²

1 - Kazan State Architect and Civil Engineering University, Kazan, Russia

2 - Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of RAS, Kazan, Russia

3 - Laboratoire de Chimie de Coordination, CNRS, France
furer@ksaba.ru

Dendrimers are a new type of compounds and the perspective materials studied by supramolecular chemistry. Heteroatom-containing dendrimers, and particularly phosphorus-containing dendrimers, have their own specificity and properties.

In this work we show the value of FT Raman spectroscopy for characterization of dendrimers. Our aim was to study the connection between the peculiarities of the structure of these compounds and their vibrational spectra.

The Raman spectra of ten generations of phosphorus-containing dendrimers containing P=S and P=O bonds with terminal benzaldehyde and P-Cl groups have been recorded and analyzed. The Raman spectra of dendrimers are determined by the ratio T_n/R_n (T_n – number of terminal groups, R_n – number of repeating units). This ratio trends to $r - 1$ (r – branching functionality of repeating unit), and becomes constant, when the generation number is higher than 3. The dependence of line full width at half height in Raman spectra on generation number is established.

The lines assigned to the core, repeating units and terminal groups of dendrimers were defined by difference spectroscopy. The influence of the encirclement on the line frequencies and intensities was studied and due to the predictable, controlled and reproducible structure of dendrimers the information, usually inaccessible is obtained. Some lines in the Raman difference spectra have characteristic EPR-like form. The strong line at 1600 cm^{-1} show marked changes of intensity in dependence of aldehyde ($-CH=O$) or azomethyne ($-CH=N$) substituents in the aromatic ring. Raman spectroscopy provides unique detailed information concerning the structure of relevant materials, which could not be obtained with any other technique.

**FTIR AND FT RAMAN SPECTROSCOPY OF
PHOSPHORUS-CONTAINING FLUORESCENT
DENDRIMERS BUILT FROM
CYCLOTRIPHOSPHAZENE CORE**

V.L. Furer¹
S. Fuchs²
J.-P. Majoral²
A.-M. Caminade²
A.E. Vandyukov³
V.I. Kovalenko³

1 - Kazan State Architecture and Civil Engineering University, Kazan,
Russia
2 - CNRS, Laboratoire de Chimie de Coordination, CNRS, Toulouse,
France
3 - Arbuzov Institute of Organic and Physical Chemistry, Kazan
Scientific Center of RAS, Kazan, Russia
furer@ksaba.ru

Due to the numerous potential applications in the fields of catalysis, materials, biology and medicine, dendrimers constitute an important class of tree-like compounds. In this work FTIR and FT-Raman spectroscopy were used for characterization of the surface-block (called "Janus") dendrimers that built from the hexafunctional cyclotriphosphazene core, obtained by the coupling of two dendrons, one having five dansyl functions and other with five carbamate ones, linked by amide or hydrazone bridge. Some model of dendrons, built from the cyclotriphosphazene core were also studied. We choose dansyl group as the fluorescent label for dendrimers. The presence of carbamate groups is important since they offer a wide range of possibilities to obtain hydrophilic functions onto the surface of dendrimers.

The characteristic feature of the IR and Raman spectra of the studied dendrimers and dendrons is their similarity to each other. The structural optimization and normal mode analysis were performed for dendrons on the basis of the density functional theory. The calculated geometrical parameters and harmonic vibrational frequencies are predicted in a good agreement with the experimental data. It was found that the dendron molecule has a concave lens structure with planar $-\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{O}$ fragments and slightly non-planar cyclotriphosphazene core. The experimental IR and Raman spectra of dendron were interpreted by means of potential energy distribution. Relying on DFT calculations a complete vibrational assignment is proposed. The strong band 1597 cm^{-1} show marked changes of the optical density in dependence of substituents in the aromatic ring. The frequencies of $\nu(\text{N-H})$ bands in the IR spectra reveal the presence of the different types of H-bonds in dendrimers. FTIR and FT-Raman spectroscopy provide unique detailed information concerning the structure of relevant materials, which could not be obtained with any other technique.

STRUCTURE OF OXIMES OF 1-METHYL-4-METHOXY-2-ETHANOYL- AND 1,4-DIMETHOXY-ETHANOYL- AND PROPANOYLBENZENE BY ^1H AND ^{13}C NMR SPECTRA AND X-RAY ANALYSIS

V.M. Ismaylov¹
I.A. Mamedov¹
S.S. Nasibov¹
N.N. Yusubov¹
V.V. Moskva²

1 - Baku State University, Baku, Azerbaijan

2 - Moscow Chemical-Technology University, Moscow, Russia
niftali-yusubov@rambler.ru

The establishing of configuration of ketoximes is a difficult task. The most promising is the establishment of the configuration ketoximes and their derivatives by the ^1H and ^{13}C NMR spectra.

In order to reveal the universality of this method for decision of the structural features of ketoximes we synthesized oximes of 4-methoxy-2-ethanoylphenol, 1,4-methoxy-2-ethanoylbenzene, 1,4-dimethoxy-2-propanoylbenzene and determined their configuration by using ^{13}C NMR and X-ray analysis. It is important to note that the synthesis of these oximes by ^1H , ^{13}C NMR and X-ray analysis produced only one isomer.

From the literature data follows that in ketoximes signal of α -methyl group, which has syn-orientation to the OH group, always reveals itself in more strong field than the signal of CH_3 group in anti-positions and is manifested in the 10-14 ppm, whereas in the spectra of Z-isomers of methylketoximes the signal of CH_3 group is in the range of 15-21 ppm.

In the ^{13}C NMR spectra of synthesized ketoximes the signal of the CH_3 group is manifested in the 18-19 ppm.

According to literature data the indicated ketoximes should be attributed to the structure of Z-isomer. However, these X-ray analysis unambiguously give the structure of the E-isomer.

Thus, on the basis of chemical shift of the carbon atom of the methyl group not always can be uniquely define the configuration of ketoximes because on the value of this chemical shift significantly affected the neighboring atoms or groups, in particular the methyl group in ortho-position of aromatic nucleus.

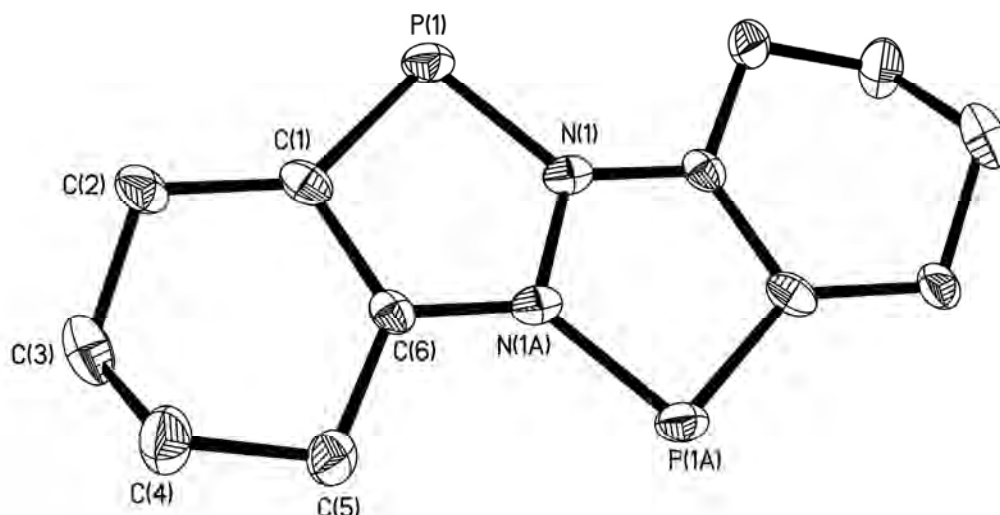
**N,N-ANNULATED DIAZAPHOSPHOLE: NEW
AROMATIC SYSTEM. STRUCTURE AND
REACTIVITY**

O.V. Lukoyanova
O.Ya. Gorak
Yu.S. Panova
V.V. Sushev
A.N. Kornev
G.A. Abakumov

G.A. Razuvaev Institute of Organometallic Chemistry RAS, Nizhny
Novgorod, Russia
olga.novikova@iomc.ras.ru

Heterophospholes are five-membered 6e aromatic systems having a two-coordinate, tervalent (σ^2 , λ^3) phosphorus which contributes one electron to the aromatic sextet.

Unique tetracyclic bis-diazaphosphole have been obtained by the reduction of the corresponding dichloroderivation.



The heterocyclic system, containing annulated five-membered rings, is entirely planar. Such arrangement enhances the effective overlap of the molecular orbitals along the fragments P-C-C-N to form a conjugated 10e-system of an essentially new type. These facts let us discuss aromaticity of the molecule. The Nuclear Independent Chemical Shift (NICS) values computed at and above the five-membered ring centers are negative.

The P-N bond lengths (1.733 Å) are in the range typical for the phosphazanes; while the N-N distance of 1.368 Å is rather shorter than that usually known for hydrazines.

Geometry of the molecule was optimized at the B3LYP/6-31G(d) level. The three highest occupied orbitals are mainly localized on the annulated heterocycles.

NBO analysis of optimized structure shows significant charge separation in the five-membered cycles: the N atoms bear partially negative charges (-0.394) while the P atoms are positively charged (+0.592); the carbon atoms, bonded to nitrogen and phosphorus, have partial charges of +0.141 and +0.422, respectively.

This work was supported by The Russian President's program "Leading Scientific Schools" (No. 7065.2010.3) and RFBR regional grant No 11-03-97029.

**QM/MM MODELING OF THE G117H
BUTYRYLCHOLINESTERASE CATALYZED
ECHOTHIOPHATE HYDROLYSIS REACTION
MECHANISM**

S.V. Lushchekina¹
P. Masson²
F. Nachon²
A.V. Nemukhin³
S.D. Varfolomeev¹

1 - N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia
2 - Institut de Recherche Biomedicale des Armees-CRSSA, La Tronche, France
3 - M.V. Lomonosov Moscow State University, Department of Chemistry, Moscow, Russia
sofya.lushchekina@gmail.com

Butyrylcholinesterase (BuChE) serves as a stoichiometric bioscavenger of organophosphorus (OP) compounds, forming a covalent bond with them. Creation of BuChE mutants capable of catalyzing the hydrolysis of OP compounds will convert the enzyme into effective catalytic bioscavenger. The G117H mutant of BuChE hydrolyzes OP compounds at slow rates. Understanding of the hydrolytic mechanism should help to improve the OPase activity of ChE-based catalytic bioscavengers. The crystallographic structure of the G117H mutant of BuChE conjugated to echotiophate was published recently [1].

We performed molecular dynamics and QM/MM studies of the G117H BuChE mutant conjugated to echotiophate in order to consider different hydrolysis mechanisms. The possible changes in His117 orientation depending on protonation state and its influence on average enzyme dynamics were considered. The hydrolysis reaction energy profiles for different possible hydrolysis mechanisms were obtained and compared with the respective profiles for aging process. The His117 protonation lowers reaction energy barriers and stabilizes reaction products both for the hydrolysis and aging processes comparing to the wild-type BuChE.

References:

[1] 1. Nachon, F. et al., X-ray crystallographic snapshots of reaction intermediates in the G117H mutant of human butyrylcholinesterase, a nerve agent target engineered into a catalytic bioscavenger. *Biochemical Journal*, 2011, 434(1): p. 73-82.

EFFICIENT METHOD OF THE SYNTHESIS OF N-SUBSTITUTED TETRAHYDROINDOLE DERIVATIVES

A.M. Maharramov

I.M. Akhmedov

I.A. Aliyev

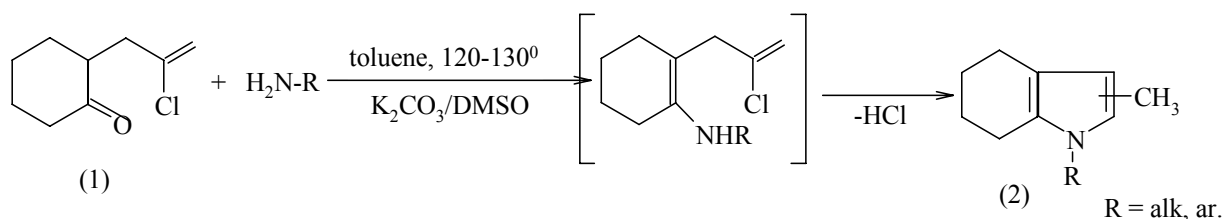
S.F. Farzaliyev

Baku State University, Baku, Azerbaijan
vgulya@mail.ru

The biological activity of some pyrrole derivatives has prompted the development of new synthetic pathways for 4,5,6,7-tetrahydroindoles with various substitution patterns [1-4]. Different derivatives of tetrahydroindoles are found in the structures of many biologically active compounds such as antibiotics, antipsychotic, antioxidants and antibacterial agents [5]. Tetrahydroindoles can also be used as ligands for transition metals.

In the literature have been described various multistep synthetic procedures, including reduction of indoles and Trofimov reaction – synthesis is the condensation of oximes cyclohexanone with acetylene in the presence of catalytic systems MOH/DMSO.

Recently, we described the synthesis of tetrahydroindoles via PTSA catalyzed amination/annulation reactions of 2(2-bromoallyl)-cyclohexanone with amines [6]. In our work we found a convenient method for the synthesis of N-substituted 4,5,6,7-tetrahydroindoles through enamines from 2(2-chloroallyl)-cyclohexanone compounds by the use of K_2CO_3 (DMSO) the following scheme:



The reaction furnished the tetrahydroindole derivatives (2) in 50-60% yields. All the synthesized compounds were identified by NMR spectroscopic and element analysis methods.

References:

1. Stetter H., Sihnhold E. *Chem. Ber.* 1955, 88, 271.
2. Chelucci G., Marchetti M. *J Heterocycl. Chem.* 1988, 25, 1761
3. Trofimov B.A. *Adv. Heterocycl. Chem.* 1990, 51, 177
4. Demir A.S., Akhmedov I.M., Sesenoqlu O. *Tetrahedron*. 2002, 58, 9793
5. Sun L, Tran N., Hubbard S., Tanq F., Lipson K., et all. *J.Med. Chem.* 2000, 43, 2655
6. Tanyeli C., Akhmedov I.M., Yazicioqlu E.Y. *Tetrahedron letters*. 2004, 45, 9627.

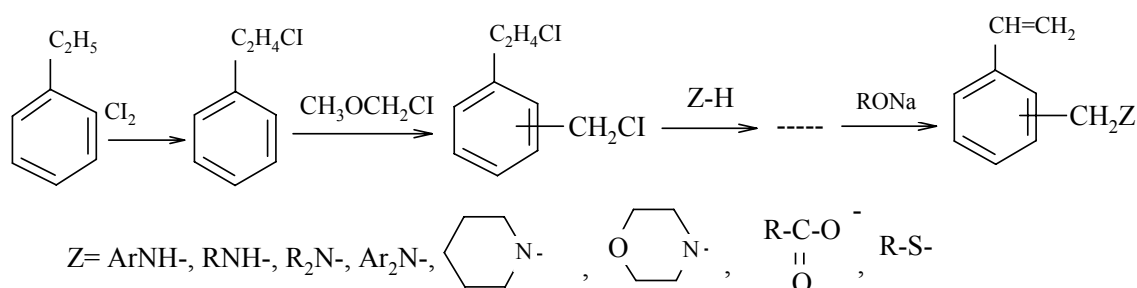
A.M. Maharramov
G.Sh. Duruskari
Kh.A. Garazadeh
A.G. Lutfaliyev
I.A. Aliyev
M.N. Magerramov

SYNTHESIS OF DERIVATIVES OF STYRENE ON THE BASIS OF ETHYLBENZOLE TRANSFORMATIONS

Baku State University, Baku, Azerbaijan
vgulya@mail.ru

Styrene derivatives have great value in quality of monomers and copolymers for reception of polymers with the set properties. For this reason to working out of methods of their reception numerous works are devoted. Throughout these works we study possibility of use of products of chlorination of ethylbenzole with the subsequent by chloromethylation of received monochlorethylbenzoles in synthesis of derivatives of styrene. It is established that under optimum conditions of chlorination the maintenance of monochlorethylbenzoles in chlorination products makes 55,8%. By data ^1H spectrum nuclear magnetic resonances the monochlorethylbenzoles consist of 90 % 1-1-1-1 - and 10 % 1-phenyl-2-chlorethanes. The chlormethylation of monochlorethylbenzoles by chlormethyl ester in the presence of chloride zinc leads to formation of chlormethyl derivatives with an exit of 51%. Further reactions of monochlorethylbenzoles with deethylamin, aniline and pyperidine are studied. It is established that monochlorethylbenzoles practically do not enter reaction with aniline and demethylamine, and with pyperidine a product yield of replacement of chlorine in 1-chlor-1-phenylethane on pyperidine fragment makes 64 %.

The offered method is based on distinction in reactionary abilities of atoms of chlorine in chlormethyl and 1-chlorethyl groups. It is established that in depence on character of a reagent reaction passes or only on chlormethyl group, or partially and on 1-chlorethyl group, dehydrochlorination reaction products leads to formation, mainly, styrene derivatives with an exit to 70%:



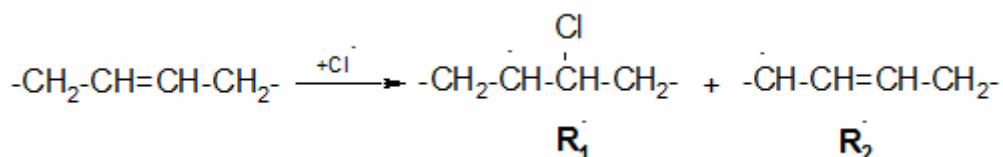
A.M. Maharramov
A.A. Azizov
N.S. Nabiyev
R.M. Alosmanov
I.A. Bunyad-zadeh

**INVESTIGATION OF DIVINYL RUBBER OXIDATIVE
CHLOROPHOSPHORYLATION BY QUANTUM
CHEMICAL ANALYSIS**

Baku State University, Baku, Azerbaijan
r_alosmanov@rambler.ru

Reaction of oxidative chlorophosphorylation can be used as simple preparation method of the phosphorus-groups containing polymers. In publications devoted to olefin type polymers have been reported that phosphorus containing group directly adds to matrix with phosphorus-carbon bonds formation, and in case of diene polymers both the addition by pointed type and through oxygen took place. It is known that this reaction proceeds by chain-radical mechanism in the presence of atomic chlorine as initiator. Future radicals interaction with PCl_3 or O_2 can be explained by initial radicals stability: more stable radical reacts with oxygen and as a result of this interaction phosphorus-containing group adds to polymer through oxygen.

In present work the electron distribution of the intermediate radical obtained as a result of attack of macromolecule with chlorine by the quantum chemical analysis has been presented.



The quantum chemical analysis have been done with AM 1 and RM 3 semiempirical methods. The calculated models on the basis of chemical structure with application of the component atoms covalent radiuses have been constructed. The atoms coordinates corresponding to pre-optimized geometric structure of the compounds have been used under electron structure optimization. It have been established that the effective charges of macro radicals R_1 and R_2 are - 0.126 and -0.111 respectively.

Hence, R_2 has more sensitivity to oxygen than R_1 , that has been established by NMR investigations of the solid phase.

**THE INFLUENCE OF MOLECULAR DYNAMICS
SIMULATIONS ON THE STRUCTURE OF
SOLVATION OF MOLECULE IN SOLVENT AND ITS
MANIFESTATION ON NMR SPECTRA**

E.R. Martynchuk¹
R.M. Aminova²
S.L. Martynchuk³

1 - E.K. Zavoisky Physical-Technical Institute, Quantum Dynamics
and Informatics Laboratory, Kazan, Russia

2 - Kazan Federal University, Physics Institute, Kazan, Russia

3 - SGT, Kazan, Russia
baisupova@mail.ru

Problem of the dynamical processes influence on the structure and chemical shifts of the solute molecule in solvent is very actual.

It is important to construct the initial structure of solvation shell containing the solvent molecules. For this purpose in this work the program for construction of initial structure of solvation shell has been elaborated by using the program language JAVA. This program was used for construct of the initial structure of solvent molecules (acetone) around ((CH₃)₃P and (CH₃)₃PCS₂) molecules. Direct molecular dynamics method has been implemented for optimization of solvation shell structures obtained with using of this program. This approach was applied for the dynamics study of the molecular cluster structures of ((CH₃)₃P and (CH₃)₃PCS₂) molecules with acetone molecules and chemical shifts calculations. For molecular configurations extracted from molecular dynamic simulations the calculations of magnetic shielding constants of ³¹P nuclei were carried out within the framework of UB3LYP/6-31(d,p) method with gauge-including atomic orbitals. It has been carried out the comparison of the dynamical processes simulation results of (CH₃)₃P and (CH₃)₃PCS₂ molecules in the acetone with data obtained by using a different methods of cluster structure modelling – molecular mechanic method, quantum mechanics/molecular mechanic method and density functional theory method (DFT) with different functionals [1].

References:

1. R.M. Aminova, E.R. Baisupova, A.V. Aganov. – *Appl. Magn. Reson.* **40**, 147-170 (2011).
-

THE REACTION OF 4-NITRO- AND 4-METHOXYPHENYLACETYLENES WITH 4,7-DI(*tert*-BUTYL)BENZO-1,3,2-DIOXAPHOSPHOLES. INFLUENCE OF SUBSTITUENT'S NATURE IN THE PHENYL MOIETY ON THE STABILITY OF OXAPHOSPHORINE CYCLE

A.S. Aniskin¹
A.V. Nemtarev¹
V.F. Mironov¹
D.S. Baranov²
S.F. Vasilevsky²
N.O. Druzhkov³
V.K. Cherkasov³

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia

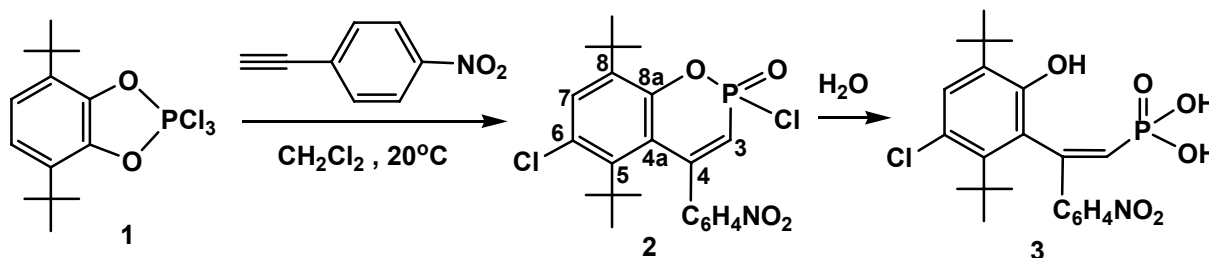
2 - Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia

3 - G.A. Razuvaev Institute of Organometallic Chemistry, Nizhni Novgorod, Russia

nemtarev@iopc.ru

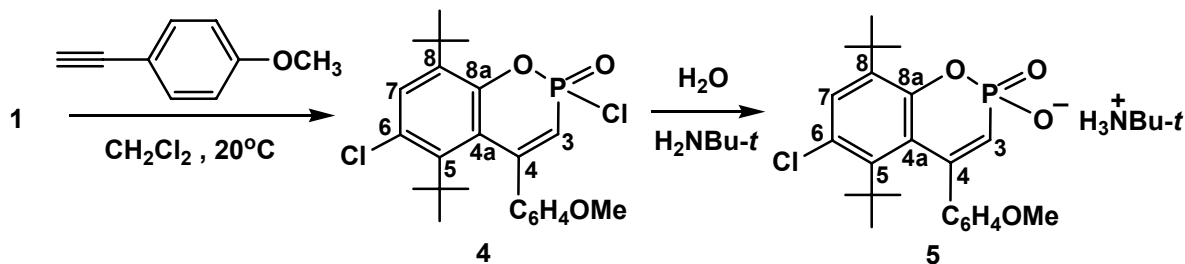
The reaction of 2,2,2-trihalogenbenzo-1,3,2-dioxaphospholes with acetylenes is known to lead to the formation of benzo[*e*]-1,2-oxaphosphorines which exhibit a considerable resistant to the action of various reagents.

Herein, the reaction of 4,7-di(*tert*-butyl)-2,2,2-trichlorobenzo-1,3,2-dioxaphosphole with substituted phenylacetylenes are discussing. 2,6-Dichloro-1,2-dihydro-5,8-di(*tert*-butyl)benzo[*e*]-1,2-oxaphosphorin-2-oxide (**2**) is formed in reaction dioxaphosphole (**1**) with 4-nitrophenylacetylene. Hydrolysis of compound (**2**) leads to the opening of oxaphosphorine's cycle and gives phosphonic acid (**3**).



The geometry of molecule (**2**) was determined by XRD (Z-configuration of C³=C⁴ bond).

Dioxaphosphole (**1**) gives with *para*-methoxyphenylacetylene benzophosphorine (**4**) with the same substituents set in the phenylene fragment. Oxaphosphorine cycle of compound (**4**) is resistant to disclosure even upon hydrolysis when heated. Thus, the result revealed a clear dependence of the substituents nature in the phenyl fragment, situated in the fourth position of the heterocycle, on the stability of oxaphosphorine's cycle in the reaction with nucleophiles. Electron withdrawing groups favor to the disclosure of the oxaphosphorine cycle.



This work was supported by Russian Foundation of Basic Research (№ 10-03-00525).

**USE OF THE THEORETICAL-INFORMATION
TOPOLOGICAL INDICES FOR CALCULATION OF
ACIDIC IONIZATION CONSTANT OF CYCLIC
CIS- AND TRANS-DICARBOXYLIC ACIDS**

**M.S. Salakhov
O.T. Greckina
B.T. Bagmanov**

Institute of Polymer Materials of Azerbaijan National Academy of
Sciences, Sumgayit, Azerbaijan
salahov_mustafa@mail.ru

We have carried out the search of the possibilities of use of discriminating capacities of the theoretical-information indices of IC_k , TIC_k , SIC_k , CIC_k ($k = 0 - 3$) on an example of configuration cis- and trans-stereoisomer 4-cyclohexene-1, 2-dicarboxylic acids (4 – CHDA) (I, II), 1-methyl-4-CHDA (III, IV), 3-methyl-4-CHDA (V – VIII), 4-methyl-4-CHDA (IX, X), 1, 2-dimethyl-4-CHDA (XI) and 4, 5-dimethyl-4-CHDA (XII) synthesized by us with the aim of finding of possible correlations $f(TI) - pK_a$ for a series of cis- and trans-configurations of the studied acids. Our calculations showed that the values of IC_0 , TIC_0 , SIC_0 , CIC_0 indices, calculated without account of hydrogen atoms in molecule for (III – X) and (XI, XII) are equal among themselves thereupon that at $k=0$ IC_k , TIC_k , SIC_k , CIC_k indices are not able to distinguish the isomer forms of the same compound. So, IC_1 , TIC_1 , SIC_1 , CIC_1 indices for isomers (III – X), and also IC_2 , TIC_2 , SIC_2 , CIC_2 indices for (III – VIII) owing to the small discriminating ability are equal among themselves. However, IC_3 , TIC_3 , SIC_3 , CIC_3 indices can be apparently used for establishment of dependence between structure and properties of the studied compounds, as they differ isomers of methyl- and dimethyl-4-CHDA depending on position of methyl groups in cyclohexene ring. It has been revealed depending on removal of methyl group on carboxyl groups in molecules of monomethylsubstituted 4-CHDA IC_3 value is decreased. Owing to the fact that TIC_k , SIC_k and CIC_k have been connected with IC_k simple functional ratios, TIC_3 and SIC_3 value is also decreased and CIC_3 value correspondingly grows. In spite of the fact that the topological indices do not consider the stereochemical peculiarities of molecules, nevertheless using IC_3 , TIC_3 , SIC_3 , CIC_3 indices in a series of monomethylsubstituted correspondingly cis- and trans isomers of methyl-4-CHDA we have revealed that pK_1 value for cis-isomers of methyl-4-CHDA grows with removal of methyl group from carboxyl groups and pK_2 and ΔpK values are correspondingly decreased. The pK_1 value of trans-isomers of methyl-4-CHDA is analogously changed. Taking into account above-mentioned, one can conclude that correspondingly for cis- and trans-isomers of methyl-4-CHDA there is a dependence of pK_1 values on IC_3 , TIC_3 , SIC_3 and CIC_3 , and also pK_2 and ΔpK on IC_3 , TIC_3 , SIC_3 and CIC_3 for cis-isomers of methyl- 4-CHDA.

**KINETIC ISOTOPE EFFECT OF THE REACTION OF
TERTIARY PHOSPHINES WITH UNSATURATED
CARBOXYLIC ACIDS AND THEIR DERIVATIVES**

**A.V. Salin
A.A. Khabibullin
V.I. Galkin**

Kazan Federal University, Department of Chemistry, Kazan, Russia
salin555@mail.ru

The kinetics of the reactions of triphenylphosphine with acrylic and maleic acids as well as acrylonitrile and acrylamide was studied by spectrophotometry in acetic and D₁-acetic acid as a solvent. Kinetic isotope effect (KIE) for these reactions was determined ($\frac{k_H}{k_D} = 1.1 \div 1.7$), establishing that proton transfer occurs in the rate limiting step of the process. A small value of KIE is due to a complex process of interaction, which includes initial equilibrium formation of phosphonium zwitterionic intermediate. Inverse KIE for the first step mostly masks normal KIE for the following proton transfer step, thus the effective value of the intrinsic KIE for the reactions is not very large. The data obtained are in a good agreement with previously proposed mechanism [1].

References:

1. Salin A.V. *et al. Zhurnal Obshei Khimii.*, 2011, **81**(5), 737.
-

**PROBING THE MECHANISM OF THE REACTION
OF TERTIARY PHOSPHINES WITH UNSATURATED
CARBOXYLIC ACIDS BY DENSITY FUNCTIONAL
THEORY**

A.V. Salin¹
R.M. Aminova²
V.I. Galkin¹

1 - Kazan Federal University, Department of Chemistry, Kazan, Russia

2 - Kazan Federal University, Department of Physics, Kazan, Russia

salin555@mail.ru

The mechanism of the reaction between trimethylphosphine and acrylic acid was investigated by using density functional theory at UB3LYP 6-31+G(d,p) level. We addressed the mechanism under bimolecular conditions, but also considered how the mechanism changed in the presence of a molecule of water. The computational results indicate that the reaction proceeds through a stepwise mechanism with initial generation of 1,3-dipolar phosphonium intermediate. The subsequent proton migration step is not a simple intramolecular process due to extremely high activation barrier for this reaction path (33.5 kcal/mol both in terms of enthalpy and Gibbs free energy in gaze phase). In the presence of a molecule of water, which services as a proton-shuttle, the activation barrier is 4.5 times as little, however even in these conditions proton transfer remains to be the rate-determining step of the whole process. The results obtained are in accordance with previous kinetic studies on this reaction [1,2]. It was shown that the form of kinetic equation, which has general third-order, depends on the nature of solvent, and this quarternization process requires involvement of third proton-donor reagent.

References:

1. Salin A.V. *et al. Phosphorus, Sulfur, and Silicon*, 2011, **186**(04), 854.
2. Salin A.V. *et al. Phosphorus, Sulfur, and Silicon*, 2011, **186**(04), 857.

**UNIFIED MODEL OF CHEMICAL BONDS AND
SYSTEM, WHICH UNITES THEM, AS
FUNDAMENTAL BASIS FOR NEW STAGE OF
DEVELOPMENT OF A.M. BUTLEROV'S THEORY
OF CHEMICAL STRUCTURE OF SUBSTANCE**

**O.S. Sirotkin¹
R.O. Sirotkin²**

1 - Kazan State Power Engineering University, School of Materials
Science and Technology, Kazan, Russia

2 - Kazan State Power Engineering University, School of Chemistry,
Kazan, Russia
rsir@mail.ru

In 1861, for the first time, the great Russian chemist A.M. Butlerov laid foundations of theory of chemical structure, which was primarily utilized in organic chemistry. This was mainly due to the fact that organic substances are covalent compounds, i.e. they exist in the form of individual chemical particles – molecules. Ionic and metallic chemical compounds were not covered by this theory, which, in our opinion, is due to absence of universal model of chemical bond.

Modern ideas of chemical bonds rest on [1-3]:

- Lewis' idea of the possibility of gradual transition from one extreme bond type (covalent, metallic, ionic) to the other through the mixed types of bonds;
- quantum-mechanical theory of Heitler and London, which allowed to demonstrate individuality (exchange integral) and distinction of chemical bond from physical types of interaction. Heitler in 1963 wrote that "it is the integral that plays decisive role in this issue", which allowed discovering, in his opinion, "the second type of atoms' interaction";
- views of L. Pauling who considered chemical bond as superposition of covalent and ionic states within development of quantum-mechanical theory of Heitler and London, and presented the wave function "as antisymmetrised product of functions, which correspond to valent lines in structural formula, or as linear combination of such products corresponding to a number of structural formulae" in the resonance theory that he proposed.

As a result, the basis of modern unified theory of chemical bond, which determines the specificity of electron-nuclear structure of any material, rests on the idea proposed by O.S. Sirotkin that any type of chemical bond should be considered as superposition on chemical bond's covalent component of metallic (in case of homonuclear bonds) or both metallic and ionic (in case of heteronuclear bonds) components of chemical interaction.

This model serves as fundamental basis for System of Chemical Bonds and Compounds (SChBC) represented as "Chemical triangle". As a result, the unified model and SChBC make it possible to develop in an evolutionary way A.M. Butlerov's theory of chemical structure in terms of broadening its versatility and practical applicability to the whole variety of metallic and nonmetallic chemical substances and materials.

References:

1. O.S. Sirotkin, Principles of unified chemistry (unitarity as basis for formation of individuality, revealing uniqueness and fundamentality of chemical science), Kazan: Fen, 2003, 252 pp.
 2. O.S. Sirotkin, R.O. Sirotkin, A.M. Trubacheva, On the necessity and procedure of taking into account the metallic component of a heteronuclear bond, Russian Journal of Inorganic Chemistry, v. 50, №1, 2005, p. 67-71.
 3. R.O. Sirotkin, O.S. Sirotkin, Chemical bond, Kazan: Kazan State Power Engineering University, 2010, 51 pp.
-

**THE ACTIVATION MECHANISM OF
CYCLOADDITION REACTIONS IN THE LIQUID
PHASE**

V.G. Uryadov¹
E.N. Ofitserov²

1 - Kazan National Exploratory Technological University, Kazan,
Russia

2 - D.I. Mendeleev Russian Chemical Engineering University,
Moscow, Russia
vguryadov@mail.ru

Theories of chemical kinetics are based on the idea of collisions of reagent molecules. This approach describes reactions in the gas phase where the energy of the molecules is determined by the translational motion. In the liquid phase the reagent molecules are in the “cage” made of solvent molecules. The formation of product takes place in this “cage” owing to overcoming the potential barrier. To this purpose the reagent molecules must have the energy store.

The cycloaddition reactions are the recognized “testing ground” for new theoretical concepts and beliefs among the organic reactions.

The aim of this work is to develop the activation mechanism of cycloaddition reaction in the liquid phase and the system of functional relations between properties of molecules and their structure in conditions of dissipative structures (DST) by Prigozhin [1].

As a physical model of the DST we consider a pulsating solvent vapor bubble in the bulk of the liquid solvent [2]. The model conforms to the following conditions:

- the vapor bubble forms the molecules taking place in chemical transformation and solvent molecules of solvation shell;
- the solvation shell should be formed by solvent molecules which are able to obtain and lose ability for the translational motion;
- the transition state is realized in the DST, the DST is an open system so the transition state of cycloaddition reaction in solution is an open system too.

According to the proposed mechanism [3], the DST is excited under the action of the reaction thermal effect energetic pulse. In the DST the overcoming of potential barrier and reorganization of molecule structure from reactants to products takes place under the influence of external perturbing force that transfers energy. The solvent molecules of solvation shell, as transferring agents of energy from reaction mixture to reagents, carry out the energy transferring of external electromagnetic radiation to a complex of molecules, involved in the chemical transformation. Mechanical inelastic collision of solvent molecules of solvation shell and reagents can be the way of transferring the acquired energy.

The proposed activation mechanism of cycloaddition reactions in solution allows for a set of periodic collisions of molecules involved in chemical transformation with molecules formed the reaction mixture. There are single collisions in the gas phase. Differences in the order and number of collisions between molecules could cause qualitative differences in organic reactions in the gas and liquid phase.

References:

- 1 Nicolis G., Prigozhin I., Self-Organization in Nonequilibrium Systems. Mir.: Moscow, 1979. 512 p. (in Russian).
2. Ofitserov E.N., Uryadov V.G. The Activation Mechanism to Diene Synthesis Reactions in Solution// Report of RAN. – 2007. – V. 416. №3. – pp. 344-347.
3. Uryadov V.G., Ofitserov E.N. The Activation Mechanism to Cyclik Additions Reactions in Solution. Monograph, Kazan state technological university. – Kazan. KSTU, 2009. – 432 p.

**THE EXPERIMENTAL AND THEORETICAL
INVESTIGATION OF THE INTERPLAY BETWEEN
THE NON-COVALENT INTERACTIONS AND THE
CRYSTAL STRUCTURES OF SOME COMPOUNDS
CONTAINING HETEROCYCLIC RING**

**J.K. Voronina
O.A. Lodochnikova
D.B. Krivolapov
I.A. Litvinov**

A.E. Arbuzov Institute of Organic and Physical Chemistry, X-ray
Laboratory, Kazan, Russia
juliavoronina@mail.ru

On the basis of the X-ray diffraction study, the indolinone fragments of the isoindigo derivatives, can have both planar and non-planar conformation. The quantum-chemical calculations have shown that the non-planar conformation is the most stable energetically for isoindigo in gas phase. It is interesting that in crystals formed by the planar and non-planar molecules the structure-forming intermolecular interactions differ. Thus, the planar molecules are bounded via the stacking interactions of the indolinone fragments, while the non-planar ones – only by the CH...O interactions.

It has been established for the racemic mixtures of the chirally related sulphones based on the mucochloric acid that the methyl derivative forms a conglomerate, while the halogen-derivatives – the real racemates. It is interesting that the crystal structures of all three samples have a lot in common: the homochiral H-bonded chains of the same type and even the analogous 3D homochiral layers additionally stabilized by the lp... π and C-H...O interactions. The quantum-chemical investigation of a number of associates has been carried out, which are formed by both the interactions observed in crystals and the hypothetical ones; the parameters of the interactions and their energy have been evaluated. However, the calculations do not explain the spontaneous resolution of the enantiomers upon the crystallization of the namely methyl-derivative.

The financial support from the Ministry of Science and Education of RF (Governmental Contract No 14.740.11.1027), grant of the President of the Russian Federation for the state support of young Russian scientists (MK-1670.2010.3) and RFBR № 09-03-00696-a.

**GREAT CHEMISTS FROM KAZAN UNIVERSITY ON
PHILATELIC MATERIALS**

R.I. Zhdanov

Kazan Federal University, Kazan, Russia
zrenad@gmail.com

Great achievements of chemists from School of chemistry at Kazan University and their input to chemistry, mainly to organic chemistry, in XIX and XX centenaries are well known and recognized. Zinin synthesis of aniline by reduction of nitrobenzene, Klaus discovery of metal Ruthenium (named in honor of Russia), Butlerov's theory of structure of organic compounds, Markownikoff's theory of interinfluence of atoms in organic molecule, Markownikoff - Zaitsev rules for addition, substitution and depletion at double bond, Zaitsev reactions for syntheses of alcohols, fatty acids and lactones, Popov rule for and oxidation of ketons, Wagner oxidation with potassium permanganate, Wagner- Meierwein rearrangement, Reformatsky reaction, Michaelis-Arbuzov rearrangement, Kamai reaction, Torgov synthesis of steroid hormones, Pudovik reaction, Abramov reaction and other discoveries represent a great input to chemical sciences. The talk is aimed to show how these discoveries and other events at Kazan University are reflected in a "mirror" of World philately. Postage stamps (coins and banknotes as well) of chemistry topics may be considered as a sort of public awareness to the benevolent work of chemists to clarify fine features of interaction between chemicals and molecular nature and mechanisms of human diseases. Accordingly, the great public response to the chemical studies follows from the postage stamps presented. The talk is based on one of the World best scientific philatelic, the author's life-time composed collection. The current philatelic items: 19 special cancellations, 20 cashes, and non-stamped 20 envelopes and 22 postcards as well issued by Russian Post Office and the Kazan Federal University, sponsored by the Government of Republic of Tatarstan, are presented in the talk. In 2011, the World Year of Chemistry, all these issues commemorate the Greatest input of the Kazan University and our Great Chemists to chemical sciences.

References:

1. Zhdanov R.I. *Science in the U.S.S.R.*, 1987, # 6, 102-103; 1988, # 1, 33; # 3, 44-45; # 4, 84-85.
2. Zhdanov R. (1988) Great chemists from Kazan' State University. *Phil. Chem. Phys. (U.S.A.)* 10 (4) 167-168.
3. Zhdanov R. (1989) Spin labeling Nobel. *Nature* 339 (6225): 500.
4. Zhdanov R. (1995) Chemical philately. The XXXVth IUPAC Congress Istanbul, *Book of Abstracts*, v.1, 535.
5. Zhdanov R., Jdanov A. (1999). Pharmacology and medicine on postage stamps. *Khim.-Pharm. Zhurnal (Rus. Chem. Pharm. Bull.)* № 4: 50-55.
6. Zhdanov R., Jdanov A. (2000). Medicine and pharmacy in philately. *Khim.-Pharm. Zhurnal. (Rus. Chem. Pharm. Bull.)* № 1: 46-53.
7. Zhdanov R., Corey E. (2009). In memorium Igor Torgov. Torgov's way to total steroid synthesis. *Steroids*. 74: 723-724.
8. Zhdanov R.I. (2009a). Scientists on Turkish banknotes will inspire young minds. *Nature*. 457: 956.
9. Zhdanov R.I. (2009b). A Toast to Mendeleev who merits more than periodic order. *Nature*. 462: 985.
10. Zhdanov R.I., Cetinkaya I., Zhdanova S.I. (2010) Stamping through scientific advances in medicine and genetics. *J. Med. Med. Sci.* 1 (1)

Section 2.

“Chiral” Organic Chemistry



Starting in 2004, NPO «TatKhimProdukt» has proved to be a reliable and trustworthy supplier of all leading scientific and educational institutions in Kazan. With us you can always order everything you need for the proper functioning of modern chemical laboratory: chemicals, glassware and consumables, laboratory equipment from famous national and international manufacturers, laboratory furniture. Among our partners are leading Russian and international companies such as Acros Organics, Sigma-Aldrich-Fluka, Alfa Aesar, Fisher Scientific, Wiegand International, Testo, Labteh, Dia-m, Helicon, LOIP and many others. We are always glad to choose the optimal purchases based on your financial resources, delivery schedules and other factors. It seems to be important for you that most of the products are supplied on producer's or official representative's prices.

Best regards,

General Director Alex Prosvirkin

Production Director Alex Yefremov

Phone/fax +7 (843) 5700226, 5700290, 2787488

www.tatcp.ru

<mailto:direct@tatcp.ru>, alex@tatcp.ru



SIGNIFICANCE OF CHIRALITY IN CHEMICAL COMMUNICATIONS

K. Mori

University of Tokyo, Department of Applied Biological Chemistry,
Tokyo, Japan
kjk-mori@arion.ocn.ne.jp

Contrary to the conventional wisdom that only pure enantiomers are bioactive, naturally occurring messengers in chemical communications are not always enantiomerically pure. For example, tribolure (4,8-dimethyldecanal), the aggregation pheromone of the red flour beetle, is a mixture of all the four stereoisomers in a ratio of $(4R,8R)/(4R,8S)/(4S,8R)/(4S,8S) = 4:4:1:1$.

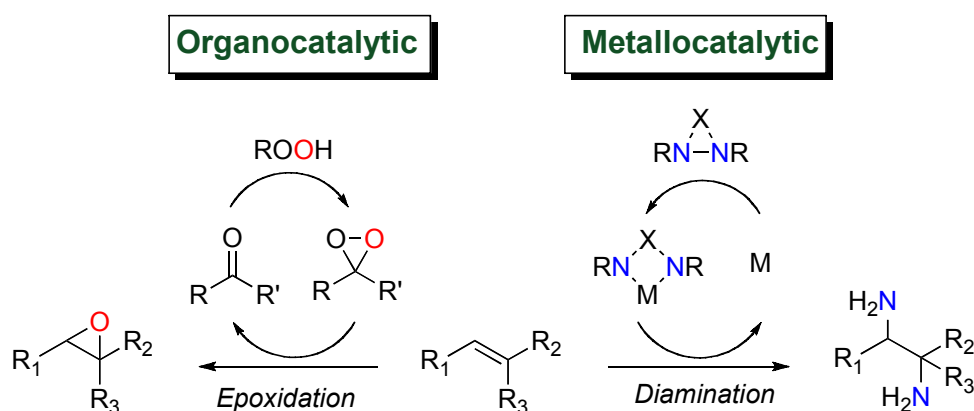
Stereochemistry-bioactivity relationships among pheromones are not simple but complicated. In the case of tribolure, a mixture with the naturally occurring ratio of 4,8-dimethyldecanal is most active. Neither (*R*)- nor (*S*)- sulcatol (6-methyl-5-hepten-2-ol) is behaviorally bioactive as the aggregation pheromone of an ambrosia beetle, whereas their mixture is active. In the case of olean (1,7-dioxaspiro[5.5]undecane), the sex pheromone of the olive fruit fly, its (*R*)-isomer is active against the males and the (*S*)-isomer is active against the females.

Enantioselective syntheses of these and other pheromones will be reviewed to show the importance of "chiral" organic chemistry in pheromone science.

**ORGANOCATALYTIC AND METALLOCATALYTIC
OXIDATION OF OLEFINS****Y. Shi**Colorado State University, Department of Chemistry, Fort Collins,
USA
yian@lamar.colostate.edu

Epoxides and diamines are important functional groups and synthetic intermediates. Epoxidation and diamination of olefins present powerful strategies to directly synthesize these compounds. Carbohydrate-based chiral ketones have been shown to be general, practical, predictable, and scalable organocatalysts for asymmetric epoxidation of olefins. In particular, the generality and practicality illustrated by fructose-derived ketone, whose results were published beginning in 1996, demonstrated the great potential of small organic molecules as catalysts for asymmetric synthesis.

Olefins are also efficiently diaminated using diaziridinone or related compounds as nitrogen source and metal as catalyst via the activation of a N-N bond. This catalytic system can also diaminate terminal olefins at allylic and homoallylic carbons via sp^3 C-H activation. Asymmetric processes have been developed for these diaminations.



**ENANTIOSELECTIVE INTRAMOLECULAR
ALKENES HYDROAMINATION CATALYZED BY
RARE-EARTH COMPLEXES SUPPORTED BY
CHIRAL BINAPHTHYLAMIDO LIGANDS**

A.A. Trifonov¹
Yu.S. Chapurina¹
J. Collin²
E. Schulz²
J. Hannedouche²

1 - G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia

2 - Equipe de Catalyse Moléculaire, ICMMO, UPS, Orsay, France
trif@iomc.ras.ru

Asymmetric intramolecular hydroamination reaction is an atom-economic and ecologic way to prepare chiral nitrogen-containing heterocyclic compounds. The synthesis of chiral alkyl- and amido rare-earth complexes supported by chiral binaphthylamido ligands will be reported. A new family of structurally defined heterobimetallic rare earth lithium ate complexes based on N-substituted binaphthylamido ligands was discovered that promoted the hydroamination/cyclization of aminoolefins with up to 87% ee. Neutral and ate rare earth alkyl complexes proved to be very efficient catalysts for enantioselective intramolecular hydroamination of aminopentenes or aminohexene at room temperature with enantiomeric excesses up to 83%. These compounds were evaluated as catalysts to promote the enantioselective hydroamination of amino-1,3-dienes. Chiral alkyl ate-complexes are shown to be efficient catalysts for the enantioselective intramolecular hydroamination of primary amines tethered to sterically demanding alkenes at high reaction temperatures. Fine tuning of their chiral environment allowed to reach enantioselectivities of up to 77% ee for the cyclisation of aminoalkenes bearing 1,2-di-substituted carbon-carbon double bond. Under harsher reaction conditions, these chiral complexes also demonstrate the ability to promote the hydroamination/ cyclisation of amine-tethered tri-substituted alkenes in enantioselectivities of up to 55% ee, as the first report of the formation of enantioenriched quaternary centres by an hydroamination reaction.

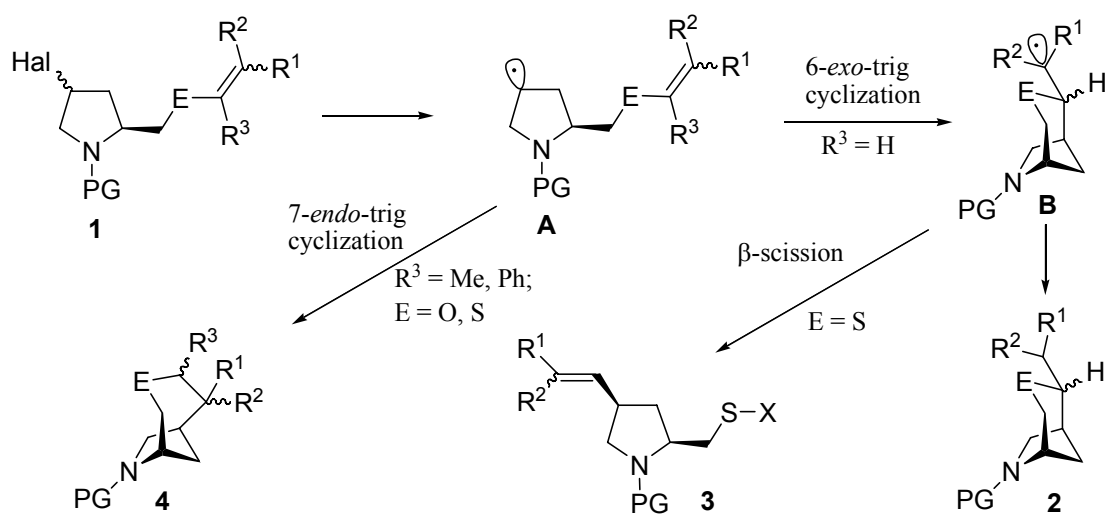
STEREOSELECTIVE CASCADE-TYPE HOMOLYTIC INTRAMOLECULAR C-ALKENYLATION VERSUS REDUCTIVE BRIDGED HETEROCYCLIZATION IN 4-HYDROXYPROLINE DERIVATIVES

E.E. Korshin
L. Konstantinovski
Y. Bilokin
M.D. Bachi

Weizmann Institute of Science, Department of Organic Chemistry,
Rehovot, Israel
edward.korshin@weizmann.ac.il

In spite of remarkable progress in formation of C–C bonds using various types of transition metal catalyzed cross-coupling reactions, an efficient and stereoselective attachment of alkenyl fragments to sp^3 -carbon stereocenter still remains a challenge for synthetic methodology. Herein we report on a novel efficient and entirely homolytic process for *cis*-stereoselective C-alkenylation through 1,5-translocation of functionalized alkenyl fragments from divalent sulfur to secondary sp^3 -carbon in the model 4-hydroxyproline derivatives **1**.

The systematic study of different variants of alkenyl fragment tethering via S-, O- or BnN-connectors, as well as the nature of the unsaturated appendage and reaction conditions reveal the general tendency which summarized schematically below. Efficient cyclization of the incipient radicals **A** according to the desired 6-*exo*-trig mode takes place in the case of α -unsubstituted alkenyl appendages. The resulted radicals **B** abstract hydrogen atom from conventional hydrogen atom donors yielding the (5+6)-bridged bicyclic systems **2**. The α -substituted radicals **A** are subjected to alternative 7-*endo*-trig route of cyclization leading to (5+6)-bridged heterocycles **4**. Being generated in the hydrogen donor free conditions, the sulfur-containing radicals **B** undergo β -scission of the weak C–S bond with formation of thiyl-radicals, which are trapped in the form of the translocated products **3** through the abstraction of allyl, styryl or tributylstannyl groups from the appropriate free radical tin mediators. Due to a bridged bicyclic nature of radical **B**, it is imperative that the homolytic cascade resulted in intramolecular C-alkenylation proceeds with absolute *cis*-stereoselectivity.



CHIRALITY IN ACTION: BEYOND THE CHIRAL DRUGS

A.A. Bredikhin

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
baa@iopc.ru

The phenomenon of chirality is considered as one of the central topics in modern organic chemistry. Considerable efforts, time and money have been spent on developing new spectacular methods of asymmetric synthesis. In this standard the ultimate goal of such studies are usually declared as the creation of chiral drugs.

Without questioning the importance and the multifaceted character of the chiral discrimination manifestations in living systems, we want to draw attention of the organic practitioners on some of the less popular but no less interesting in themselves aspects of chiral recognition phenomena. In this report we have used our own results obtained for a narrow class of organic compounds, namely terminal glycerol aromatic ethers $\text{Ar-O-CH}_2\text{CH(OH)CH}_2\text{OH}$ and their simple derivatives, to illustrate:

- chiral recognition of the "host-guest" type, including
 - recognition in solutions;
 - recognition on the gravity sensor surface;
- chiral recognition in self-assembly processes, including
 - spontaneous resolution of enantiomers during crystallization;
 - the formation of molecular nanogels;
 - the formation of periodic structures during gelation process;
 - the formation of new class of thermotropic liquid crystals.

TANDEM OF ORGANOCATALYSIS AND IONIC LIQUIDS: NOVEL OPPORTUNITIES FOR ASYMMETRIC ORGANIC SYNTHESIS

S.G. Zlotin
O.V. Maltsev
A.S. Kucherenko
D.E. Siyutkin
S.V. Kochetkov

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia
zlotin@ioc.ac.ru

The asymmetric organocatalysis is a rapidly growing area of modern organic chemistry. However industrial applications of this methodology require recoverable immobilized forms of organocatalysts. We have synthesized novel types of immobilized catalysts by tagging them to ionic groups (ionic liquid fragments). As a result, they have acquired lower solubility in organic solvents and simplified regeneration. Unlike known polymer-tagged catalysts, our products possess tunable catalytic properties and their synthesis and transformations can be monitored by conventional spectroscopic methods.

In the presence of α -aminoacid-derived ionic catalysts, prochiral ketones react with aldehydes in organic or aqueous media to afford chiral aldols with extremely high diastereo- (*dr* до 99:1) and enantioselectivities (up to 99% *ee*), which are similar to respective values of enzymatic reactions. In the presence of α,α -diarylprolinol-derived catalysts, α,β -unsaturated aldehydes add C- or N-nucleophiles to afford corresponding Michael adducts (yield up to 98% and up to 99% *ee*). Using this methodology we synthesized key intermediates for the preparation of the most active enantiomers for CNS disorder medications and important β -amino acids. Furthermore, we revealed undesirable side reactions poisoning the catalysts (ESI-MS mass spectrometry) and found a solution (inert atmosphere) to significantly increasing their operation period (more than 10 cycles).

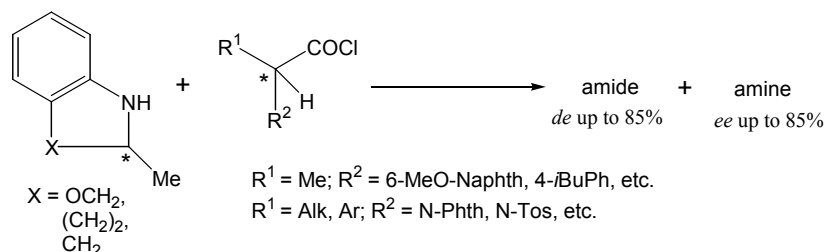
The work was financially supported by the Ministry of Education and Science of the Russian Federation (contract No 02.740.11.0630) and by the RFBR (grants Nos. 09-03-00384 and 09-03-12164).

V.P. Krasnov
G.L. Levit
D.N. Kozhevnikov
M.I. Kodess
D.A. Gruzdev
E.N. Chulakov
V.N. Charushin

ACYLATIVE KINETIC RESOLUTION OF RACEMIC AMINES WITH PROFENS AND AMINO ACIDS DERIVATIVES

Postovsky Institute of Organic Synthesis of RAS, Ekaterinburg, Russia
ca@ios.uran.ru

Preparation of enantiomerically pure amines as a result of acylative kinetic resolution (KR) has attracted considerable interest. In addition to the efforts on creation of new acyl transfer catalysts, a significant attention is given to design of the agents capable of stereoselective acylation. We showed that efficient KR of heterocyclic amines can be achieved while using 2-arylpropionyl and N-protected amino acids derivatives as resolving agents.



The aim of the present work was to study the effect of structure of resolving agent on the efficiency of KR.

It was shown that the use of 2-arylpropionyl chlorides provides a significant difference in the reaction rates of *R*- and *S*-amines (selectivity factor *s* up to 60), which makes it possible to apply some of these compounds for preparative KR of racemic amines. Amino acids derivatives were less selective (*s* up to 20), but they are diverse in a structure and are of specific interest for elucidation of stereo and electronic factors that determine the stereochemical outcome of the process.

To explain the peculiarities of KR process in the course of acylation of racemic amines with chiral acyl chlorides we used quantum-chemical calculations (DFT-D/B3LYP/TZVP, COSMO solvation model) and NMR spectroscopy.

The work was financially supported by RFBR (grant 10-03-00084), the State Program for Supporting of Leading Scientific Schools of the RF (grant NSh 65261.2010.3), the State Contract 02.522.12.2011 and by the Ural Division of RAS (grants 09-P-3-2001, 09-I-3-2004).

**PHOSPHORUS BASED MACROCYCLIC LIGANDS:
SYNTHESIS AND APPLICATIONS**

A.A. Karasik¹
 A.S. Balueva¹
 E.I. Musina¹
 R.N. Naumov¹
 S.N. Ignatyeva¹
 E. Hey-Hawkins²
 O.G. Sinyashin¹

1 - A. E. Arbuzov Institute of Organic and Physical Chemistry,
 Russian Academy of Sciences, Kazan, Russia

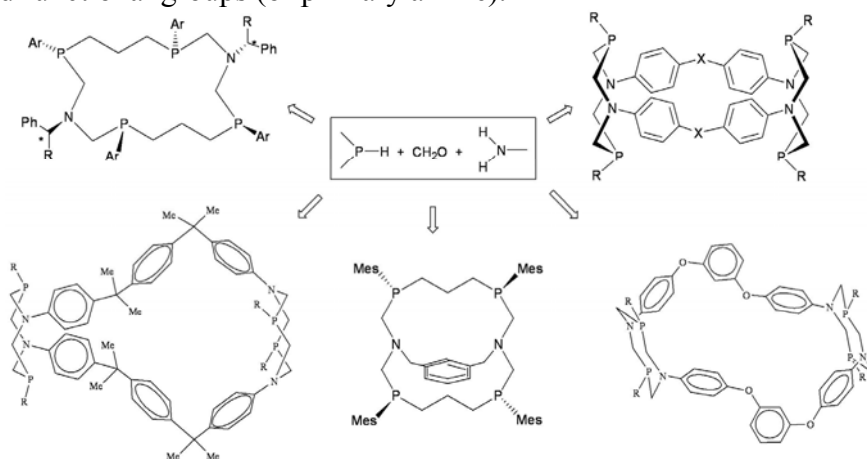
2 - Institut für Anorganische Chemie der Universität Leipzig, Leipzig,
 Germany
 anna@iopc.ru

The macrocycles are perspective building blocks for the creating of nanosized molecular devices and nanomaterials on the "bottom-up" principle. Incorporation of phosphorus atom into the macrocyclic skeleton lead to the specific properties. First of all P(III) donor centers are soft that is why the specific coordination ability to the soft metal ions should appear. Secondly the well-known ability of P(III) species to form transition metal based catalysts of various organic reactions should be modified by additional bonding of metal centers or organic substrates with macrocycle fragments via dative or weak interactions. Thirdly the specific reactivity and the structural variability of phosphorus could be utilized for the additional functionalization of the macrocyclic objects or for the rational design of macrocyclic molecular devices. However there are some noticeable problems concerning the availability of P-based macrocycles. In contrast with the "common" heteroatoms such as O and N the inversion barrier of P(III) is higher. So compounds containing two or more phosphorus atoms are usually obtained as a mixture of stereomers, which require separation in order to obtain the individual macrocycles. Another problem is the known instability of phosphines to oxidation. So, the availability of the P-containing macrocyclic compounds is one of the key points for their use in the fields of catalysis, supramolecular chemistry and nanomaterials.

At the present time three main strategies for macrocyclic synthesis may be identified:

1. macrocyclization under high-dilution conditions; 2. template synthesis of macrocycles; 3. covalent self-assembly of macrocycles

An effective strategy of P,N-containing macrocycles design had been developed which is based on covalent self-assembly processes in the course of Mannich-type condensations in three-component systems: primary phosphine (or secondary diphosphine) – formaldehyde – diamine with spatially divided functional groups (or primary amine).



This approach allowed authors to obtain various types of macrocyclic phosphines, namely cage cyclophanes with 1,5-diaza-3,7-diphosphacyclooctane fragment in the basic framework, cyclophanes with linear P,N-containing spacers, P,N-containing corands and the first P,N-containing cryptand with four phosphine centers.

References:

1. A.A. Karasik, O.G. Sinyashin in *Phosphorus Compounds Advanced Tools in Catalysis and Material Sciences*, Berlin, Springer, 2011, Chapter 14, P. 377-448
2. A.A. Karasik, A.S. Balueva, O.G. Sinyashin *C. R. Chimie* 13 (2010) 1151–1167.

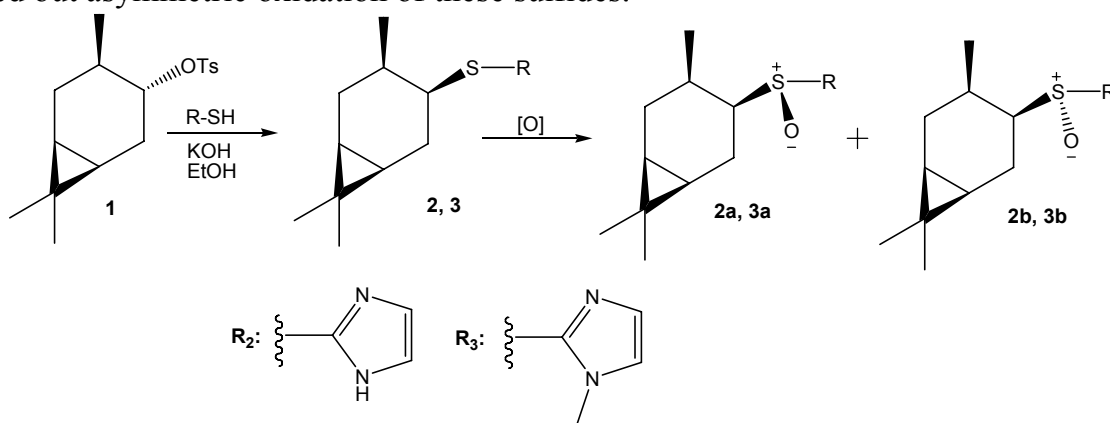
SYNTHESIS AND ASYMMETRIC OXIDATION OF CARANYL CONTAINING HETEROCYCLIC SULFIDES

M.Ya. Demakova
D.V. Sudarikov
S.A. Rubtsova
A.V. Kuchin

Institute of Chemistry, Komi Science Center, Ural Division of RAS,
Russia
my-demakova@rambler.ru

Optically pure and diastereomerically enriched sulfoxides are of interest as physiologically active substances and widely used in asymmetric synthesis [1]. For example, some of these compounds are used as antioxidants and antidepressants [2]. Series of chiral sulfoxides containing heterocycles are used in clinical therapy of functional diseases [3].

In this paper we synthesized 2-(((1R,3S,4R,6S)-4,7,7-trimethylbicyclo(4.1.0)-hept-3-yl)sulfanyl)-1*H*-imidazole (**2**) and 1-methyl-2-(((1R,3S,4R,6S)-4,7,7-trimethylbicyclo(4.1.0)-hept-3-yl)sulfanyl)-1*H*-imidazole (**3**) with yields 82 and 86% respectively. Further we carried out asymmetric oxidation of these sulfides.



As an oxidant were used *m*-CPBA (*meta*-chloroperoxybenzoic acid) and CHP (cumene hydroperoxide). The results of the oxidation are presented in the table.

Sulfide		Oxidant	
		<i>m</i> -CPBA	CHP/VO(acac) ₂
2	Yield, %	87	89
	<i>de</i>	45	48
3	Yield, %	88	92
	<i>de</i>	42	46

Structures of the obtained compounds are confirmed by NMR, IR spectroscopy and element analysis data.

References:

- 1) Prilezhaeva E.N. Synthesis and properties of sulfur organic compounds/ Edited by Belen'kiy. Moscow: Khimia, 1998. 162 p. [in russian]
- 2) Minoru U. Chem. Farm. Bull., 1989, 37, 21
- 3) Youssef M. S. K., Ahmed R. A. // Phosphorus, Sulfur, and Silicon and the Related Elements. 2006, 181:5, P. 1123-1199.

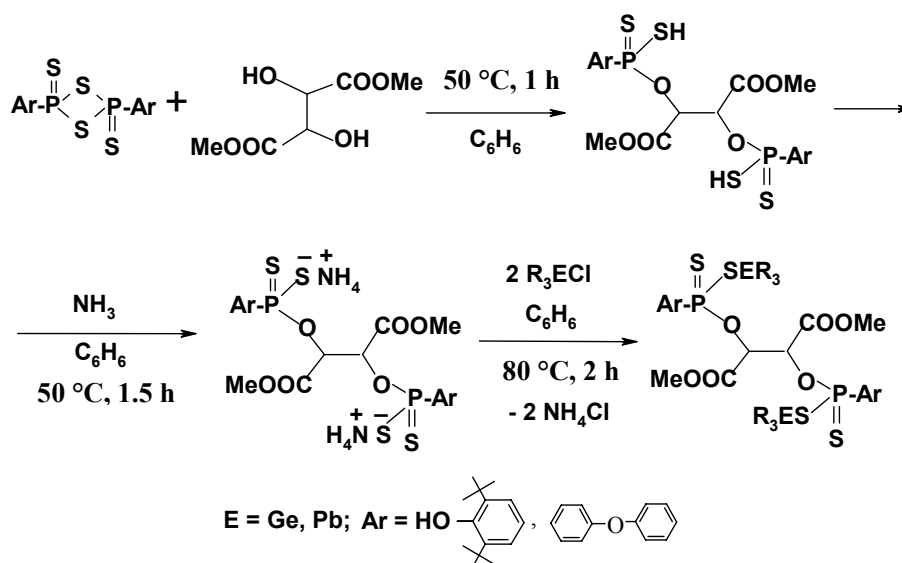
The study is supported by Russian Foundation of Basic Researches (grant № 10-03-00933-a).

G.T. Gabdullina
Ye.M. Martianov
L.A. Almetkina
I.S. Nizamov
R.A. Cherkasov

OPTICALLY ACTIVE S-GERMYL AND S-PLUMBYL DERIVATIVES OF ARYLBISDITHIOPHOSPHONIC ACIDS ON THE BASIS OF DIMETHYL L-TARTRATE

Kazan (Volga region) Federal University, Kazan, Russia
isnizamov@mail.ru

Thiophosphorylated derivatives of chiral natural compounds are necessary to develop convenient methods of preparing new types of drugs. The substantial interest in dithiophosphonic acids and their S-organoelement derivatives is due to their potential biological activity. We have recently prepared bisaryldithiophosphonic acids by the reactions of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with tri(ethylene glycol) and 1,4-butanediol and their S-silyl, S-germyl, S-stannyl and S-plumbyl derivatives [1]. In continuation of our approach, we have manage to involve dimethyl *L*-tartrate in the reactions with 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides. Optically active arylbisdithiophosphonic acids obtained were transformed into the corresponding diammonium salts.



Novel S-germyl and S-plumbyl derivatives of aryldithiophosphonic acids were prepared on the basis of the reactions of ammonium salts of corresponding acids with triorganylschlorogermans, chloroplumbanes and diphenyl dichloroplumbane. The S-germyl and S-plumbyl derivatives of aryldithiophosphonic acids with chiral centers possess appreciable antimicrobial activities.

References:

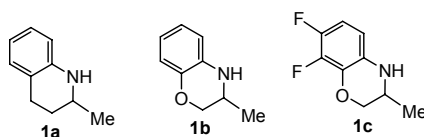
- [1] Nizamov I.S., Gabdullina G.T., Nizamov I.D., Nikitin Ye.N., Al'metkina L.A., Cherkasov R.A. *Phosphorus, Sulfur, and Silicon*. 2010. Vol. 185. P. 732-742.

INVERSION OF STEREOSELECTIVITY IN THE ACYLATION OF HETEROCYCLIC AMINES WITH N-PROTECTED (S)-AMINO ACYL CHLORIDES. EFFECT OF N-PROTECTION

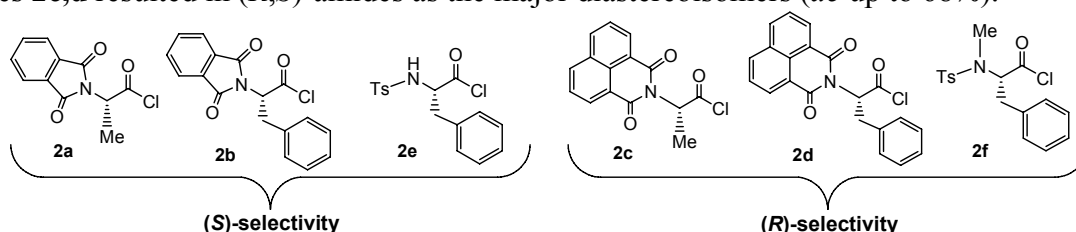
D.A. Gruzdev
G.L. Levit
V.P. Krasnov

Postovsky Institute of Organic Synthesis of the Russian Academy of
Sciences (Ural Division), Ekaterinburg, Russia
gruzdev-da@ios.uran.ru

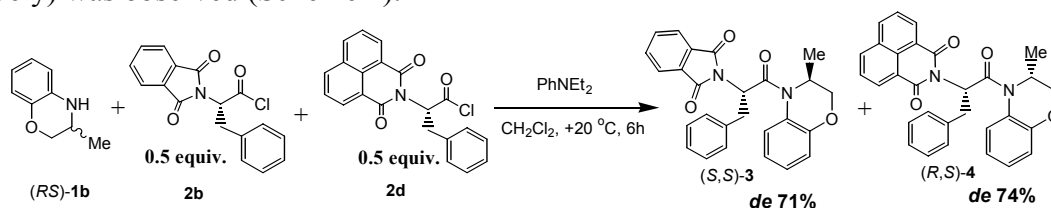
Acylative kinetic resolution of racemic amines is under active investigation for the last years. Previously we showed that acylation of heterocyclic amines **1a,b** with *N*-phthaloyl-(*S*)-alanyl and *N*-phthaloyl-(*S*)-phenylalanyl chlorides^{1,2} (**2a,b**) leads to the predominant formation of (*S,S*)-amides (*de* up to 74%).



In the present work we demonstrated that the change in *N*-protection from phthaloyl to 1,8-naphththaloyl leads to the inversion of stereoselectivity. Acylation of racemic amines **1a-c** with acyl chlorides **2c,d** resulted in (*R,S*)-amides as the major diastereoisomers (*de* up to 68%).



Kinetic resolution of amine **1b** with acyl chlorides **2b** and **2d** in CH₂Cl₂ at +20 °C led to amides (*S,S*)-**3** (*de* 60%) and (*R,S*)-**4** (*de* 63%), respectively. We carried out the parallel kinetic resolution of **1b** using the equimolar mixture of chlorides **2b** and **2d** with of the same (*S*)-configuration. In this case the formation of amides (*S,S*)-**3** and (*R,S*)-**4** (*de* 71 and 74%, respectively) was observed (Scheme 1).



Scheme 1.

It was also shown that *N*-tosyl-(*S*)-phenylalanyl (**2e**) and *N*-methyl-*N*-tosyl-(*S*)-phenylalanyl (**2f**) chlorides exhibit the opposite stereoselectivity in acylation of amine **1c**. Thus, the kinetic resolution of **1c** using **2e** in toluene resulted in (*S,S*)-amide (*de* 24%), while acylation of **1c** with *N*-methylated compound **2f** under the same conditions led to (*R,S*)-amide (*de* 73%).

Thus, it was shown that the minor changes in the structure of chiral acylating agent is accompanied by significant change in the stereochemical result of kinetic resolution of heterocyclic amines up to the total inversion of stereoselectivity.

References:

1. Krasnov V.P., Levit G.L., Kodess M.I. et al. // *Tetrahedron: Asymmetry*, 2004, 15, 859-862.
2. Gruzdev D.A., Levit G.L. Krasnov V.P. et al. // *Tetrahedron: Asymmetry*, 2010, 21, 936-942.

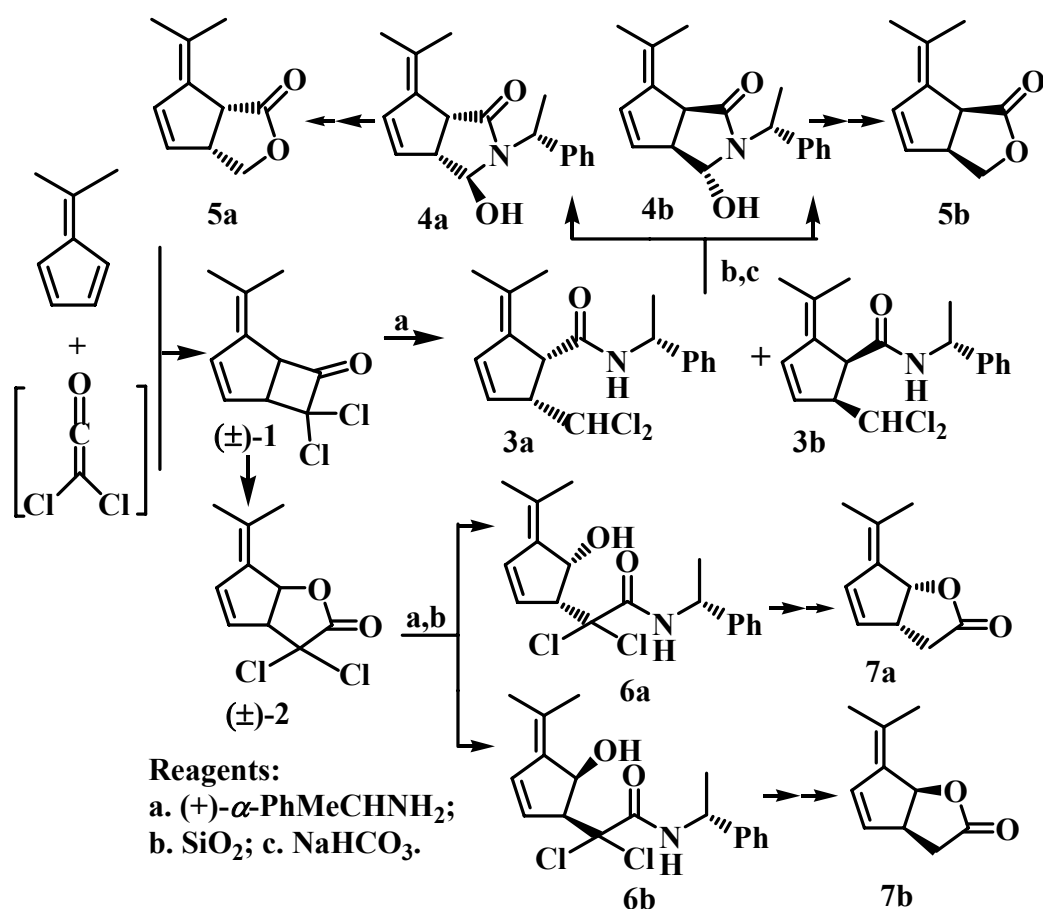
The work was financially supported by RFBR (grant 10-03-00084), the State Program for Supporting of Leading Scientific Schools of the RF (grant NSh 65261.2010.3), the State Contract 02.522.12.2011 and by the Ural Division of RAS (grants 09-P-3-2001, 09-I-3-2004, 10-3-NP-322).

N.A. Ivanova
N.P. Akhmetdinova
Z.R. Valiullina
V.A. Akhmetyanova
M.S. Miftakhov

CHIRAL BLOCKS FROM [2+2]-CYCLOADDUCT OF DICHLOROKETENE AND DIMETHYLFULVENE

Institute of Organic Chemistry, Ufa Scientific Centre of the Russian Academy of Sciences, Russia
ivanova_NA@anrb.ru

Obtaining chiral block - synthons from available raw materials is an important "component" of an enantiospecific synthesis of physiologically active compounds. Using as a «source of chirality» (+)- α -methylbenzylamine from [2+2]-cycloadducts dimethylfulvene and dichloroketene were developed hemorational syntheses of optically active *exo*-isopropylidenecyclopentenones **5a, 5b** и **7a, 7b**.



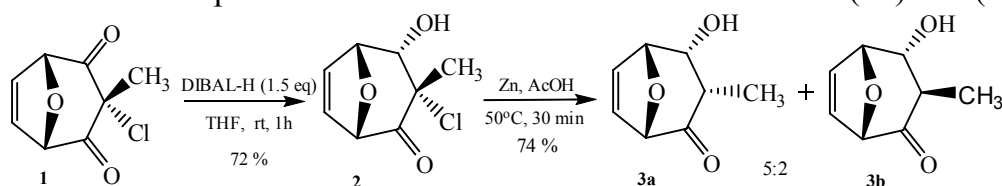
This work was supported by the state contract the Ministry of Education and Science № 4.740.11.0367 (with BashSU).

D.A. Khlevin
S.E. Sosonyuk
M.V. Proskurnina
N.S. Zefirov

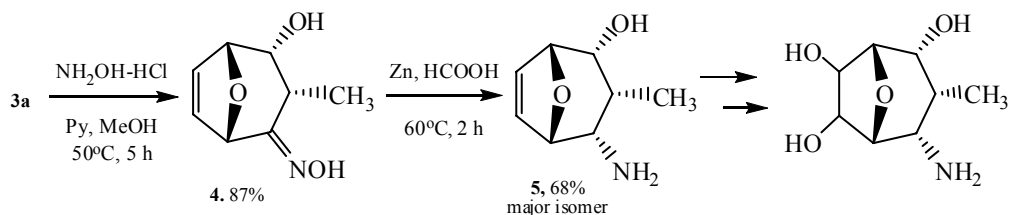
NEW POLYHYDROXYAMINOCYCLOHEPTANES AS A PERSPECTIVE GLYCOSIDASE INHIBITORS

Moscow State University, Chemistry Department, Moscow, Russia
khlevin@mail.ru

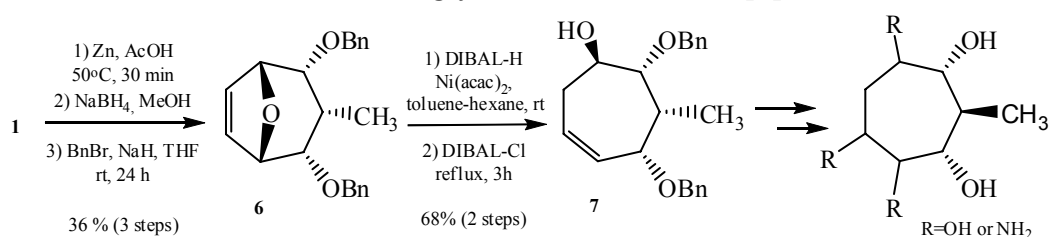
Stereoselective approach to polyhydroxyaminocycloheptanes as potential glycosidase inhibitors from available diketone (**1**) [1] was proposed. Introduction of amino function in 8-oxabicyclo[3.2.1]octane framework was intriguing as the route to calystegine analogs – potential glucosidase inhibitors [2]. Reduction of diketone (**1**) by DIBAL-H followed by dechlorination led to a separable mixture of ketoalcohol stereoisomers (**3a**) and (**3b**).



The major isomer (**3a**) was involved in a reductive amination process. Amine (**5**) was separated from the reaction mixture as individual isomer. We assume it could be transformed to a potential glycosidase inhibitor by double bond bishydroxylation.



Expanding our strategy we have developed a route to monocyclic cycloheptane derivatives. Benzyl protected diol (**6**) was synthesized from compound (**1**), then using DIBAL-H mediated reductive ring opening in the presence of nickel complexes unsaturated compound (**7**) was obtained. We consider this alcohol as a precursor for aminoderivatives with the structure close to some known glycosidase inhibitors [3].



Configuration of products was determined by X-ray and NMR experiments. Proposed strategy is flexible and allows to obtain a wide range of mono- and bicyclic aminopolyols with different given regio- and stereochemistry.

References:

1. Tafeenko, V. A., Aslanov, L. A., Proskurnina, M. V., Sosonyuk, S. E., Khlevin, D. A. *Acta Cryst.* **2009**, E65, 1580
2. Asano, N., Nash, R. J., Molyneux, R. J., Fleet, G. W. J. *Tetrahedron: Asymmetry*. **2000**, 11, 1645–1680
3. Gravier-Pelletier, C., Maton, W., Dintinger, T., Tellier, C., Le Merrer, Y. *Tetrahedron*. **2003**, 59, 8705–8720.

SYNTHESIS AND MEMBRANE TRANSPORT PROPERTIES OF OPTICALLY ACTIVE α -AMINOPHOSPHINE OXIDES

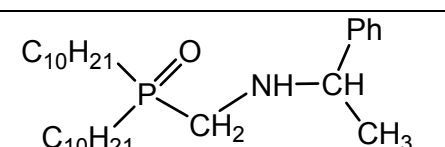
S.A. Koskin
A.R. Garifzyanov
R.A. Cherkasov

Kazan Federal University, A.M. Butlerov Institute of Chemistry,
Kazan, Russia
scioris@yandex.ru

In recent years the increased interest to aminophosphine oxides due to their ability to form the different structure complexes that allowing use them in the processes of liquid and membrane extraction of inorganic and organic substrates. Besides presence of optically active centers and centers of specific interaction in molecules enables apply α -aminophosphine oxides for concentration and separation of optical isomers of organic compounds.

Therefore we have developed a method of synthesis the functionalized α -aminophosphine oxides based on a three-component Kabachnik-Fields reaction with formaldehyde, phosphinic acid, amines or amino acid. The introduction of chiral centers in the α -aminophosphine oxides carried out by involving to Kabachnik-Fields reaction of reagents with chiral carbon and phosphorus atoms – (R)-, (S)-methylbenzylamines, (S)-alanine, (S)-valine, (S)-leucine, (S)-glutamic acid and mixtures of enantiomers decylphenylphosphinic acid. The synthesis conditions were chosen to achieve maximum yield (85-95%). Enantiomers of compounds derived from racemic decylphenylphosphinic acid were separated by crystallization of tartrates. The structure of the obtained compounds was conformed by ^1H NMR, IR-spectroscopy.

For obtained (R)- and (S)-didecyl-(N-1-phenylethanamino)methylphosphine oxides have been studied the membrane transport of the tartaric and aspartic acid stereoisomers (Table) and stereoselectivity of the transfer found.

Carrier		Flow*10 ⁶ mol*min/m ²			
		Tartaric acid		Aspartic acid	
		D-form	L-form	D-form	L-form
	(R)	17.4	13.6	1.75	4.70
	(S)	6.43	10.27	6.33	3.66

Ye.M. Martianov¹
 L.A. Almetkina¹
 I.S. Nizamov¹
 R.A. Cherkasov¹
 D.B. Krivolapov²
 I.A. Litvinov²

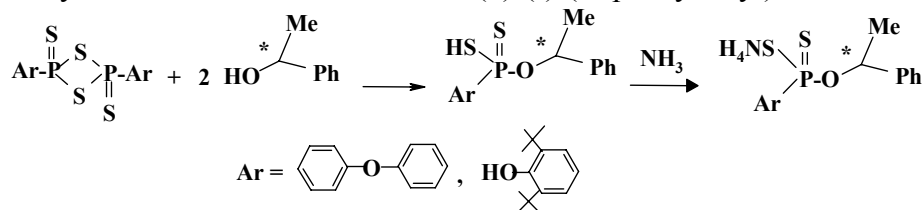
PHENYLETHANOL, PHENYLETHYL AMINES AND AMINOSILANES CONTAINING CHIRAL CENTRES IN THIOPHOSPHORILATION REACTIONS

1 - Kazan (Volga region) Federal University, Kazan, Russia

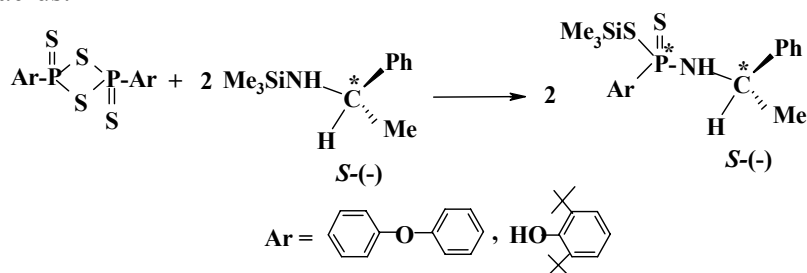
2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia

isnizamov@mail.ru

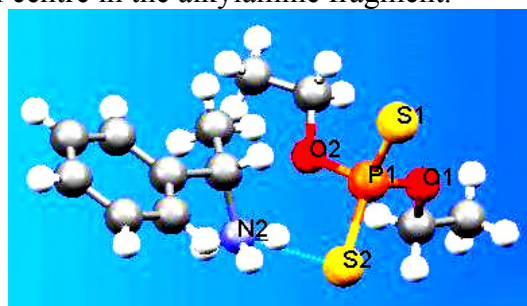
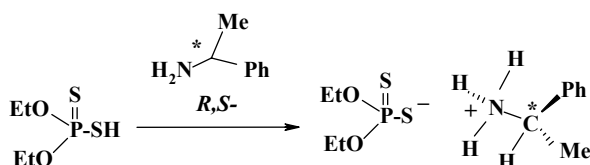
Tetracoordinated phosphorus organic thioacids, their ammonium salts and esters containing chiral centres are interest from the point of fundamental organic chemistry and the development of facile methods of obtaining new products with biological activity. The interest in chiral tetracoordinated phosphorus organic thioacids and their derivatives is due to their potential metabolic regulation activity. We have obtained racemic dithiophosphoric and aryldithiophosphonic acids by the reactions of tetraphosphorus decasulfide and 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with *R,S*- α -phenylethanol. These thioacids were transformed into the corresponding ammonium salts by the treatment of ammonia and (*S*)-(-)-(α -phenylethyl) amine.



Aminosilanes obtained on the basis of enantiomeric pure (*S*)-(-)-(α -phenylethyl) amine, (*R*)-(+)-(α -phenylethyl) amine and racemic α -phenylethyl amine were also involved in the reactions with 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides to form *S*-trimethylsilyl esters of amino-dithiophosphonic acids.



The reaction of O,O-diethyl dithiophosphoric acid with (*R,S*)- α -phenylethylamine serve as a method for obtaining dithiophosphates bearing a chiral centre in the alkylamine fragment.



Its structure was established by X-ray single crystal diffraction.

**HIGH PERFORMANCE NMR ANALYSIS OF
ENANTIOMERIC PURITY AND ABSOLUTE
CONFIGURATION OF CHIRAL ALCOHOLS AND
AMINES ON A MICROGRAM SCALE**

**N.V. Orlov
V.P. Ananikov**

Zelinsky Institute of Organic Chemistry, Russian Academy of
Sciences, NMR Laboratory, Moscow, Russia
onv@ioc.ac.ru

Nowadays NMR spectroscopy has become a powerful tool for analysis of chiral compounds. An important prerequisite before NMR analysis is conversion of enantiomers into magnetically nonequivalent diastereomers by means of chiral derivatizing agents (CDAs). Though great number of various CDAs were introduced over last years¹ the derivatization procedure remains time- and reagent consuming operation which limits its use as a routine tool for rapid analysis of reactions of asymmetric synthesis and catalysis.

Recently we have developed new derivatization procedure for analysis of chiral alcohols and amines which can be performed directly in NMR tube². No preliminary purification of diastereomers formed is required to obtain various NMR spectra (both 1D and 2D) of high quality which allows determination of enantiomeric purity of various chiral alcohols and amines with high accuracy within several minutes including sample preparation time. 5-10 mg of chiral samples is enough for standard analysis though even 0.01 mg of chiral samples can be successfully analyzed using standard NMR hardware. The method developed is applicable to determination of absolute configuration as well using both double and single derivatization techniques³. The scope of the "in tube" derivatization procedure and experimental details of analysis will be discussed.

References:

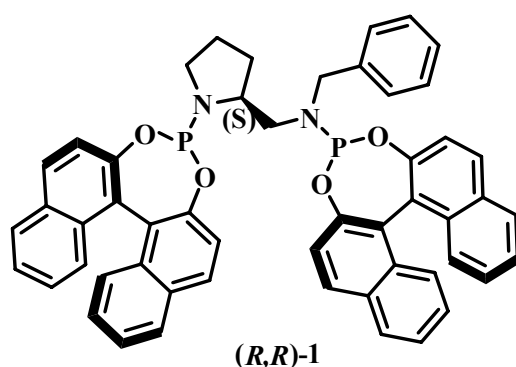
1. a) J. M. Seco, E. Quinoa, R. Riguera, *Chem Rev.*, **2004**, 104, 17; b) T. J. Wenzel, C. D. Chisholm, *Prog. Nucl. Magn. Reson. Spectrosc.*, **2011**, 59, 1.
 2. a) N. V. Orlov, V. P. Ananikov, *Chem. Commun.*, **2010**, 46, 3212; b) N. V. Orlov, V. P. Ananikov, *Green Chem.*, **2011**, 13, *ASAP*, DOI: 10.1039/C1GC15191F.
 3. J. M. Seco, E. Quinoa, R. Riguera, *Tetrahedron: Asymmetry*, **2001**, 12, 2915.
-

The work was supported by the Research Grant MK-1434.2010.3.

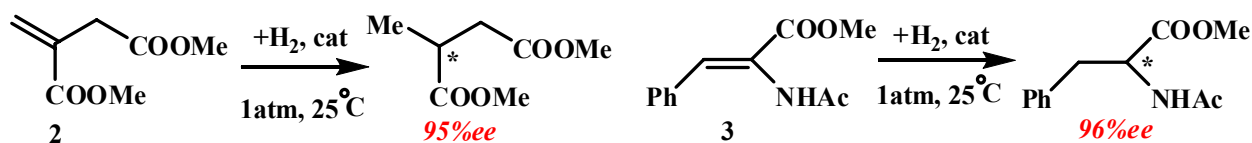
A. Boerner³

shaa78@mail.ru

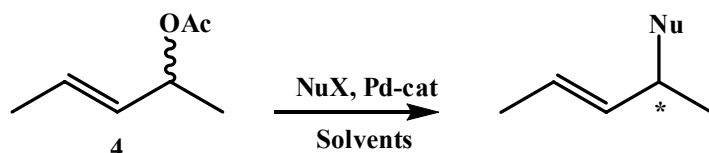
(*S,S*)-1



Scheme 1



Scheme 2



Nu = N(CH₂)₄, X = H, up to 67% *ee*

Kazan, Russia, 2011

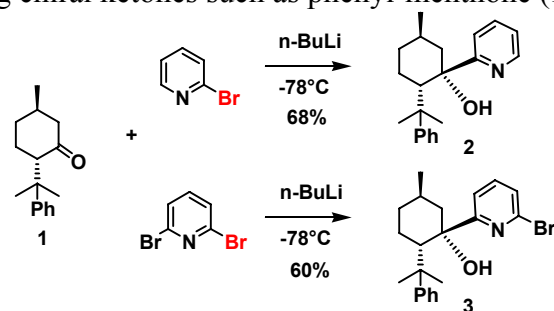
BROMINE-LITHIUM EXCHANGE UNDER IN SITU-QUENCH CONDITIONS: AN EFFICIENT ONE-POT SYNTHESIS OF CHIRAL LIGANDS FOR TRANSITION METAL CATALYSIS

Ja. Velder
A. Saiai
M. Mitani
H.-G. Schmalz

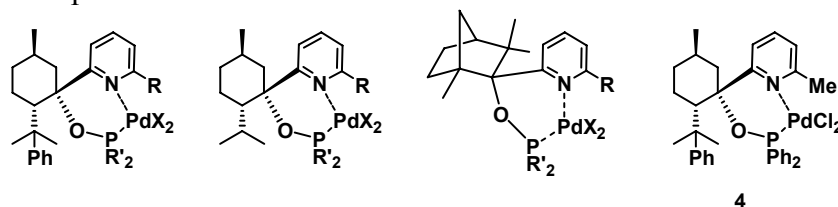
Institute of Organic Chemistry, University of Cologne, Cologne, Germany
janna.velder@uni-koeln.de

In contrast to commonly applied protocols, reactions of organolithium compounds need not necessarily be conducted in a stepwise fashion. In this context, we have recently demonstrated that the generation of lithioarenes by bromine-lithium exchange can be performed in many cases in the presence of an electrophile. This in-situ-quench (ISQ) protocol is operationally simple, offers new opportunities for the synthesis of valuable compounds and is even suitable for application in flow microreactors. [1]

In our research on the synthesis of new chiral ligands for metal catalysis we have now applied the ISQ methodology [2] to the synthesis of chiral alcohols (**2** and **3**) by alkylation of mono- or dibromoarenes employing chiral ketones such as phenyl-menthone (**1**), fenchone or menthone.

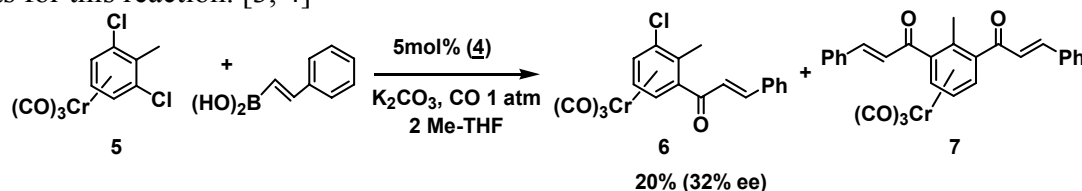


This way, we were able to synthesize several new N,O-ligands, which were then used for the preparation of Pd-complexes:



R = H, Br, Ph, Me; R' = Ph, *t*-Bu, *c*-HeX, *i*-Pro; X = Cl, I

The Pd-complex **4** performed well in a carbonylative Suzuki coupling to give the mono-coupling product (**6**/ent-**6**) in 32% ee, which is a better result than those achieved with well-known catalysts for this reaction. [3, 4]



References:

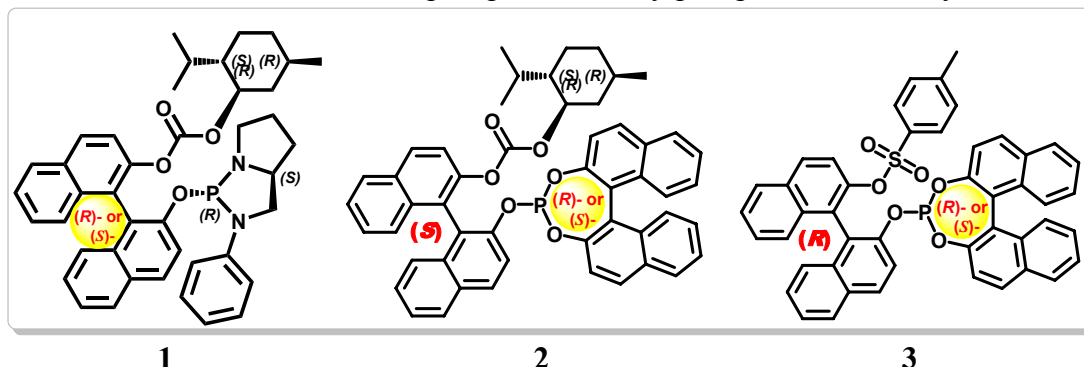
- [1] S.El Sheikh, H.-G. Schmalz. *Curr. Opin. Drug Discov. Devel.* **2004**, 7, 882.
- [2] S. Goto, J. Velder, S. El Sheikh, Y. Sakamoto, M. Mitani, A. Adler, A. Becker, J. Neudörfl, J. Lex, H.-G. Schmalz. *Synlett* **2008**, 1361.
- [3] B. Gotov, H.-G. Schmalz. *Org. Lett.* **2001**, 3, 1753.
- [4] A. Böttcher, H.-G. Schmalz. *Synlett* **2003**, 1595.

THE NEW BINOL-BASED DIAMIDOIPHOSPHITES AND ARYLPHOSPHITES IN ASYMMETRIC METALLOCOMPLEX CATALYSIS

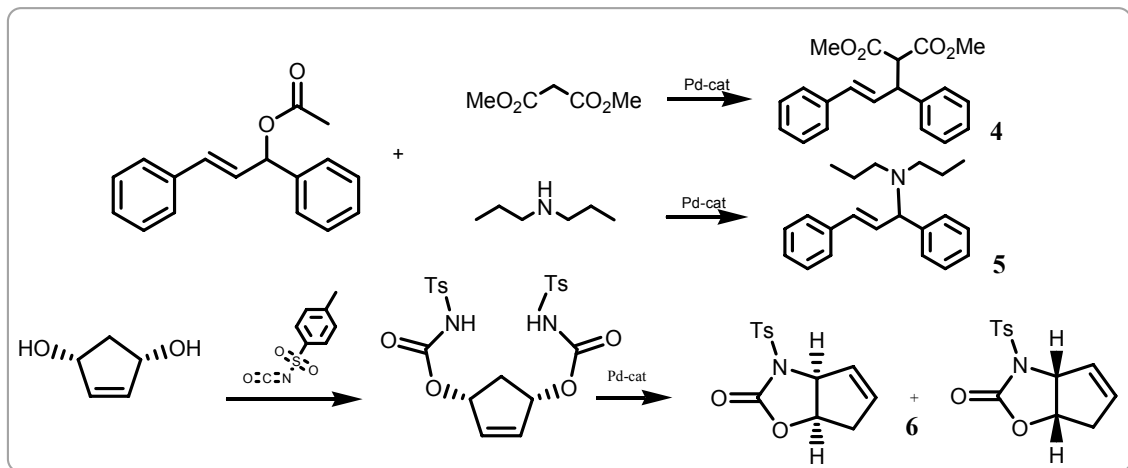
S.V. Zhiglov¹
M.N. Gavrilova¹
I.V. Chuchelkin¹
E.A. Rastorguev²
K.N. Gavrilov¹

1 - Ryazan State University, Department of Chemistry, Ryazan, Russia
2 - Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia
s.zhiglov@rsu.edu.ru

The new BINOL-based diamidoiphosphites and arylphosphites **1-3** was synthesized:



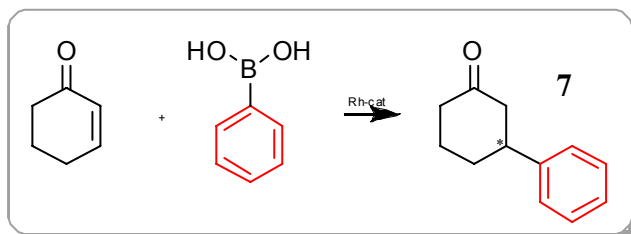
These Pd (II) complexes were used in Pd-catalyzed allylation and desymmetrization:



Novel aryl phosphites provided high enantioselectivity in the Pd-catalyzed allylic substitution of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate (*ee* up to 96% with (**S**)-**1**) and dipropylamine (up to 95% *ee* with (**R**)-**1**). Up to 67% *ee* in Pd-catalyzed desymmetrization of N,N-ditosyl-meso-cyclopent-4-ene-1,3-diol biscarbamate were obtained with (**S**)-**3**.

Ligands **1-3** were next evaluated in the Rh-catalyzed addition of phenylboronic acid to cyclohexenone. Diamidophosphite (**R**)-**1** demonstrated excellent *ee* (98%). Ligands (**R**)-**2** and (**S**)-**3** provided lower asymmetric induction (65% and 88 % *ee*).

The combination of high enantioselectivity, low cost, and easy synthesis of the ligands makes them very attractive for further catalytic applications.



We acknowledge the financial support from the Russian Foundation for Basic Research (Grant No. 11-03-00347-a) and a grant President of the Russian Federation for Young Candidates of Sciences (No. MK-3889.2010.3).

ASYMMETRICAL HYDRO-, HYDROTIOPHOSPHORUS COMPOUNDS AND SOME THEIR FUNCTIONALLY SUBSTITUTED DERIVATIVES

O.A. Aimakov¹
J.V. Oleynikova²
N.B. Kasenova²
N.I. Svintsitskaya²

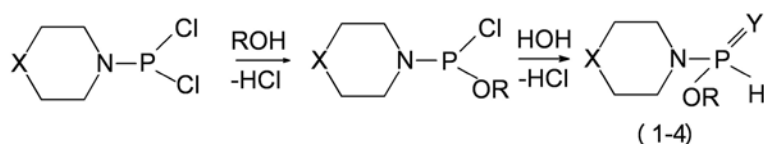
1 - Kokshetau State University of S.Ualihanov, Kokshetau,
Kazakhstan

2 - Saint-Petersburg State Institute of Technology (Technical
University), St.-Petersburg, Russia
 aimakov@rambler.ru

Hydrophosphorus and hydrothiophosphorus organic compounds are of considerable interest for researchers owing to their unusual reactivity connected with presence of hydrophosphorus and hydrothiophosphorus groups in the molecules.

Our research group is engaged in investigation of the chemistry and application of the hydrophosphorus and hydrothiophosphorus compounds which possess a high reactivity and allow to synthesize various classes of organophosphorus compounds containing phosphorus-carbon, phosphorus-nitrogen, phosphorus-sulphur and phosphorus-carbon-nitrogen fragments in the molecule.

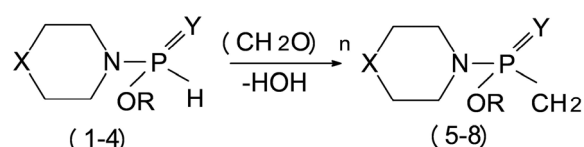
Here we developed the synthesis of hydroxy- and hydrophosphorus organic compounds with various radicals. The scheme of the synthesis of N-piperidino-O-ethyl(isopropyl) phosphonic acid derivatives (1-4) is shown below (scheme 1).



X = O, CH₂; R = Et, i-Pr; Y = O, S

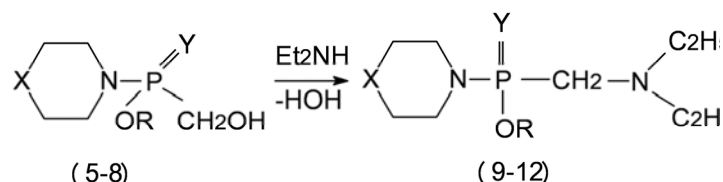
Scheme 1.

The condensation reaction of compounds (1-4) with paraformaldehyde leading to the formation of derivatives (5-8) was investigated (scheme 2).



Scheme 2.

Obtained 1-hydroxyphosphonic derivatives (5-8) were treated then by diethylamine to give 1-(N,N-diethylamino)phosphonic derivatives (9-12) (scheme 3).



Scheme 3.

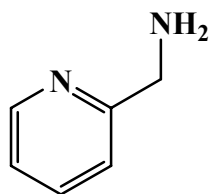
Obtained compounds (9-12) are widely applied as intermediate synthesis products of pesticides and complexing agents, polymers stabilizers, additives to oils, and biologically active substances.

NEW PICOLYLAMINE TEMPLATE ORGANO-CATALYST FOR ENANTIOSELECTIVE ALDOL REACTIONS

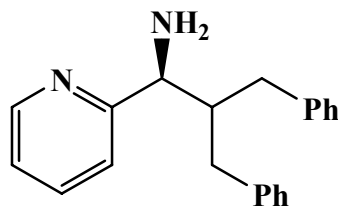
M. Naveed Umar^{1,2}
 Thomas Nugent²
 Ahtaram Bibi²

1 - University of Malakand, Pakistan
 2 - Jacobs University Bremen, Germany
 onv@ioc.ac.ru

Picolylamine template organocatalyst containing only one stereogenic center has been identified for fast aldol reactions (16–48 h). Using 2–5 mol% of (*R*)- or (*S*)-PicAm-2, cyclohexanone (3.3 equiv) readily undergoes aldol reactions with *o*-, *m*-, and *p*-substituted aromatic aldehyde partners (limiting reagent), including the poor electrophile 4-methylbenzaldehyde (95–99% ee). Furthermore, functionalized cyclic ketone substrates have been converted into four aldol products 9–12 using the lowest catalyst loading (5.0 mol%) to date with the highest yield and enantioselectivity.



2-picolylamine: promising new organocatalyst template



aldol organocatalyst example
 PicAm-2

Section 3.

Advanced Methods of Organic Synthesis

Ecopharm company was founded in 1996 by a group of chemists had been working in the field of science for a long time. The goal of our enterprise establishing is complex task solution in laboratories equipping.

At present Ecopharm company is Volga region leader in the sphere of chemicals, chemical raw materials, laboratory apparatus delivering and equipping of laboratories of different sorts. Experienced company specialists who are chemical-engineering university graduates, skillfully and in a short space of time help our customers to equip their laboratories from zero level or to complete equipping of laboratories with necessary facilities and devices.

Additionally, complete laboratory equipment "turnkey" is possible. Equipment is carried out as individual orders, as well as the original design projects. We provide designing and layout of workplaces, shops and laboratories, conducting after-sales service.

The activity of our company is not limited by delivering of chemicals and equipping of laboratories but it also develops in some industrial directions. One of them is manufacturing of laboratory and educational institution furniture including furniture produced according to custom designs as well as scientific and research laboratory accessories. Many laboratories of large food, machine-building, chemical and other enterprises are equipped with furniture produced by our company.

Our company sets up and completes the production with the newest most technologically advanced equipment.

Ecopharm company is the official dealer of a number of foreign corporations - manufacturers of industrial and laboratory equipment that allows to pick out the products to each customer at special prices individually. We supply a wide range of products from companies with a worldwide reputation:

OHAUS- Japan (scales), **SHIMADZU** - Japan (the widest range of analytical equipment), **SARTORIUS** – Germany (laboratory equipment), **IMPLEN** – Germany (spectrophotometers of a new generation with patented technology "drop sampling"), **SHINKO** – Japan (weighing equipment), **METTLER TOLEDO** – Switzerland (scales, pH meters, analytical instrumentation for thermal analysis, titrators, electrochemical equipment, laboratory), **DAIHAN** – Korea (laboratory equipment), **ULAB** – Germany (advanced laboratory equipment), **J.T. Baker** – Netherlands-USA (chemicals of high purity, pharmacopoeial standards and polietilenglikolievye basics), **RHEOTEST** – Germany (viscometers and rheometers rotamers), **HAIER** – Germany (biochemical equipment), **TRILOGICA** – Germany (viscometers, rheometers, moisture analyzers, dilatometry, bursting machines, laboratory equipment), **HUBER** – Germany (the widest range of thermostats), **LEKI** – China (scales and spectrophotometers), **SNOL-THERM** – Russia (muffle, tube, tube furnaces, ovens), **CEMICO** – Russia (electrochemical devices), **ESCO** – Singapore (chemical and bioreactors), **INFRASPAK-ANALYT** – Russia (electrochemical devices), **UNICO** – (spectrophotometers), **LUMEX** – Russia (fluorometry, high performance liquid chromatography, capillary electrophoresis) etc. In addition, we perform the installation, commissioning and maintenance of the equipment. We provide counseling and conduct after-sales service, so our client is always in the spotlight.

Among our respected customers: Kazan Federal University, Kazan National Science and Technology University, Perm State National Research University, Ufa State Oil Technical University, Chuvash State University, Izhevsk State Technical University, Udmurt State University, Tatneft Plc, Vyatcky State University, KazanOrgsintez Plc, Nizhnekamskneftekhim Plc, Sibur-chemprom Plc, Sibur-Petrocheml Plc, KAMAZ Plc, Bashneft Plc, TAIF ST, Tatarstan Airlines and many others .

Address:

Ecopharm Company

Sibirsky trakt, 34/1 box 193

420029 Kazan, Russia

phone/fax: +7(843) 299 00 78

fax: +7(843) 272 19 72

e-mail: info@ecopharm.ru

THE PREPARATION OF FUNCTIONAL
N-HETEROCYCLES AND THEIR APPLICATION IN
MATERIALS CHEMISTRY

D.W. Bruce

University of York, Department of Chemistry, Heslington, UK
duncan.bruce@york.ac.uk

Materials chemistry studies the collective behaviour of compounds that display useful properties based on responses not related to chemical reactivity, rather that depend upon, for example, electronic structure, optical and magnetic response, and photophysics. Nitrogen heterocycles are of interest in this regard as, for instance, the nitrogen centre can perturb the electronic structure of conjugated aromatic systems, or can act as a Lewis base to facilitate interactions such as hydrogen bonding or metal coordination.

- a) 4-Alkoxy stilbazoles form **halogen** bonds to electron-poor halides such as iodine found in highly fluorinated materials, and complexes between such stilbazoles and iodopentafluoro-benzene have been characterised crystallographically. Depending on the alkoxy chain length, these complexes show liquid crystal properties and the lecture will describe systematic studies both of the halogen bond strength and of structure/property relationships, with analogies being made to related hydrogen-bonded systems.
- b) Substituted phenylpyridines are classically prepared using metal-catalysed cross-coupling methodologies, but they may also be obtained using the Boger reaction, an inverse electron demand Diels-Alder reaction for which key starting compounds are 1,2,4-triazines. This chemistry may be used to prepared 1,3-(2-pyridin-2-yl)benzenes, whose platinum(II) complexes are promising, efficient chromophores for application in **Organic Light-Emitting Diodes (OLEDs)**. Similarly, the same chemistry can lead to 2,5-diphenylpyridines whose platinum(II) and iridium(III) complexes are also of interest in OLEDs. Preparation of suitable substituted heterocycles led to metal complexes that combine liquid crystallinity and OLED properties; the combination of these properties will be described.

**NOVEL SYNTHESSES OF CARBOCYCLES AND
HETEROCYCLES VIA IODINE, PALLADIUM AND
ARYNE CHEMISTRY**

R.C. Larock

Iowa State University, Chemistry Department, Ames, USA
larock@iastate.edu

Efficient syntheses of a wide variety of heterocycles and aromatic hydrocarbons have been achieved by the iodocyclization of functionally-substituted alkynes and subsequent palladium-catalyzed cross coupling. Palladium also catalyzes a wide variety of annulation and cyclization reactions useful in carbocycle and heterocycle synthesis. Unique approaches to such substrates are also provided by palladium migration chemistry. Finally, arynes readily undergo a number of annulation reactions, including palladium-catalyzed processes, useful for carbocycle and heterocycle synthesis.

SOME SERENDIPITIES IN MY RESEARCH LIFE

S. Tsuboi

Tsuboi Institute of Science and Technology, Japan
stsuboi6@mac.com

Some serendipities found during my research life in Okayama University for 40 years will be presented. Some of them are summarized as shown below.

- (1) Vinylogous Favorskii rearrangement was found out for the treatment of chloral acetone and γ -chlorinated α,β -unsaturated ketones with alkaline.¹⁾
- (2) A new pyridone synthetic method was discovered by the thermal treatment of imidates of propargyl alcohols and N-cyanopyrrolidine with Professor Larry E. Overman in California University, Irvine.²⁾
- (3) Thermal treatment of β -allenic esters with alumina catalyst in aprotic solvents yielded (*2E,4Z*)-dienoic esters in 57-87% yields with 91-100% stereoselectivity. This method was applied for the synthesis of some natural products such as insect pheromones and leukotrienes, including (*E,Z*)-diene structure.³⁾
- (4) A novel synthesis of tricyclo[5.1.0.0^{3,5}]octane-2,6-dione derivatives **1** via double Michael addition-induced cyclopropanation reactions was reported. Treatment of 2,4-alkadienoic esters with lithio dichloromethane at -95 °C gave tricyclooctane-2,6-diones **1** as a sole product.⁴⁾

References:

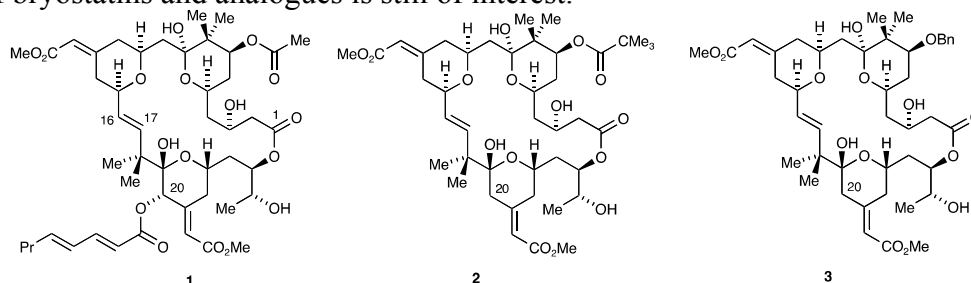
- 1) Akira Takeda and Sadao Tsuboi, *J. Org. Chem.*, **38**, 1709 (1973).
- 2) L. E. Overman, S. Tsuboi, J. P. Roos, G.F. Taylor, *J. Am. Chem. Soc.*, **102**, 747 (1980).
- 3) A. Takeda, T. Masuda, S. Tsuboi, *J. Org. Chem.*, **47**, 4478 (1982).
- 4) S. Tsuboi, X. Ye, K. Kunito, T. Ono, *Tetrahedron*, **57**, 3035 (2001).

APPROACHES TO THE SYNTHESIS OF SOME BIOLOGICALLY ACTIVE COMPOUNDS

A. Green
A. Lee
J. Thomas

The University of Manchester, The School of Chemistry, Manchester, UK
e.j.thomas@manchester.ac.uk

The bryostatins are macrocyclic natural products with potent anti-cancer activity due in part to protein kinase C inhibition.¹ They also show a range of other biological activities including cognition enhancement. Representative examples include the widely studied bryostatin 1 (**1**) and bryostatin 10 (**2**)² which lacks an oxygen function at C(20). Five total syntheses of bryostatins have been described to date,³ together with a formal synthesis,⁴ syntheses of close analogues⁵⁻⁷ and many partial syntheses.^{1a,8} Moreover, analogues with simplified C(1)-C(16) fragments have been prepared with improved biological activity.⁹ However the isolation of bryostatins from natural sources is difficult and only limited quantities are available for SAR studies.^{2b,10} For these reasons the synthesis of bryostatins and analogues is still of interest.⁸



Approaches to 20-deoxybryostatins, a biologically active sub-group of the bryostatins that has yet to succumb to total synthesis, will be discussed with reference to the synthesis of the 20-deoxybryostatin **3**.^{11, 12}

References:

- (a) K. J. Hale, M. G. Hummersone, S. Manaviazar and M. Frigerio, *Nat. Prod. Reports*, 2002, **19**, 413; (b) J. H. Sharp, M. K. Winson and J. S. Porter, *Nat. Prod. Reports*, 2007, **24**, 659.
- (a) G. R. Pettit, Y. Kamano and C. L. Herald, *J. Org. Chem*, 1987, **52**, 2848; (b) Y. Kamano, H-p. Zhang, A. Hino, M. Yoshida, G. R. Pettit, C. L. Herald and H. Itokawa, *J. Nat. Prod.*, 1995, **58**, 1868; (c) Y. Kamano, H-p. Zhang, H. Morita, H. Itokawa, O. Shiota, G. R. Pettit, D. L. Herald and C. L. Herald, *Tetrahedron*, 1996, **52**, 2369.
- (a) M. Kageyama, T. Tamura, M. H. Nantz, J. C. Roberts, P. Somfrai, D. C. Whritenour and S. Masamune, *J. Am. Chem. Soc.*, 1990, **112**, 7407; (b) D. A. Evans, P. H. Carter, E. M. Carreira, A. B. Charette, J. A. Prunet and M. Lautens, *J. Am. Chem. Soc.*, 1999, **121**, 7540; (c) K. Ohmori, Y. Ogawa, T. Obitsu, Y. Ishikawa, S. Nishiyama and S. Yamamura, *Angew. Chem., Int. Ed.*, 2000, **39**, 2290; (d) B. M. Trost and G. Dong, *J. Am. Chem. Soc.*, 2010, **132**, 16403; (e) G. E. Keck, Y. B. Poudel, T. J. Cummins, A. Rudra and J. A. Covell, *J. Am. Chem. Soc.*, 2011, **133**, 744.
- S. Manaviazar, M. Frigerio, G. S. Bhatia, M. G. Hummerstone, A. E. Aliev and K. Hale, *Org. Lett.*, 2006, **8**, 4477.
- G. E. Keck, Y. B. Poudel, D. S. Welch, M. B. Kraft, A. P. Truong, J. C. Stephens, N. Kedei, N. E. Lewin, and P. M. Blumberg, *Org. Lett.*, 2009, **11**, 593.
- B. M. Trost, H. Yang, O. R. Thiel, A. J. Frontier and C. S. Brindle, *J. Am. Chem. Soc.*, 2007, **129**, 2206.
- B. Bradshaw, M. Ball, R. Dumeunier, T. J. Gregson, S. MacCormick and E. J. Thomas, *Tetrahedron Lett.*, 2006, **47**, 2223.
- (a) K. J. Hale and S. Manaviazar, *Chemistry - an Asian Journal*, 2010, **5**, 704; (b) A. P. Green, S. Hardy, A. T. L. Lee and E. J. Thomas, *Phytochem. Rev.*, 2010, **9**, 501.
- (a) P. A. Wender, B. A. DeChristopher and A. J. Schrier, *J. Am. Chem. Soc.*, 2008, **130**, 6658; (b) P. A. Wender and V. A. Verma, *Org. Lett.*, 2008, **10**, 3331.
- D. E. Schaufelberger et al., *J. Nat. Prod.*, 1991, **54**, 1265.
- J. Allen, A. P. Green, A. Hardy, N. Heron, A. T. L. Lee, and E. J. Thomas, *Tetrahedron Lett.*, 2008, **49**, 6352.
- A. P. Green, A. T. L. Lee and E. J. Thomas, *Chem. Commun.*, 2011, in print.

THE NATURE OF THE CATALYST IN TRANSITION-METAL-CATALYZED CARBON-HETEROATOM AND CARBON-CARBON BONDS FORMATION REACTION

V.P. Ananikov

Zelinsky Institute of Organic Chemistry, Moscow, Russia
val@ioc.ac.ru

Recently we have developed a series of catalytic reactions to accomplish carbon-heteroatom (C-I, C-P, C-S, and C-Se) bonds formation reactions leading to functionalized alkenes and carbon-carbon (C-C) bond formation as a route to functionalized dienes [1]. The synthetic approach involves atom-economic addition reactions of easily available reagents – alkynes, thiols, disulfides, diselenides, iodine, and H-phosphonates. Transition metal catalysts furnish multistep highly regio- and stereoselective transformations under mild conditions, thus resulting in design of practical one-pot procedures.

The question of principal importance is the nature of catalytic transition metal species. Our mechanistic NMR, ESI-MS studies and theoretical [1] showed that homogeneous and nanoparticle catalysts may both be present under studied conditions and connected by leaching/agglomeration. The techniques will be presented and discussed to distinguish the metal species under catalytic conditions and to determine their role in the reaction.

Complex nature of catalyst active centers interconversion between different metal complexes and particles points out for supramolecular organization of catalytic systems in solution.

References:

- [1] (a) *Chem. Rev.*, 2011, 111, 1596; (b) *Dalton Trans.*, 2011, 40, 4011; (c) *Curr. Org. Synth.*, 2011, 8, 2; (d) *Chem. Asian J.* 2011, 6, 306; (e) *J. Organomet. Chem.* 2011, 696, 400; (f) *Chem. Eur. J.* 2010, 16, 2063; (g) *Adv. Synth. Catal.* 2010, 352, 2979; (h) *Organometallics* 2010, 29, 5098; (i) *Mendeleev Commun.* 2010, 20, 125; (j) *J. Mol. Cat. A: Chem.* 2010, 324, 104; (k) *Eur. J. Inorg. Chem.* 2009, 1149; (l) *Chem. Eur. J.* 2008, 14, 2420; (m) *J. Am. Chem. Soc.* 2007, 129, 7252; (n) *J. Am. Chem. Soc.* 2002, 124, 2839.
-

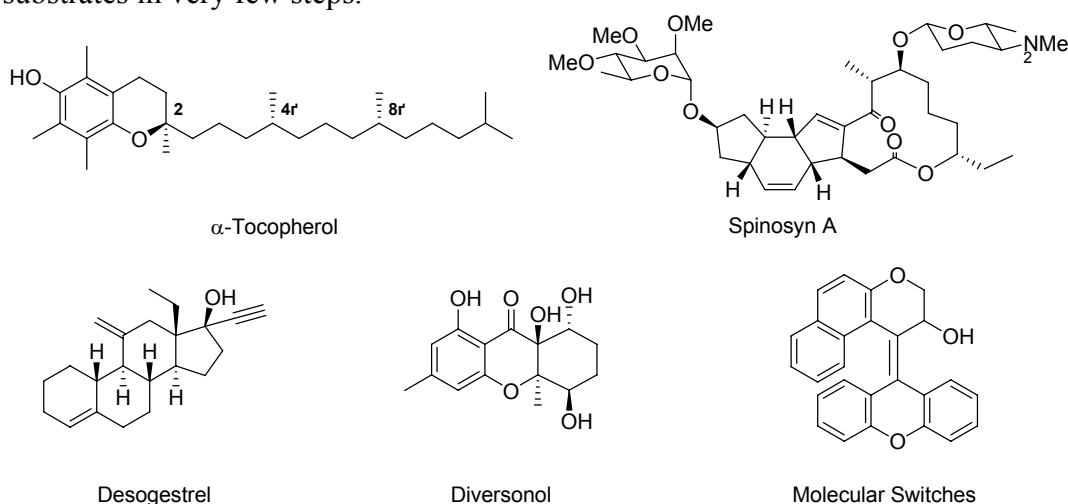
MULTIPLE Pd-CATALYZED TRANSFORMATIONS FOR THE SYNTHESIS OF NATURAL PRODUCTS, DRUGS AND MATERIALS

L.F. Tietze

Institute of Organic and Biomolecular Chemistry, Georg-August-University Göttingen, Göttingen, Germany
ltietze@gwdg.de

The development of novel highly efficient procedures for the synthesis of natural products, drugs, agrochemicals and materials is an important topic in academic and industrial chemistry. These procedures must not only be compatible with our environment and allow the preservation of our resources but they should also have economical advantages. In such an approach the proportion of the number of steps and the increase of complexity is a valuable standard for the quality of a synthesis.

A general way to improve synthetic efficiency and also address the above mentioned criteria is the design of multiple transition metal catalyzed transformations either in a sequential or a domino fashion. This methodology allows the formation of complex compounds starting from simple substrates in very few steps.¹



In the lecture the use of multiple Pd-catalyzed transformations for the efficient synthesis of α-tocopherol², spinosyn³, steroids⁴, diversonol⁵ and molecular switches⁶ will be presented.

References:

- (1) a) Tietze, L. F.; Brasche, G.; Gericke, K. *Domino Reactions in Organic Synthesis*, Wiley VCH, Weinheim **2006**;
b) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115–136; c) Tietze, L. F.; Beifuss, U. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131–163; d) Tietze, L. F.; Levy, L. The Mizoroki-Heck Reaction in Domino Processes in "The Mizoroki-Heck Reaction" (Ed.: M. Oestreich) Wiley-VCH, Chichester, **2009**, p. 281–344; Tietze, L. F.; Düfert, A. *Pure Appl. Chem.* **2011**, *82*, 1375–1392.
- (2) Tietze, L. F.; Stecker, F.; Zinngrebe, J.; Sommer, K. M. *Chem. Eur. J.* **2006**, *12*, 8770–8776.
- (3) Tietze, L. F.; Brasche, G.; Stadler, C.; Grube, A.; Böhnke, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 5015–5018 and unpublished work.
- (4) Tietze, L. F.; Krimmelbein, I. *Chem. Eur. J.* **2008**, *14*, 1541–1551.
- (5) Tietze, L. F.; Spiegl, D. A.; Stecker, F.; Major, J.; Raith, C.; Grosse, C. *Chem. Eur. J.* **2008**, *14*, 8956–8963 and unpublished work.
- (6) Tietze, L. F.; Düfert, A.; Lotz, F.; Sölter, L.; Oum, K.; Lenzer, T.; Beck, T.; Herbst-Irmer, R. *J. Am. Chem. Soc.* **2009**, *131*, 17879–17884. Tietze, L. F.; Düfert, A.; Hungeland, T.; Oum, K.; Lenzer, *Chem. Eur. J.* **2011**, on line and unpublished work.

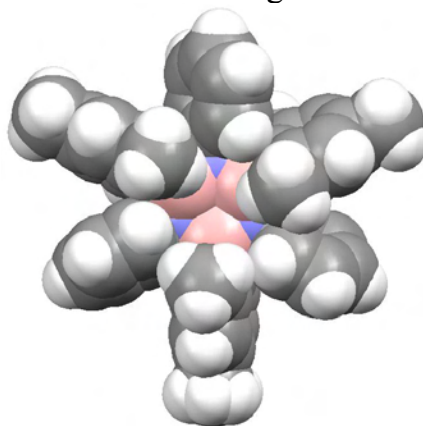
**DOPED π -CONJUGATED ORGANIC EMITTERS:
SYNTHESIS, PROPERTIES AND
SUPRAMOLECULAR ORGANIZATION**

D. Bonifazi

University of Namur (FUNDP), Department of Chemistry, Namur,
Belgium

davide.bonifazi@fundp.ac.be

The development of organic-based polymers and of their hybrid derivatives paves the way to materials with a continuously tunable energy gap from the IR to the deep UV. Specifically, there is a growing demand for light-emitting devices (LEDs) in the deep UV region, for a variety of applications where high photon energy is necessary for either processing or sensing/characterisation purposes (UV lamps for photodynamic therapy, water sterilization systems, "solar-blind" photodetectors, to name a few). A possible engineering strategy meeting these requirements would be to tune the electronic properties of the material by combining molecules with a similar carbon-based structures replacing every pair of carbon atoms rings by boron and nitrogen atoms. In this respect, borazine rings (Stock in 1926) are good candidates. However, the sensitivity toward water has hampered their exploitation in current technologies. In this report, we will describe the synthetic efforts toward the synthesis of water-stable borazine derivatives. Fluorescence studies in solution and at the solid state showed the presence of a strong UV-emission band in the UV region (300 nm, $\Phi = 7.5\%$). The synthesis of unprecedented unsymmetrical borazine derivatives and borazene linear modules will be shown as well. Novel H-bonding interactions involving boronic acids will be also discussed showing their potentials as alternative molecular synthones in molecular recognitions.



References:

Unpublished results; S. Kervyn and D. Bonifazi, EU patent EP11158909, filed 18.3.2011, pending ; *Pure Appl. Chem.*, **2011**, 83, 899-912 ; L. Maggini and D. Bonifazi* *Chem. Soc. Rev.* **2011**, DOI:10.1039/C1CS15031F ; S. Mohnani and D. Bonifazi* *Coord. Chem. Rev.*, **2010**, 254, 2342-2362. D. Bonifazi,* S. Mohnani and A. Llanes-Pallas *Chem. Eur. J.*, **2009**, 15, 7004-7015.

SYNTHESIS OF CYCLIC PEROXIDES

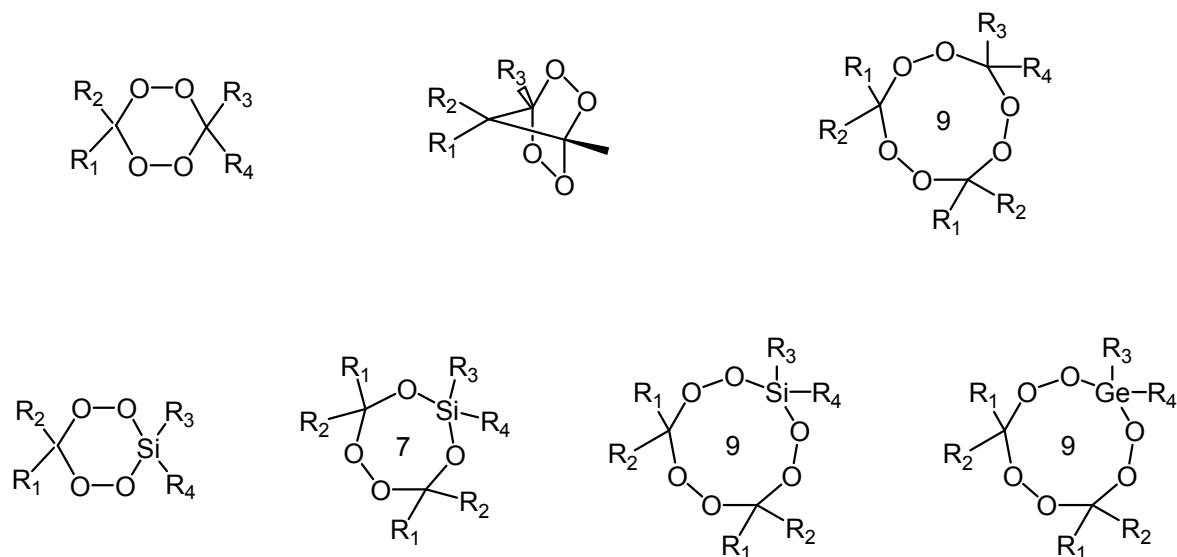
A.O. Terentyev

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia
terentev@ioc.ac.ru

In the past two decades, organic peroxides have come to the attention of chemists and researchers in the field of drug design because certain representatives of these compounds exhibit antimalarial and antitumor activities. This has stimulated the development of methods for the synthesis of these compounds.

Nowadays, cyclic compounds, such as tetraoxanes, ozonides, and trioxanes, are considered as the most promising synthetic peroxides having such activities. Some of these compounds exhibit high activity comparable to or higher than that of the natural peroxide artemisinin, which is widely used for the treatment of malaria. The design of explosives based on cyclic peroxides is of particular interest. For example, triacetone triperoxide is one of the most sensitive known explosives, whose power is similar to that of trinitrotoluene.

This report describes the synthesis of cyclic organic, organosilicon and organogermanium peroxides.



This work is supported by the Program for Support of Leading Scientific Schools of the Russian Federation (Grant NSh 4945.2010.3) and the Grant of the Russian Foundation for Basic Research (Grant 11-03-00857-a).

CYCLIZATION OF FUNCTIONALIZED (BUTA-1,3-DIYNYL)ARENES IN THE SYNTHESIS OF ENEDIYNE SYSTEMS FUSED TO HETEROCYCLES

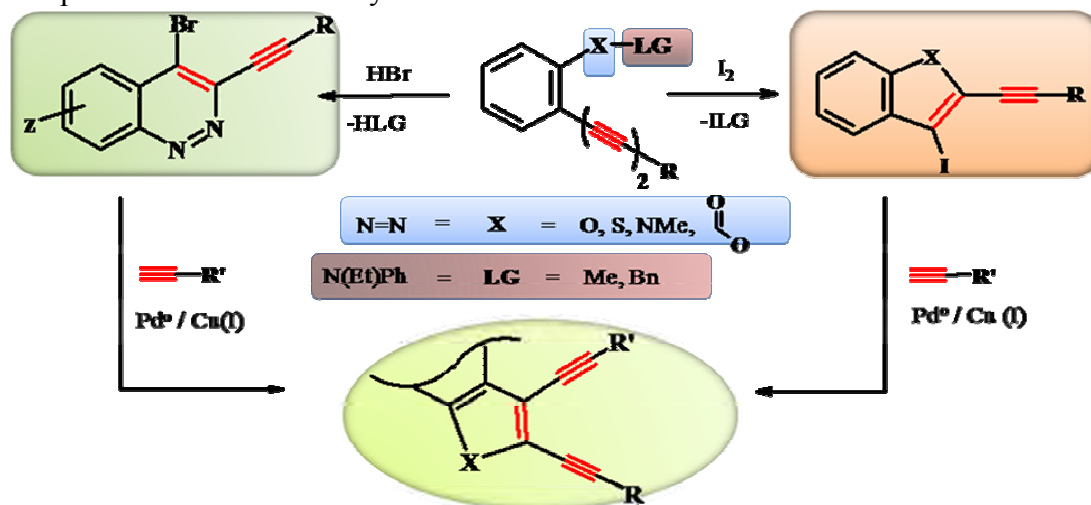
I.A. Balova

Saint-Petersburg State University, Department of Chemistry,
Saint-Petersburg, Russia
irinabalova@pobox.spbu.ru

Enediynes antitumor antibiotics, belonging to a small family of natural compounds, are among the most potent antineoplastic agents ever discovered¹. Natural enediynes are too scarce for practical use, additionally, have low antitumor selectivity, therefore, there is a significant interest in developing syntheses of artificial enediynes compounds.

Heterocycles possessing an enediyne system are promising objects for the investigation of general patterns of action and structure-activity relationships. However there is no general method to construct (Z)-3-ene-1,5-diyne system attached to a variety of heterocycles. Reported syntheses of such systems usually include transformation of functional groups to the ethynyl moieties or double cross-coupling of terminal acetylenes with dihaloheteroarenes, which are not widely accessible.

Recently we demonstrated the cyclization of *ortho*-functionalized (buta-1,3-diyne)arenes to be a short route towards heterocycles, having ethynyl moieties and halogen at neighboring atoms^{2,3}. This cyclization and followed Pd/Cu catalyzed cross-coupling with terminal acetylenes is promising approach to enediynes systems fused to various heterocycles. Moreover this synthetic methodology can get these connections to advance clearly defined position of substituents at both triple bonds which is important for further enediynes modification.



The proposed methodology for obtaining of cinnolines, benzannulated *S,N,O*-five-membered heterocycles, isocumarines will be discussed as well as examples of enediyne systems synthesis.

References:

1. K.C. Nicolaou, G. Zuccarello, C. Riemer, V.A. Estevez, W.M. Dai. *J. Am. Chem. Soc.*, **1992**, *114*, 7360; R.-G. Shao. *Curr. Mol. Pharm.*, **2008**, *1*, 50.
2. O. V. Vinogradova, V. N. Sorokoumov, I. A. Balova. *Tetrahedron Lett.* **2009**, 6358.
3. N. A. Danilkina, S. Bräse, I. A. Balova. *Synlett*, **2011**, 517.

This project is supported by Saint-Petersburg State University (grants 12.38.14.2011, 12.41.246.2011) and RFBR (grant 11-03-00048-a).

**SYNTHESIS, INTRA- AND INTERMOLECULAR
TRANSFORMATIONS OF *N*-AMINOAZIRIDINE
DERIVATIVES**

M.A. Kuznetsov
A.S. Pankova
V.V. Voronin

Saint-Petersburg State University, Organic Chemistry Department,
Saint-Petersburg, Russia
mak@mail.wplus.net

Oxidative addition of various *N*-aminoheterocycles to diverse unsaturated compounds is a general way to prepare a wide range of *N*-aminoaziridine derivatives. We have shown recently that, along with a traditionally used *N*-aminophthalimide (API) and 3-aminoquinazolinones, the easily available unsaturated cage *N*-aminoimides can be used in this reaction successfully, affording the corresponding *N*-aminoaziridines in good yields.

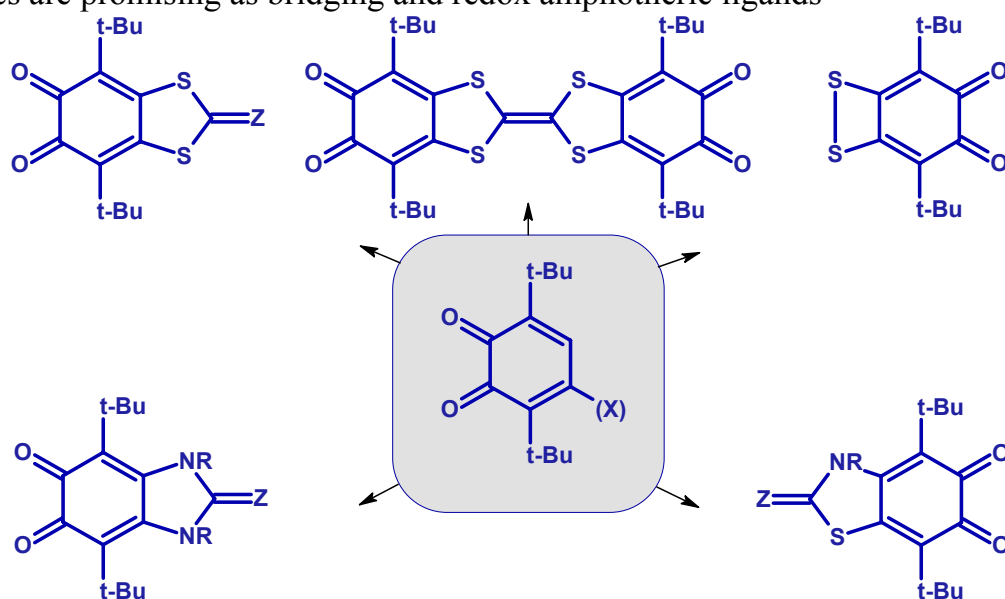
API oxidation in the presence of different 5-membered aromatic alkenylheterocycles (pyrazoles, 1,2,4- and 1,3,4-oxadiazoles, thiophenes) leads to adducts on exocyclic double bonds, aziridinylheterocycles. But furanes (both with alkenyl substituents, and without them) provide 5-membered ring opening products – (*Z*)-alk-2-en-1,4-diones monohydrazones – under the same conditions. The very special case is the oxidative addition of API to thiophene and selenophene, that provides bis-adducts, *trans*-fused 5-thia(seleno)-3,7-diazatricyclo[4.1.0.0^{2,4}]heptanes, only.

A strained three-membered ring causes a high activity of aziridines, and most of its transformations include a cleavage of C-N bonds or C-C bond (the latter one leads to octet-stabilized 1,3-dipoles, azomethyne ylides) for strain energy relief. As a result, the heating of *N*-aminoaziridine derivatives can cause its isomerization to corresponding hydrazones and imines. Thermolysis of aziridines with unsaturated substituents (>C=C<, >C=O, -N=N-) on carbon atoms leads to pyrrolines, 1,3-oxazoles and 1,2,3-triazoles. Intra- and intermolecular 1,3-dipolar cycloaddition of intermediate azomethine ylides on C=C, C≡C, and even C≡N bonds gives the corresponding 5-membered nitrogen heterocycles and polycyclic compounds.

**CHEMISTRY OF STERICALLY HINDERED
O-QUINONES. FUNCTIONALIZATION WITH
ANNELATED DITHIOL, THIAZOLE, IMIDAZOLE
AND TETRATHIAFULVALENE MOIETIES****V.A. Kuropatov**G.A. Razuvaev Institute of Organometallic Chemistry of RAS, Nizhny
Novgorod, Russia
viach@iomc.ras.ru

o-Quinone is a stronger acceptor as compared with p-quinone, in addition it can act as a chelating ligand to form stable complexes with various transition and non-transition metals. Moreover, transition metals in such complexes can change their oxidation state when the metal environment is altered. Modification of quinone skeleton is required to tune steric and redox characteristics, or to add auxiliary functionalities such as coordination sites or redox active centers.

We have studied 1,4-addition and substitution reactions in 3,6-di-tert-butyl-o-quinones and developed the methods for selective preparation of o-quinones annelated with 1,3-imidazole, thiazole, dithiole and dithiete ring. A variety of functionalized o-quinone derivatives have been synthesized. Several of these compounds such as TTF and dithiete derivatives are promising as bridging and redox amphoteric ligands

 $R = \text{H, Ph, Me}; Z = \text{O, NH, N}^+\text{R}_2$

Synthetic methods used in preparation of these compounds do not require complicated protection-deprotection procedures. Chemical properties of new quinones and their reduced and oxidized forms will be discussed.

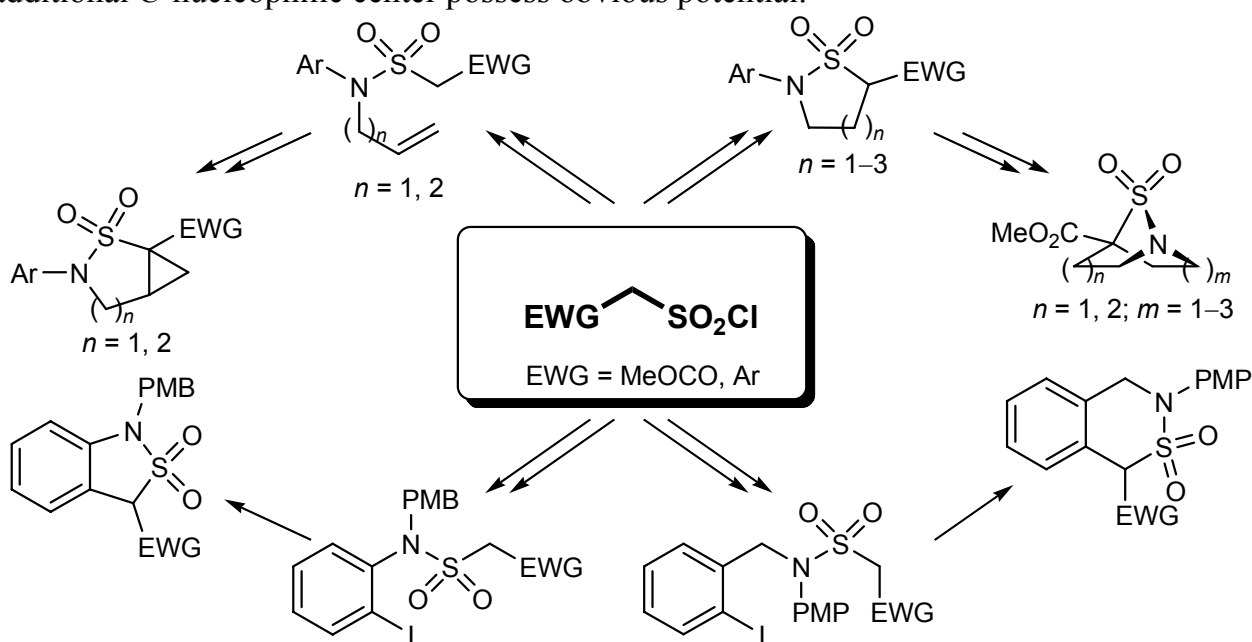
We gratefully acknowledge the financial support of the Russian Foundation for Basic Research, grant 10-03-00788-a and the Program for support of Leading Scientific Schools NSh-7065.2010.3. This work was made according to FSP "Scientific and scientific-pedagogical cadres of innovation Russia" for 2009–2013 years (GK-P839 from 25.05.2010).

SYNTHESIS OF SULTAMS BY CYCLOALKYLATION OF ALPHA-SUBSTITUTED METHANESULFONAMIDES

St. Perersburg State University, Department of Chemistry,
St. Petersburg, Russia
vsokolo@mail.ru

V.V. Sokolov

Acyclic sulfonamides can commonly be prepared by sulfonylation of amines, but synthesis of sultams is not so easy. One of the possible solutions is the intramolecular cycloalkylation (arylation) of sulfonamides. In this connection sulfonamides bearing an additional C-nucleophilic center possess obvious potential.



Therein we report intermolecular cycloalkylations of (methoxycarbonyl)methanesulfonanilides in $\text{K}_2\text{CO}_3/\text{DMF}$ system and α -toluenesulfonamides under wide range of the conditions by 1, ω -dihaloalkanes to give monocyclic sultams with various ring sizes. The intramolecular variant of the same reaction allows to obtain bicyclic sultams with sulfonylcyclopropane moiety.

For all the obtained sultams 4-methoxyphenyl (PMP) or 4-methoxybenzyl (PMB) group was removed from the nitrogen with CAN under mild condition. To the best of our knowledge, there have been no reports concerning the analogous cleavage of *N*-PMP-sulfonamides.

The cycloalkylation of the sultams bearing a secondary amide function leads to bicyclic compounds with the sulfur atom in the apex position. At the present time in literature only one sultam from this new class is represented. Our method shows a possibility to create a wide range of different bicyclic systems based on simple variations of the alkylation agents and starting material.

The intramolecular *C*-arylation of (methoxycarbonyl)methanesulfonamides with Pd(OAc)₂/Ph₃P/NaH allowed to synthesize benzo-annelated sultams.

**3,4-DICHLORO-2(5H)-FURANONES: USEFUL
SYNTHONS FOR THE PREPARATION OF A
VARIETY OF O-, N- AND S-HETEROCYCLES**

A.R. Kurbangalieva¹

A.S. Ezhova¹

O.A. Lodochnikova²

E.A. Berdnikov¹

G.A. Chmutova¹

1 - A.M. Butlerov Chemical Institute, Kazan Federal University,
Kazan, Russia

2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia

Almira.Kurbangalieva@ksu.ru

2(5H)-Furanone derivatives are naturally occurring and extremely useful heterocyclic compounds in various branches of medicine, agriculture, technology, and organic synthesis. The present work deals with a new synthetic applications of 3,4-dichloro-2(5H)-furanones based on the reactivity toward sulfur-containing mono- and binucleophilic reagents. These applications illustrate that mucochloric acid and its 5-alkoxy derivatives can provide a simple and convenient entry to a wide variety of interesting and previously unknown sulfur-containing heterocyclic compounds and are mainly concerned with the selective and efficient preparation of variously thiosubstituted 2(5H)-furanone derivatives.

The utilization of binucleophilic reagents (2-mercaptoethanol, 1,2-ethanedithiol, 1,3-propanedithiol, 1,2-phenylenedimethanethiol) in the reactions with 3,4-dichloro-2(5H)-furanones conducted under basic and acidic conditions, allowed us to obtain novel fused and spiro bicyclic sulfur heterocycles, as well as various *bis*-thioethers with a sulfur-containing chain, connecting two 2(5H)-furanone units. The diastereomeric mixtures of *bis*-thioethers were separated into the individual components by fractional crystallization.

A series of sulfones and sulfoxides were prepared by selective oxidation of the corresponding mono- and dithioderivatives of 2(5H)-furanone. A simple and efficient approach to the synthesis of various derivatives of 5-hydroxy-3-pyrrolin-2-one was developed via reactions of corresponding thioethers of 5-alkoxy-2(5H)-furanones with ammonia, amines and nitrogen-containing binucleophiles. Regio- and stereochemical aspects of these reactions are discussed; possible mechanistic schemes of reactions of substitution, cyclization and opening of cyclic furanone structure, leading to isolated products are suggested on the basis of the obtained synthetic results. Novel furanone and pyrrolinone based compounds have been characterized in detail by NMR spectroscopy and single crystal X-ray diffraction.

*The financial support from the Ministry of Science and Education of Russian Federation
(Governmental Contract No 02.740.11.0633) is gratefully acknowledged.*

A NOVEL REARRANGEMENT OF QUINOXALIN-2(1H)-ONES FOR THE SYNTHESIS OF 2-HETEROARYL-BENZIMIDAZOLES

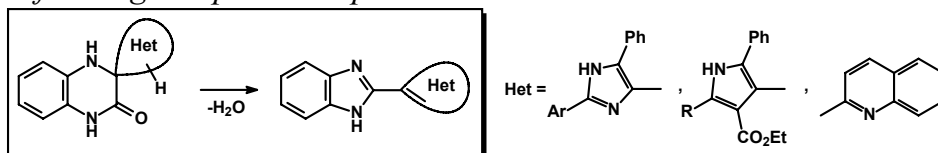
A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
mamedov@iopc.ru

V.A. Mamedov

We have recently discovered a highly efficient and versatile reaction for the synthesis of benzimidazoles **3**, **6** and **9** on the basis of the novel ring contraction of 3-benzoyl(3-alkanoyl)- (**1**), 3- α -chlorobenzyl- (**4**) and 3-arylacylidene- (**7**) quinoxalin-2(1H)-ones with 1,2-diaminebenzenes, α -picoline and hydrazine hydrate correspondingly.

As can be seen from these generalized schemes of reactions the key step in all the three cases is the formation of spiro-compounds of the **2**, **5** and **8** types respectively. As a result of the cascade reactions all the compounds are transformed into benzimidazole derivatives, containing heterocyclic systems. These systems act as spiro-fragments in the intermediate compounds **2**, **5** and **8**.

These results appeared sufficient to propose a hypothesis that “any of the spiro-derivatives of 1,2,3,4-tetrahydroquinoxalin-3-one with at least one mobile hydrogen atom in their spiro-forming component are on their way to the benzimidazole derivative, with the spiro-forming component in position 2”.



The report demonstrates the generality of this assumption, indicating how the benzimidazole derivative is synthesized via spiro-compounds which makes it unnecessary to use only 3-aryl(3-alkanoyl)- (**1**), chloralkyl- (**4**), or arylacetylidene- (**7**) quinoxalin-2(1H)-one derivatives. Any other derivatives can be used to form spirocompounds.

Pyrazinones in this rearrangement are transformed into imidazoles.

References:

1. Mamedov V.A., Saifina D.F., Rizvanov I.Kh., Gubaidullin A.T. *Tetrahedron Lett.* **2008**, 49, 4644.
2. Mamedov V.A., Saifina D.F., Gubaidullin A.T., Saifina A.F., Rizvanov I.Kh. *Tetrahedron Lett.* **2008**, 49, 6231.
3. Mamedov V.A., Murtazina A.M., Gubaidullin A.T., Hafizova E.A., Rizvanov I.Kh. *Tetrahedron Lett.* **2009**, 50, 5186.
4. Mamedov V.A., Saifina D.F., Gubaidullin A.T., Ganieva V.R., Kadyrova S.F., Rakov D.M., Rizvanov I.Kh., Sinyashin O.G. *Tetrahedron Lett.* **2010**, 51, 6503.
5. Mamedov V.A., Zhukova N.A., Beschastnova T.N., Gubaidullin A.T., Balandina A.A., Latypov S.K. *Tetrahedron*, **2010**, 66, 9745.

Acknowledgement. We thank the Russian Foundation for Basic Research (Grant № 10-03-00413) for financial support.

**NOVEL SYNTHESIS OF OXYGEN HETEROCYCLES
VIA PRINS AND OXONIUM-ENE CYCLIZATION**

A.K. Saikia

Indian Institute of Technology Guwahati
asaikia@iitg.ernet.in

Prins cyclization has long been used for the synthesis of oxygen heterocyclic compounds particularly substituted tetrahydropyrans. Similarly, oxonium-ene reactions are powerful tool for the construction of various cyclic ethers. These cyclic ethers are found in biologically active molecules and natural products. We have developed a few methodologies for the synthesis of substituted tetrahydropyrans using Sakurai-Hosomi-Prins-Ritter, Sakurai-Hosomi-Prins-Friedel-Crafts and Prins-Friedel-Crafts reactions.¹ Further, oxonium-ene cyclization reaction has also been under investigation for the synthesis of oxabicyclo[3.3.1]nonanone,² oxabicyclo[3.3.1]nonene and substituted tetrahydropyrans. Detailed results will be presented in the meeting.

References:

1. (a) Reddy, U. C.; Raju, B. R.; Kumar, E. K. P.; saikia, A. K. *J. Org. Chem.* **2008**, 73, 1628. (b) Reddy, U. C.; Bondalapati, S.; Saikia, A. K. *Eur. J. org. Chem.* **2009**, 1625. (c) Reddy, U. C.; Bondalapati, S.; Saikia, A. K. *J. Org. Chem.* **2009**, 74, 2605. (d) Reddy, U. C.; Saikia, A. K. *Synlett* **2010**, 7, 1027.
2. Saha, P.; Reddy, U. C.; Bondalapati, S.; Saikia, A. K. *Org. Lett.* **2010**, 12, 1824.

**FLUORINE, AN ELEMENT FOR (ALMOST) ALL
EVENTS. RECENT ADVANCES IN
FLUOROORGANIC CHEMISTRY**

G.-V. Roeschenthaler

Jacobs University Bremen, School of Engineering and Science,
Bremen, Germany
g.roeschenthaler@jacobs-university.de

Organofluorine compounds with its unique properties have become indispensable in a broad variety of applications, e.g. in modern LCD displays, as drugs with high efficacy, as pesticides, as anesthetics and in membranes of fuel cells. More than 50% of substances developed in the Life Science sector have at least *one* fluorine atom in their structure. Fluorinating the target molecules tunes their lipophilicity, their ability to form hydrogen bonds, the strength of electrostatic interactions and moreover influences stereoelectronic properties, controls the conformation and metabolic stability.

Novel reagents for nucleophilic fluorination, a new family of salts with delocalized, lipophilic cations applicable for the “Halex Process”, will be presented. Effective substitutes for the difficult to handle sulfur fluorides, SF₄ und DAST, namely compounds (R₂N)₂CF₂ and R₂NCF₂R will be described. The first examples of preparative 1,4-perfluoroalkylation and regioselective 1,4-trifluormethylation of α,β -enones using a “*protect-in-situ*” method will be discussed. Novel perfluoroalkyl borates and -boronates could be used as potential partners for Petasis or Suzuki reactions. A new method for the introduction of C₂F₅ groups and of CF₂-containing building blocks including CF₂P(O)(OEt)₂ into organic molecules and the „electrophilic” perfluoroalkylation of selected nucleophiles will be presented. Furthermore, the introduction of SF₅ in organic substrates and the role of hypervalent sulphur will be discussed.

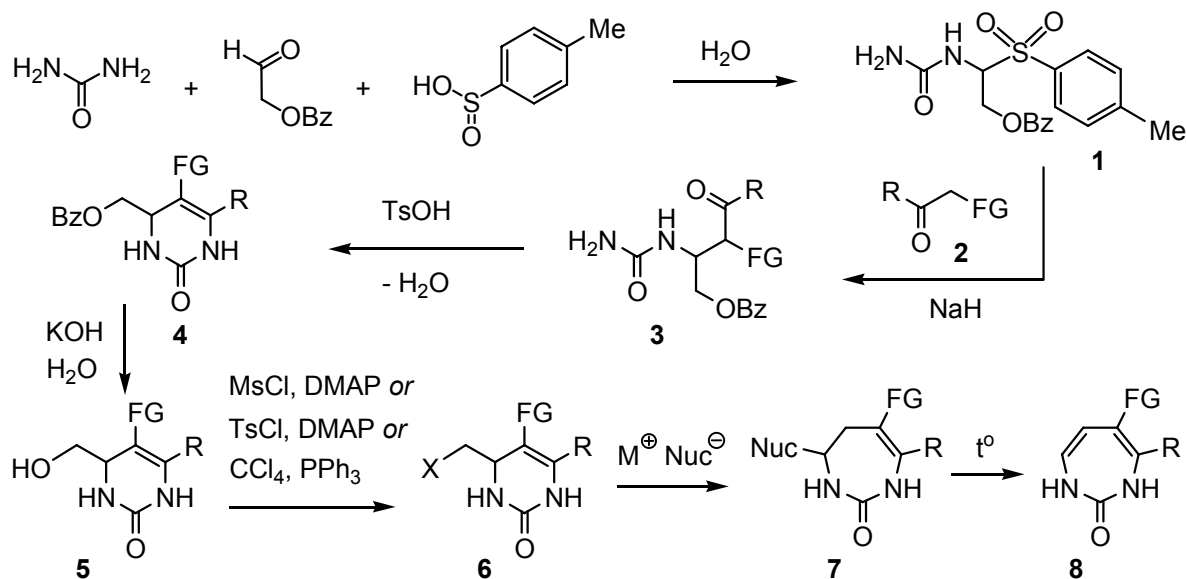
RECENT ADVANCES IN THE SYNTHESIS OF TETRAHYDRO- AND DIHYDRO-1*H*-1,3-DIAZEPIN-2-ONES

A.D. Shutalev
A.A. Fesenko
L.A. Trafimova

Moscow State Academy of Fine Chemical Technology, Department of
Organic Chemistry, Moscow, Russia
shutalev@orc.ru

Up to date, functionalized tetrahydro-1*H*-1,3-diazepin-2-ones and dihydro-1*H*-1,3-diazepin-2-ones remain practically unknown. Here we report a general method of their preparation based on synthesis of 4-tosyloxymethyl-, 4-mesyloxymethyl- and 4-chloromethyl-1,2,3,4-tetrahydropyrimidin-2-ones followed by ring expansion promoted by nucleophilic agents.

Readily available urea **1** served as a starting compound. Reaction of **1** with sodium enolates of α -functionalized ketones **2** afforded oxoalkylureas **3** in high yields. Treatment of **3** with TsOH in refluxing EtOH or MeCN led to dehydration of intermediate cyclic isomers to give tetrahydropyrimidin-2-ones **4** in yields up to 93 %.



R = Me, Bu, Ph, CF₃, COOEt, COOMe; FG = COOEt, COOMe, Ac, Bz, SPh, Ts; X = MsO, TsO, Cl

M⁺Nuc⁻ = NaCN, NaCH(COOEt)₂, NaSPh, NaOMe,
sodium succinimide, potassium phthalimide, NaBH₄, etc.

Hydrolysis of benzoates **4** easily proceeded at room temperature in the presence of KOH in aqueous EtOH to give 4-hydroxymethyl-substituted tetrahydropyrimidines **5**. Reaction of the latter with MsCl/DMAP, TsCl/DMAP or PPh₃/CCl₄ yielded pyrimidines **6** which were converted into various diazepines **7** after treatment with nucleophiles. Heating of the obtained **7** (Nuc = OMe, SPh) in solvents at 100–110 °C provided 2,3-dihydro-1*H*-1,3-diazepin-2-ones **8** as a result of elimination of methanol or PhSH.

**REGIO- AND STEREOSELECTIVE HECK
ARYLATION OF CINNAMATES AND ALLYLAMINE
DERIVATIVES USING ARENEDIAZONIUM SALTS**

P. Prediger¹
J.G. Taylor²
C.R.D. Correia¹

1 - State University of Campinas, Organic Chemistry Department,
Campinas, Brazil

2 - Federal University of Ouro Preto, Chemistry Institute, Ouro Preto,
Brazil

roque@iqm.unicamp.br

The Heck arylation of cinnamates and allylamine derivatives is a known process that still faces many challenges in controlling the product outcome such as the regioselectivity (β - or γ -arylation) and the stereoselectivity (*E/Z* ratio). We reevaluated these Heck arylations by employing arenediazonium salts and discovered a straightforward methodology for the efficient Heck arylation of these simple molecules with exceptional synthetic potential. Arylations were achieved in a highly stereo- and regioselective manner within short reaction times (1-3h), at temperatures ranging from rt to 80 °C. Arylation of both allylamine derivatives provided the 1,2-adduct almost exclusively regardless of the bulkiness of the carbonylic system present on the heteroatom. The allylamines were functionalized as amides, carbamates, biscarbamates, sulphonamides and phosphoramides. Minor side products in both cases were identified as the isomerized olefin and the 1,1-adducts only. Arylation was also insensitive to the electronic nature of the arenediazonium salts displaying excellent results with electron donating, electron deficient and electron neutral salts. An alternative approach to the enantioselective synthesis of γ,γ -diaryl propanols and γ,γ -diaryl propylamines was also developed. This approach relies on the Heck arylation of cinnamic esters followed by the enantioselective reduction of the Heck adducts in good to excellent enantioselectivity using chiral CuH complexes. The results concerning the development of this new synthetic methodology and its applications will be presented.

**MECHANISM AND SYNTHETIC CAPABILITIES OF
THE VIC-(ALKYNYL)ARENEDIAZONIUM SALTS
CYCLIZATION REACTION**

**L.G. Fedenok
I.I. Barabanov
V.S. Bashurova
G.A. Bogdanchikov**

Institute of Chemical Kinetics and Combustion, Siberian Branch of the
Russian Academy of Sciences, Novosibirsk, Russia
fedenok@kinetics.nsc.ru

Cyclization of *ortho*-(alkynyl)benzene diazonium salts, discovered more than a century ago,¹ has been used until recently exclusively as a method of obtaining cinnoline derivatives.² However, it was revealed during the investigation of 1-alkynyl-9,10-anthraquinone-2-diazonium chloride cyclization that in this case the ring closure proceeds to give not the 6-membered pyridazine cycle, but a 5-membered pyrazole.³ The revealed difference stimulated the studies of the cyclization mechanism of *vic*-(alkynyl)arenediazonium salts in the series of both benzene and quinones.⁴⁻⁸ Experimental data and quantum chemical calculations demonstrated that there are common features in the cyclization mechanisms of *ortho*-alkynylbenzene- and *vic*-alkynylanthra(or naphtho)diazonium salts.^{4,7,8} A multistage cyclization mechanism was proposed; it is principally different from the generally accepted single-stage mechanism of cyclization of *ortho*-alkynylbenzene diazonium salts.⁹⁻¹¹ In the course of investigation, an intermediate product of cyclization was detected, isolated and characterized. It has a 5-membered structure of the 3*H*-pyrazole cycle. It was established that, depending on reaction conditions and substrate structure, stabilization of the intermediate occurs either with the conservation of the heterocycle size and the formation of indazole derivatives or with cycle expansion and the formation of cinnoline derivatives. We demonstrated how the variation of reaction conditions allows us to obtain either cinnoline or indazole derivatives with a high yield from the same initial substrates.⁵

References:

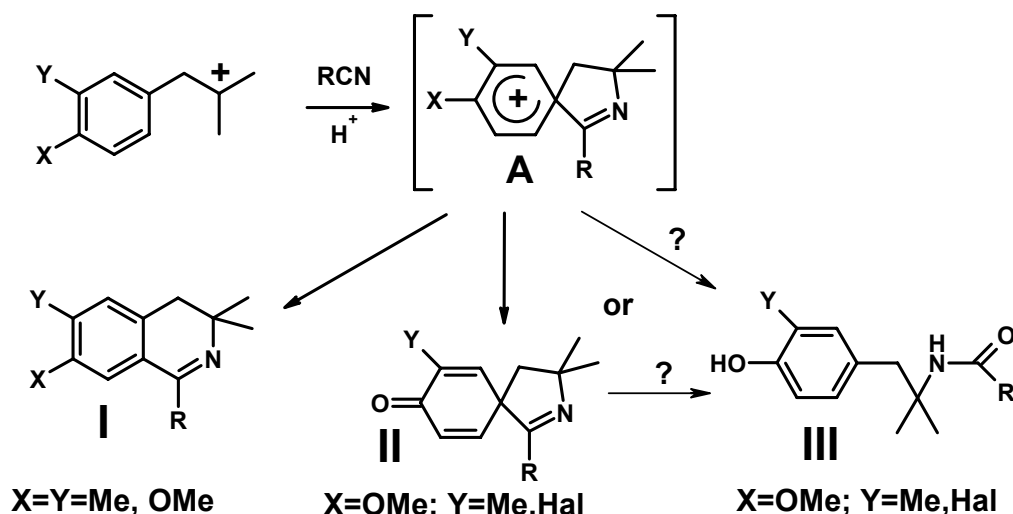
- [1] V. Richter, *Ber. Dtsch. Chem. Ges.* **1883**, 16, 677.
- [2] Porter, A.E.A. Diazines and Benzodiazines. In *Comprehensive Organic Chemistry*; Barton, D.H.R.; Ollis, W.D., Eds. Pergamon Press: Oxford, 1979; Vol.4, pp. 122-124.
- [3] M.S. Shvartsberg, I.D. Ivanchikova, and L.G. Fedenok, *Tetrahedron Lett.* **1994**, 35, 6749-6752.
- [4] L.G. Fedenok, I.I. Barabanov, and I.D. Ivanchikova, *Tetrahedron Lett.* **1999**, 40, 805-808.
- [5] L.G. Fedenok, I.I. Barabanov, and I.D. Ivanchikova, *Tetrahedron*. **2001**, 57, 1331-1334.
- [6] L.G. Fedenok, and N.A. Zolnikova, *Tetrahedron Lett.* **2003**, 44, 5453-5455.
- [7] L.G. Fedenok., I.I. Barabanov, V.S. Bashurova, and G.A. Bogdanchikov, *Tetrahedron*. **2004**, 60, 2137-2145.
- [8] L.G. Fedenok., M.S. Shvartsberg, V.S. Bashurova, and G.A. Bogdanchikov, *Tetrahedron Lett.* **2010**, 51, 67-69.
- [9] K. Schofield, and J.C.E. Simpson, *J. Chem. Soc.* **1945**, 520-526.
- [10] K. Schofield, and T. Swain, *J. Chem. Soc.* **1949**, 2393-2399.
- [11] S.F. Vasilevsky, and E.V. Tretyakov, *Liebigs Ann.* **1995**, 5, 775-779.

SYNTHESIS OF THE PARTIALLY HYDROGENATED NITROGEN-CONTAINING HETEROCYCLES: HOW DOES RITTER-TYPE HETEROCYCLIZATION PROCEED?

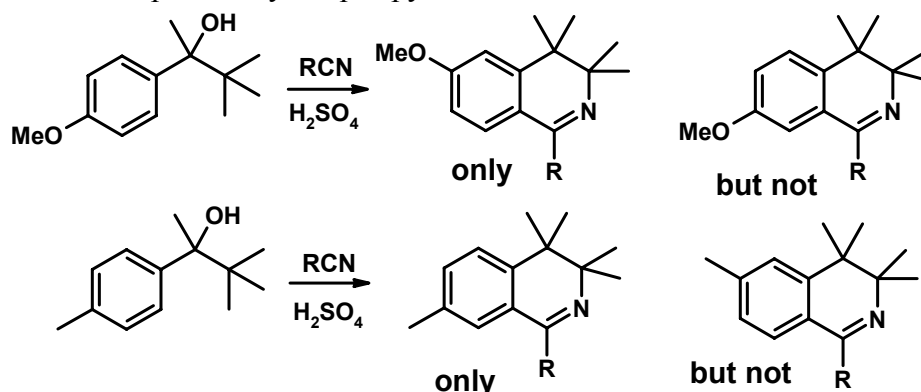
Yu.V. Shklyaev
Yu.S. Rozhkova
T.S. Vshivkova
O.G. Stryapunina

Institute of Technical Chemistry of UB of RAS, Organic Synthesis
 Department, Perm, Russia
yushka@newmail.ru

The report summarizes the author's works on synthesis of 3,4-dihydroisoquinolines (**I**), spiropyrrolines (**II**), polyhydroindoles (**IV**), neospiranes (**V**), polyhydrocarbazoles (**VI**) and classical products of Ritter reaction (**III**) as well. Basing on the obtained data there has been done an assumption that all the Ritter-type heterocyclizations proceed through the *ipso*- σ -complex of A-type generation, the 1,2-sigmatropic shift in which results in isoquinolines **I** formation. Water addition to complex **A** produces spiropyrrolines **II**, the dienone-phenol rearrangement of which gives rise to amides **III**.



There has been demonstrated that carbenium-ion generation via retropinacolin rearrangement completely excludes the possibility of spiropyrrolines **II** formation even for anisoles.



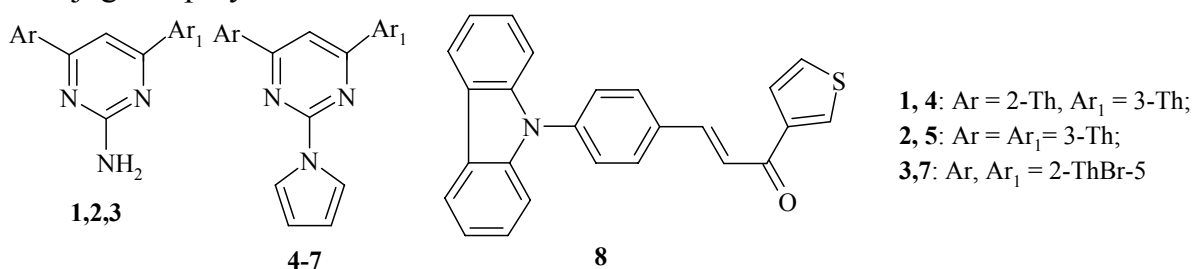
The work was financially supported by Russian Foundation for Basic Research (project no 10-03-00138), by RAS Presidium's programs (nos 18, 21) and by programs of collaboration between of the UB and SB RAS scientists.

NEW PYRIMIDINES WITH THIOPHENE MOIETIES IN THE CONJUGATED BACKBONE: SYNTHESIS, ELECTROCHEMICAL PROPERTIES

G.G. Abashev¹
T.S. Syrchikova²
E.A. Sosnin¹
E.V. Shklyayeva³

1 - Institute of Technical Chemistry, UB RAS, Perm, Russia
 2 - Perm State University, Chemical Department, Perm, Russia
 3 - Natural Sciences Institute of Perm University, Perm, Russia
 gabashev@psu.ru

In the creation of electronic devices such as light-emitting diodes, solar cells *at alii* [1] an important role belongs to the conjugated oligomers and polymers, which backbones include simultaneously electron-excess heterocycles like thiophene, pyrrole, carbazole and electron-deficient heterocycles like pyrimidine, triazine, pyridine [2]. Formerly we have synthesized a series of 4,6-disubstituted pyrimidines with thiophene and pyrrole moieties linked with the pyrimidine core via α -C atom of heterocycle [3]. It was shown that some of these compounds could be electrochemically polymerized. Recently by cyclization of corresponding chalcones with guanidine we have prepared pyrimidines **1-2** which thiophene fragments are connected with the pyrimidine core via β -C thiophene atom. In this case both α -C atoms of thiophene cycles remain free and could be engaged into polymerization process. With an aim to realize Ni(0)-catalyzed polymerization we have synthesized pyrimidine **3** with two terminal bromine atoms. Further by interaction of pyrimidines **1-3** with DMTHF in AcOH media there were prepared pyrrolopyrimidines **4-7**. Condensation of 3-acetylthiophene and 4-(9-carbazolyl)benzaldehyde has resulted in chalcone **8** further converted into corresponding pyrimidine. Investigation of cyclic voltammograms has demonstrated that all the prepared compounds are able to be electrochemically polymerized into conjugated polymers.



References:

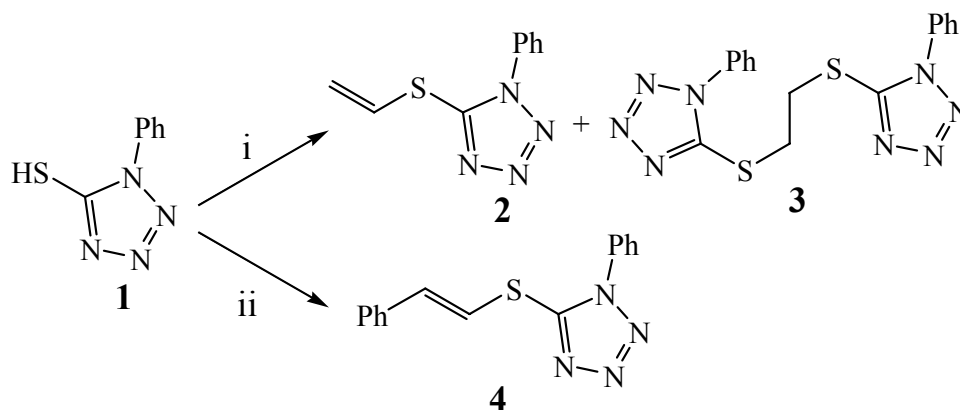
- [1] G.G.Wallace, P.R.Teasdale, G.M.Spinks, L.A.P.Kane-Maguire, Conductive Electroactive Polymers: Intelligent Polymer Systems, 3rd Ed., CRC Press, Taylor&Francis Group, Boca Raton-London-New York, 2009, 282 pp.
- [2] R.P. Ortiz, J. Casado, V. Hernandez, J.T.L Navarrete et al // Chem.Eur. J., 2009, 15, 5023.
- [3] A.Yu. Bushueva, E. V. Shklyayeva, G. G. Abashev // Mendeleev Commun., 2009, 19, 229.
- [4] E.V. Shklyayeva, A.Yu. Bushueva, V.A. Romanova, G.G. Abashev // Russ. J. Org. Chem., 2010, 46, 938.

The work was financially supported by Russian Foundation for Basic Research (project no 10-03-96038).

NEW VINYL MONOMERS OF HIGH NITROGEN
CONTENT: DERIVATIVES OF
5-MERCAPTOTETRAZOLEP.A. Aleshunin
V.A. OstrovskiiSt. Petersburg State Institute of Technology, Chemistry and
Technology of Organic Nitrogen Compounds, St. Petersburg, Russia
apa-ti@mail.ru

Vinyl derivatives of tetrazole are promising monomers whose polymerization products are applied as binders of energy-rich materials and materials of medical purpose: superabsorbents of moisture, components of filtering materials, and of polymer membranes [1]. Besides, vinyltetrazoles attain strong interest as reagents for the synthesis of new functional tetrazole derivatives [2].

In this study the vinylation of 1-phenyl-5-mercaptotetrazole **1** with 1,2-dibromoethane in the presence of triethylamine in acetonitrile environment led to the formation of 1-phenyl-5-vinylthiotetrazole **2** in 85% yield. Dimer **3** formed as a side product in 15 % yield.

i: $\text{Br}(\text{CH}_2)_2\text{Et}_3\text{N}$, MeCN, refluxii: $\text{BrCH}=\text{CHPh}$, [Cu]-cocktail, Cs_2CO_3 , DMF, 70°C

The vinylation of tetrazole **1** with (*E*)-(2-bromovinyl)benzene in the presence of a catalytic quantity of copper salts provided (*E*)-styrylthiotetrazole **4** in 95% yield.

References:

1. Kizhnyayev, V.N., Vereshchagin, L.I., *Usp. Khim.*, **2003**, 72, 159.
2. Ostrovskii, V.A., Koldobskii, G.I., Trifonov, R.E., *Compr. Heterocycl. Chem. III*, **2008**, 6, 257.

The study was carried out under a financial support of RFFR (grant 11-08-00757-a).

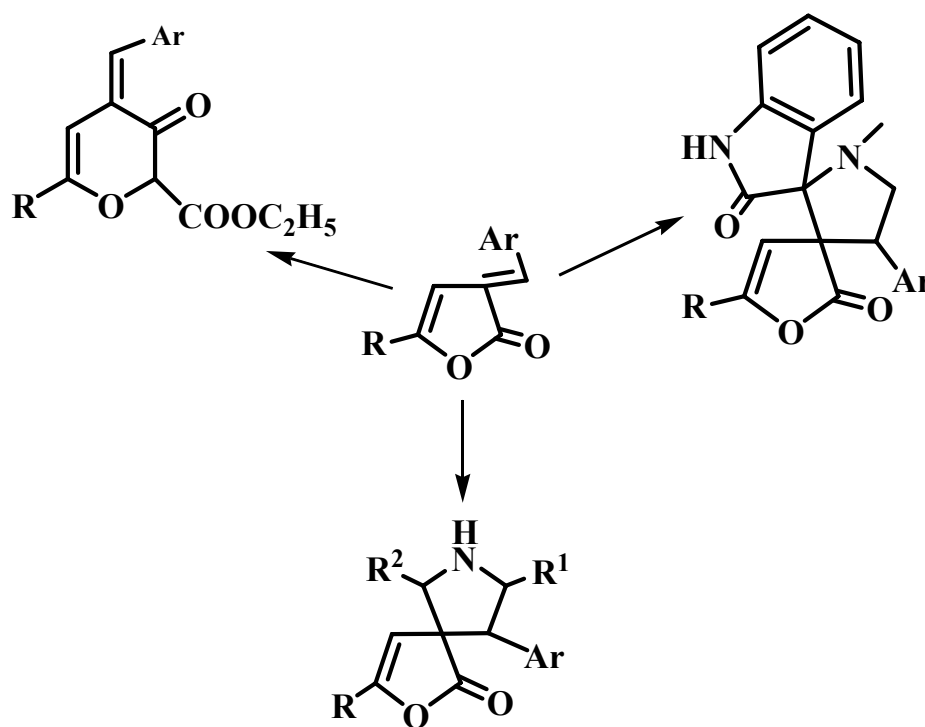
T.V. Aniskova
A.Yu. Yegorova
O.V. Buruhina
A.A. Aniskov
I.E. Kamneva

CYCLOADDITION REACTION OF ARYLMETHYLIDENE-3H-FURAN-2-ONES

Saratov State university, Institute of Chemistry, Saratov, Russia
aniskovatv@mail.ru

Synthetic capabilities of arylmethyldene-3H-furan-2-ones are determined by the presence in the structure of those compounds of several reaction centers: the carbonyl group and the exocyclic double bond. This fact determines various chemical transformations for the structures that can occur as the conservation lactone ring and with its expansion or contraction cycle.

Considered compounds were introduced in reactions with diazoacetic ester and with various azomethine ylides:



It was established, that the use of diazoacetic ester reaction proceeds with the expansion of the furane's ring and lead to formation pyranones. 1,3-dipolar cycloaddition of azomethine ylides to arylmethyldene-3H-furan-2-ones lead to formations of spiropyrrolidines. The structures of the synthesized compounds were confirmed by IR, NMR ^1H , ^{13}C , $^1\text{H}^{13}\text{C}$ HSQC, NOESY 1D spectroscopy data.

The study was carried out under a financial support of the Russian foundation of basic research (grant no 03-00640-a) and grant of the president R.F. MK-2054.2011.3

SYNTHESIS AND SPECTROSCOPIC STUDIES OF NOVEL COVALENTLY LINKED PYRENE-ARYL AZIDE SYSTEMS

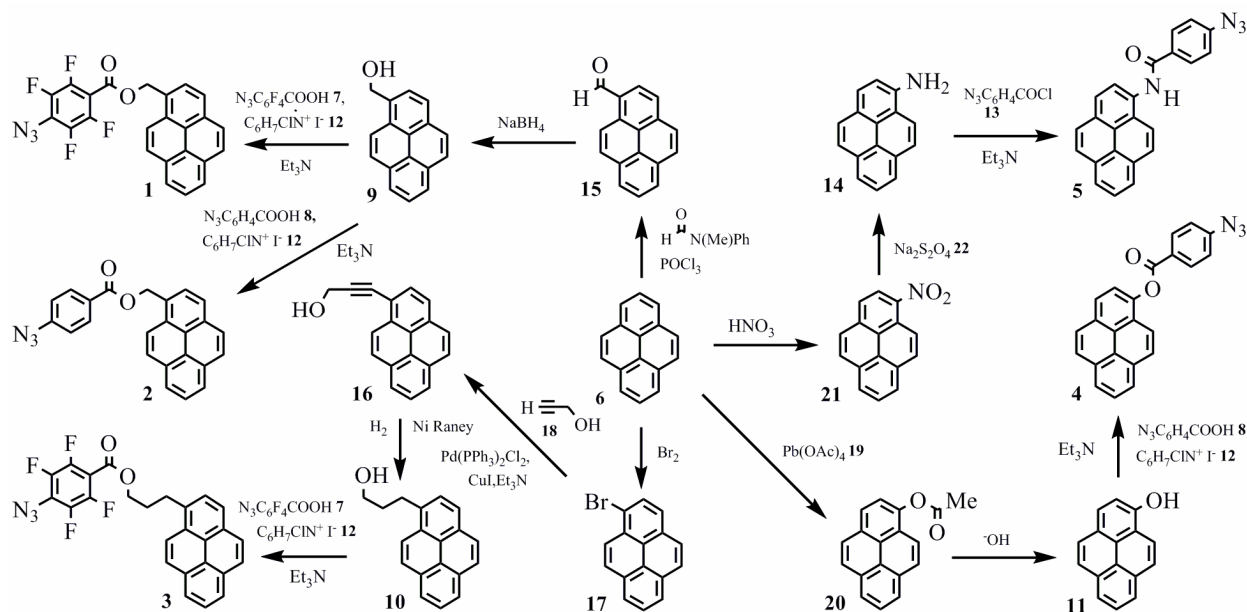
I.I. Barabanov¹A.V. Polukhin¹E.A. Pritchina¹N.P. Gritsan¹L.V. Kuibida¹G.T. Burdzinski²M.S. Platz²

1 - Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

2 - The Ohio State University, Department of Chemistry, Columbus, Ohio, USA

barabanov@kinetics.nsc.ru

A series of covalently linked systems (**1-5**) containing pyrene and aryl azido residues has been synthesized from pyrene (**6**). These compounds are models of the binary reagents used in the photoaffinity labeling of biopolymers. The esters (**1-4**) were prepared by interaction of *p*-azidotetrafluorobenzoic (**7**) and *p*-azidobenzoic (**8**) acids with pyren-1-ylmethanol (**9**), 3-(pyren-1-yl)propan-1-ol (**10**) and 1-hydroxypyrene (**11**), respectively. The esterification was promoted by 1-methyl-2-chloropyridinium iodide (**12**). The amide **5** was synthesized by condensation of *p*-azidobenzoyl chloride (**13**) with 1-aminopyrene (**14**).



The alcohol **9** was obtained from **6** by the Vilsmeier-Haack reaction followed by reduction of pyrene-1-carboxaldehyde (**15**). The alcohol **10** was synthesized by hydrogenation of 3-(pyren-1-yl)propyn-1-ol (**16**), which was prepared by bromination of **6** followed by the Sonogashira cross-coupling reaction of 1-bromopyrene (**17**) with propargyl alcohol (**18**). The synthesis of 1-hydroxypyrene (**11**) was based on the oxidation of **6** by lead tetraacetate (**19**) into 1-acetoxypyrene (**20**) followed by hydrolysis of **20**. 1-Aminopyrene **14** was synthesized by nitration of **6** into 1-nitropyrene (**21**) and reduction of **21** with sodium hydrosulfite. All pyrene derivatives were isolated in yields of 30-90%.

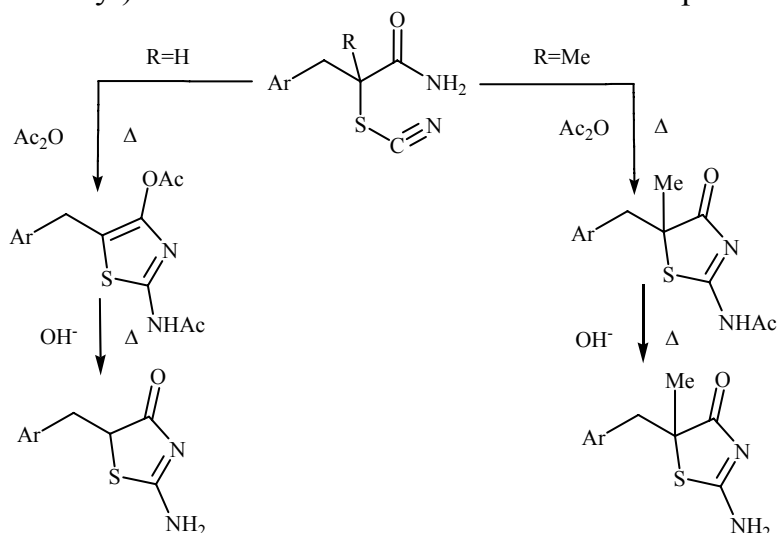
The primary processes which follow photoexcitation of **1** and **3** have been studied using femtosecond transient absorption spectroscopy and computational chemistry. Both the electron and energy transfer from pyrene to aryl azide moiety were found to be responsible for the photosensitization of the aryl azide decomposition.

HETEROCYCLIZATION OF ARYLSUBSTITUTED MONO- AND BISTHIOCYANATOAMIDES

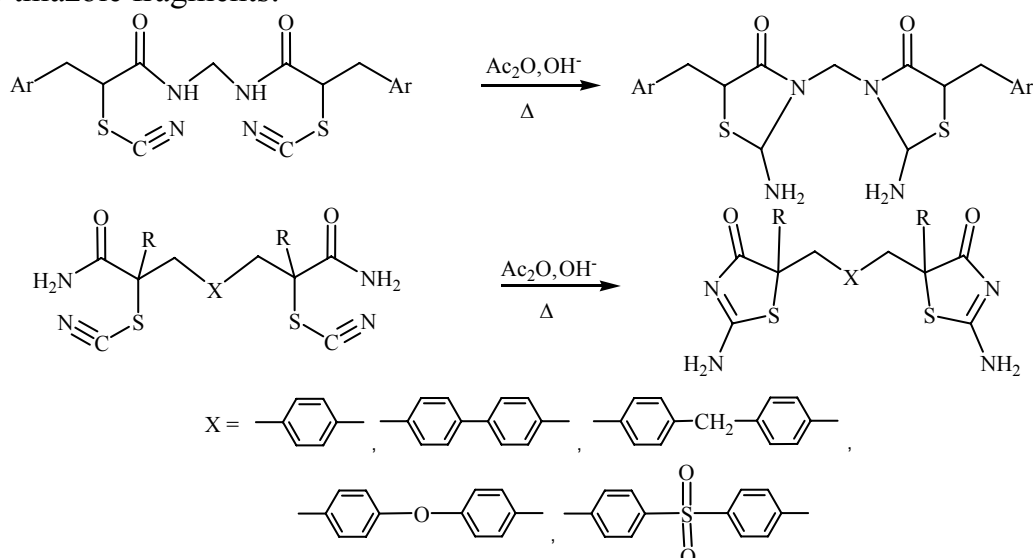
V.S. Baranovsky
B.D. Grishchuk

Ternopil V. Hnatiuk National Pedagogical University, Chemistry
Department, Ternopil, Ukraine
baranovsky@tnpu.edu.ua

By heterocyclization of thiocyanatoarylation products of acrylamide, methacrylamide and N,N-methylenebisacrylamide in acetic anhydride a new 5-arylsubstituted acetylic derivatives of thiazole-4-one are obtained. These compounds are easily deacetylated to 2-amino-5-benzyl-(5-methyl)-thiazole-4-ones in alkaline medium as presented on the scheme:



Bisthiocyanatoamides in similar conditions are formed a heterocyclic compounds with two thiazole fragments:



The structure of synthesized compounds was confirmed by IR, MS, ^1H NMR, ^{13}C NMR, HMBC and HMQC spectra.

The studies of biological activity revealed that 2-amino-5-benzyl-(5-methyl)-thiazole-4-ones have very high antifungal activity and may be the basis for new antimicrobial broad-spectrum drugs.

ANTIOXIDATION ACTIVITY OF SOME CALIX[4]RESORCINOLS DURING THE OXIDATION OF STYRENE

L.I. Vagapova¹
T.A. Barsukova²
A.R. Burilov¹
S.V. Bukharov²
Kh.E. Kharlampidi²
G.N. Nugumanova²

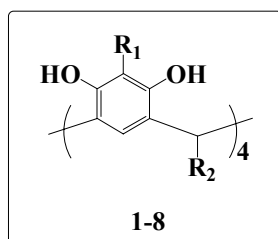
1 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia

2 - The Kazan State Technological University, Kazan, Russia
vagapovan@mail.ru

Organic materials that must be exposed to air, such as foods, plastics, rubber, cosmetics, drugs etc., undergo a spontaneous oxidation leading to degradation with loss of their physico-chemical, organoleptic properties. So the problem of searching for new compounds that could prevent oxidation is still important.

It is well known that polyphenols represent the class of compounds that are able to inhibit oxidation process of different substrates. Calix[4]resorcinols are polyphenolic macrocyclic compounds, containing in its structure 4 resorcinols units and having a wide possibility for its modification. So, the construction of new antioxidants on the basis of calix[4]resorcinols seems to be very perspective.

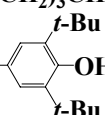
The oxidation of styrene initiated by AIBN (azobisisobutyronitrile) and inhibited by calix[4]resorcinols (1-8) in chlorobenzene solution was investigated. Antioxidant activity was characterized by rate constants of interaction of inhibitor with peroxide radical.



$R_1=H, R_2=CH_3, C_7H_{15}, C_9H_{19}(1-3)$;

$R_1=CH_2N(CH_3)CH_2CH(OMe)_2, R_2=CH_3(4)$;

$R_1=CH_2NH(CH_2)_3CH(OEt)_2, R_2=C_7H_{15}(5)$;

$R_1=H_2CS-$  $, R_2=CH_3, C_7H_{15}, C_9H_{19}(6-8)$

It was shown that all examined calix[4]resorcinols are able to inhibit oxidation process. The most effective inhibitory activity has compound **6** and it exceeds the activity of well-known stabilizers (thioalkofen MMB(TB3) and antioxidant BHT(ionol).

This work was supported by Federal Target Program "Scientific and Scientific-Pedagogical Personnel in Innovation Russia", 2009-2013, state contract No.P837

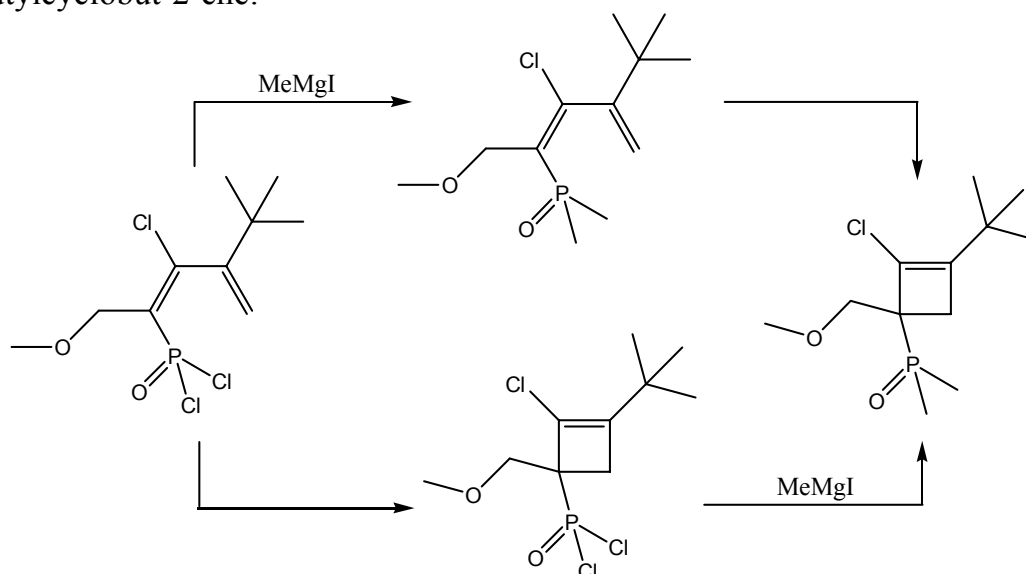
CYCLOBUTENYLPHOSPHINE OXIDES

A.S. Bogachenkov
B.I. Ionin

Saint-Petersburg State Institute of Technology (Technical University),
Department of Organic Chemistry, Saint-Petersburg, Russia
alexterve@gmail.com

Cyclobutenyl derivatives are hardly available compounds, and their properties are virtually unexplored. In the Department of Organic Chemistry of SPbSTI^{1,2} have been reported that in some cases 1-substituted 2-chloro-3-*tert*-butyl-1,3-butadiene-1-phosphonic acid dichlorides readily undergo 1,3-butadiene $\rightarrow$ cyclobutene isomerization, that makes available cyclobutenyl dichlorophosphonates. It was reported³ that dialkyl esters of 1-substituted 2-chloro-3-*tert*-butyl-1,3-butadiene-1-phosphonic acids do not isomerize to the corresponding cyclobutenes.

We found that 1-methoxymethyl-2-chloro-3-*tert*-butyl-1,3-butadiene-1-dimethylphosphine oxide (first obtained by organomagnesium synthesis from 1-methoxymethyl-2-chloro-3-*tert*-butyl-1,3-butadiene-1-dichlorophosphonate) by heating at 120°C for 1.5 h undergo cyclization to form 1-methoxymethyl-2-chloro-3-*tert*-butylcyclobut-2-enyl-1-dimethylphosphine oxide. Structure of the latter is confirmed besides physical methods by synthesis from 2-chloro-1-dichlorophosphono-1-methoxymethyl-3-*tert*-butylcyclobut-2-ene:



Similarly, from the corresponding cyclobutene dichlorophosphonates by organomagnesium synthesis were obtained previously not described diethyl- and diphenyl phosphine oxides. Structure of all obtained phosphine oxides was confirmed by NMR (^1H , ^{13}C , ^{31}P), IR spectroscopy, and for 1-methoxymethyl-2-chloro-3-*tert*-butylcyclobut-2-enyl-1-dimethylphosphine oxide by X-ray diffraction method.

References:

- (1) Ionin B.I., Brel' V.K., Prudnikova O.G., Struchkov Yu.T. Chernega A.N., Petrov A.A. Doklady AN SSSR, **1985**, 284, 359.
- (2) Prudnikova O.G., Brel' V.K., Ionin B.I., Petrov A.A. Zh. Obshch. Khim., **1987**, 57, 1472.
- (3) Brel' V.K., Doctorate diss., Chemical Sciences. St. Petersburg: SPbTI, **1993**.

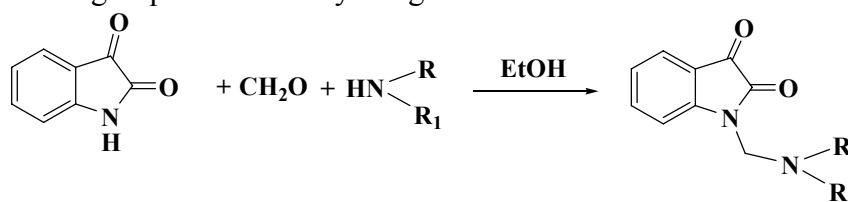
L.I. Musin
A.V. Ilin
A.V. Bogdanov
D.B. Krivolapov
I.A. Litvinov
V.F. Mironov

NOVEL DIVERSELY SUBSTITUTED ISATIN DERIVATIVES: SYNTHESIS AND REACTIONS WITH TRIS(DIETHYLAMINO)PHOSPHINE

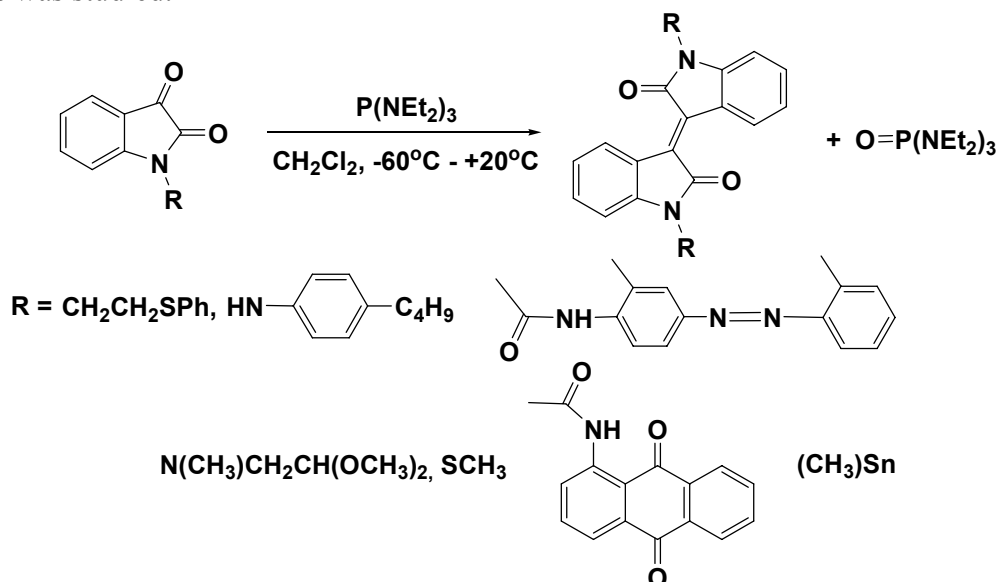
A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
bogdanov@iopc.ru

Isatin (indole-2,3-dione) and its derivatives play an important role in the pharmaceutical and dye industry. Drug substances containing isatin moiety may cure diseases such as epilepsy, tuberculosis, and bulimia. As it was established earlier, isatin N-Mannich bases, containing morpholine and piperidine groups, possess moderate activity against certain Gram-negative bacteria. These compounds are widely used in the synthesis of a number of heterocycles, in particular in the synthesis of isoindigo. Isoindigo [*1H,1'H*-bis(indolin-3-yliden)-2,2'-dione] derivatives attract a great attention mostly as the substances which show a specific biological activity (anti-leukemia, antiproliferative, anti-inflammatory etc.). Thus, 1-(β -*D*-glucopyranosyl)-isoindigo was found to be an anti-leukemia drug as well as 1-methylisoindigo that is applied in China since 80th of past century.

Herein we describe the synthesis of novel isatin derivatives bearing various alkyl, aminomethyl and thio-groups as well as dye fragments.



The reactions of isatins obtained with tris(diethylamino)phosphine to form isoindigo derivatives was studied.



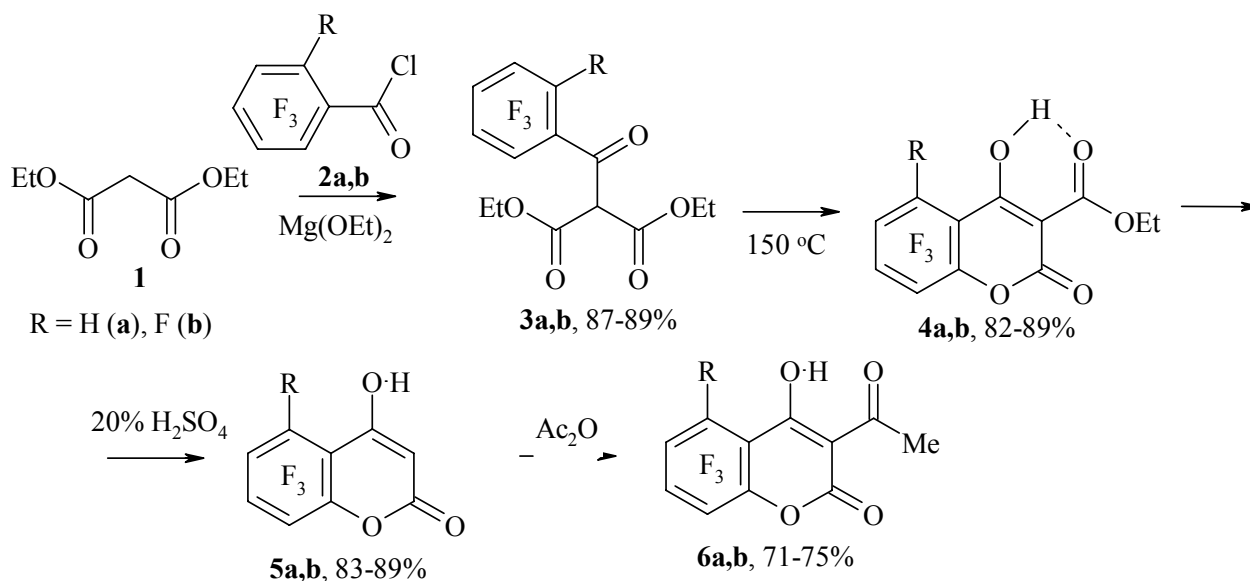
Financial support by the Council on Grants of the President of the Russian Federation (grant MK-1670.2010.3), Russian Foundation for Basic Research (grant No. 09-03-00933) and by the Program No. 1 of the Division of Chemistry and Material Sciences of Russian Academy of Sciences is gratefully acknowledged.

THE NEW WAY TO SYNTHESIS OF 4-HYDROXPOLYFLUOROCOUMARINS

Ya.V. Burgart
D.N. Bazhin
K.V. Scherbakov
V.I. Saloutin

Institute of Organic Synthesis, Ural Division of Russian Academy of Sciences, Ekaterinburg, Russia
 burgart@ios.uran.ru

We have found that the acylation of diethylmalonates **1** by polyfluorobenzoylchlorides **2a,b** results in the formation of diethyl(polyfluorobenzoyl)malonates **3a,b**. The thermal cyclization of esters **3a,b** allows to obtain 3-ethoxycarbonyl-4-hydroxypolyfluorocoumarins **4a,b**. The formation of coumarins **3a,b** proceeds without catalyst, bases and solvent. Acid hydrolysis of 3-ethoxycarbonylcoumarins **4a,b** affords 4-hydroxypolyfluorocoumarins **5a,b**, acylation of which by acetic anhydride yields 3-acetyl-4-hydroxypolyfluorocoumarins **6a,b**. The discovered thermal transformation of diethyl(polyfluorobenzoyl)malonates **3a,b** is an alternative way to 4-hydroxypolyfluorocoumarins **5, 6** that were used to get *via* chromone-coumarin rearrangement [1].



References:

1. V.I. Saloutin, Z.E. Skryabina, I.T. Bazil, S.P. Kisil. *J. Fluor. Chem.* 1999, **94**, 83.

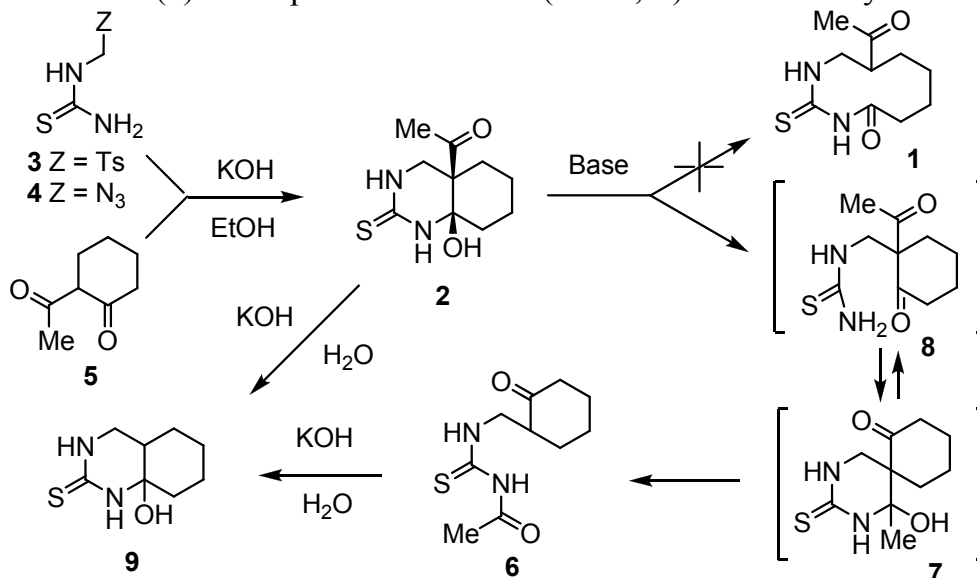
This work was financed by the Program of UB RAS (project N 09-I-3-2004) and the State Program for Support of Leading Scientific School (project No. 65261.2010.3).

AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE BASE-CATALYZED REARRANGEMENT OF 4A-ACETYL-8A-HYDROXYDECAHYDROQUINAZOLINE-2-THIONE

D.A. Cheshkov
A.D. Shutalev

Moscow State Academy of Fine Chemical Technology, Department of Organic Chemistry, Moscow, Russia
cheshkov_d@mail.ru

Recently we showed that 4-acyl-4-hydroxyhexahydropyrimidine-2-thiones/ones being treated with bases undergo C₍₄₎-C₍₅₎ bond cleavage to give corresponding *N*-acyl-*N'*-(3-oxoalk-1-yl)thioureas or -ureas [1]. To apply this rearrangement to the synthesis of 10-membered cyclic thiourea **1**, we prepared 4a-acetyl-8a-hydroxydecahydroquinazoline-2-thione (**2**) by reaction of *N*-(tosylmethyl)thiourea (**3**) or *N*-(azidomethyl)thiourea (**4**) with 2-acetylcyclohexanone (**5**) in the presence of KOH (EtOH, rt) in 72–79 % yields.



We found that treatment of pyrimidine **2** with base (NaH, DBU, etc.) at room temperature failed to give the desired cyclic thiourea **1**. In this reaction the ureide **6** was obtained as a single product in 88 % yield. Obviously the rearrangement **2** → **6** includes isomerisation of **2** into spirocyclic pyrimidine **7** via **8** followed by C–C bond cleavage. The DFT studies at the B3LYP/6-31+G(d,p) level showed that this reaction is controlled by stereoelectronic factors. Plausible explanation of the obtained data was proposed.

We found that treatment of **2** or **6** with aqueous solution of KOH resulted in formation of 8a-hydroxydecahydroquinazoline-2-thione (**9**).

References:

1. Shutalev A.D., Kishko E.A., Alekseeva S.G. *Chem. Heterocycl. Compd.* **1999**, 35, 750.

ACYLATIVE KINETIC RESOLUTION OF 2-METHYL-1,2,3,4-TETRAHYDROQUINOLINE USING 2-ARYLPROPIONYL CHLORIDES

E.N. Chulakov
G.L. Levit
A.A. Tumashov
D.N. Kozhevnikov
V.P. Krasnov

Postovsky Institute of Organic Synthesis of RAS (Ural Division),
Ekaterinburg, Russia
chulakov@ios.uran.ru

Acylative kinetic resolution (KR) is widely used to obtain the optically pure amines, the use of chiral acylating agents being of particular interest. Earlier we showed that (2*S*)-2-(6-metoxynapht-2-yl)propionyl chloride is an effective agent for KR of 7,8-difluoro-2,3-dihydro-3-methyl-4*H*-[1,4]benzoxazine – a key intermediate in the synthesis of antibacterial agent levofloxacin.

In this work we present the results of KR of 2-methyl-1,2,3,4-tetrahydroquinoline (**1**) using 2-arylpropionyl chlorides **2a-c** under various conditions. To determine the optimal conditions for KR we used the resolving agents in racemic form. In this case, the stereo selectivity factor is equal to the ratio of the diastereoisomeric amides formed.

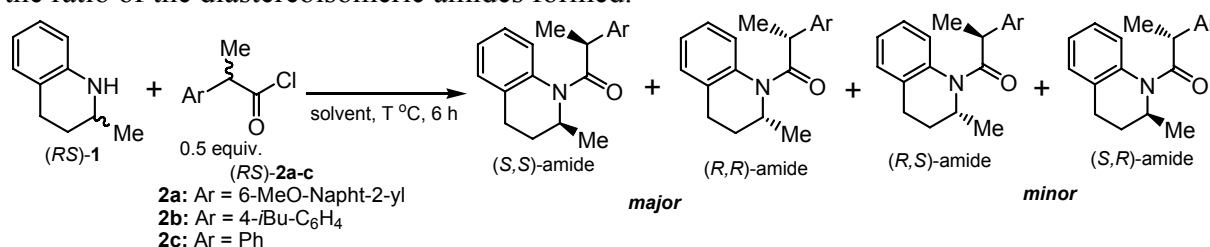


Table. Stereochemical results of acylation of amine **1** with acyl chlorides **2a-c**

Acylating agent	Solvent	<i>dr</i> = (<i>S,S</i>)/(<i>R,S</i>) or (<i>R,R</i>)/(<i>S,R</i>)	
		+20 °C	–20 °C
2a	PhMe	96.8/3.2	98.0/2.0
	CH ₂ Cl ₂	93.8/6.2	92.3/7.7
2b	PhMe	97.0/3.0	98.1/1.9
	CH ₂ Cl ₂	91.8/8.2	93.8/6.2
2c	PhMe	95.9/4.1	97.5/2.5
	CH ₂ Cl ₂	88.8/11.2	89.5/10.5

It was found that acylation of amine **1** with acyl chlorides **2a-c** results in predominant formation of (*S,S*)[(*R,R*)]-amides. In all cases the most selective acylation of **1** was observed in toluene at –20 °C. Acylation in dichloromethane was less selective (see Table). Ibuprofen chloride (**2b**) was found to be more selective resolving agent in comparison with naproxen chloride (**2a**) and 2-phenylpropionyl chloride (**2c**). Thus, in the case of acylation of amine **1** in toluene at +20 °C with acyl chloride **2b** the diastereoisomeric ratio (*dr*) of the amides formed was 97.0/3.0. The decrease in the reaction temperature from +20 to –20 °C provided an improvement in stereoselectivity (*dr* 98.1/1.9).

The reaction of amine **1** with **2c** was calculated (DFT-D/B3LYP/TZVP) in dichloromethane (COSMO solvation model) at 293 K. Difference in the computed free energy of activation for (*S,S*)[(*R,R*)]- and (*S,R*)[(*R,S*)]-diastereomers (12.2 and 15.2 kcal/mol, respectively) agrees with the measured diastereoisomeric ratio. Weak $\pi\pi$ -interactions stabilizes the (*S,S*)[(*R,R*)] transition state due to the parallel position of aromatic rings of the reagents.

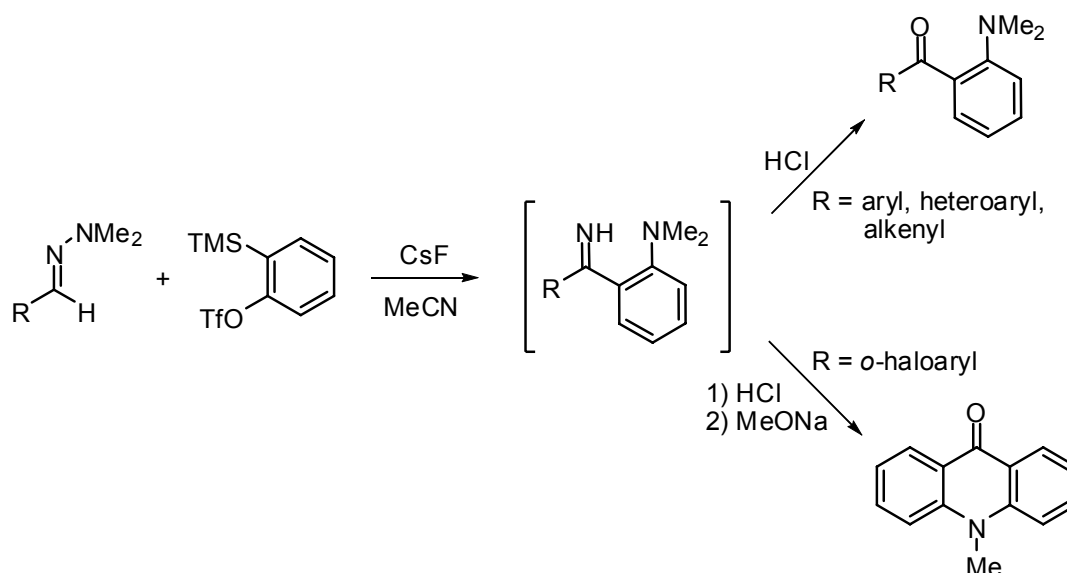
The work was financially supported by RFBR (grant 10-03-00084), the State Program for Supporting of Leading Scientific Schools of the RF (grant NSh 65261.2010.3), the State Contract 02.522.12.2011 and by the Ural Division of RAS (grants 09-P-3-2001, 09-I-3-2004, 10-3-NP-322).

SYNTHESIS OF *ORTHO*-(DIMETHYLAMINO)ARYL KETONES AND ACRIDONES BY THE REACTION OF 1,1-DIALKYLHYDRAZONES WITH ARYNES

A.V. Dubrovskiy
R.C. Larock

Iowa State University, Department of Chemistry, Ames, IA, USA
anton@iastate.edu

A novel, efficient, and expedient route to biologically and pharmaceutically important *o*-(dimethylamino)aryl ketones and acridones has been developed starting from readily available aldehydes, 1,1-dimethyl hydrazine, and commercially available *o*-(trimethylsilyl)aryl triflates. The reaction proceeds under mild conditions, tolerates a wide range of functional groups, and provides final products in good to excellent yields.



N-ACYLBENZOTRIAZOLE MEDIATED MICROWAVE ASSISTED SYNTHESIS OF PROTECTED AND NOVEL UNPROTECTED FERROCENYOYLAMIDOAMINO ACIDS

S.F. Ekti Dal¹
D. Hur¹
G.A. Varol²
E. Hur²

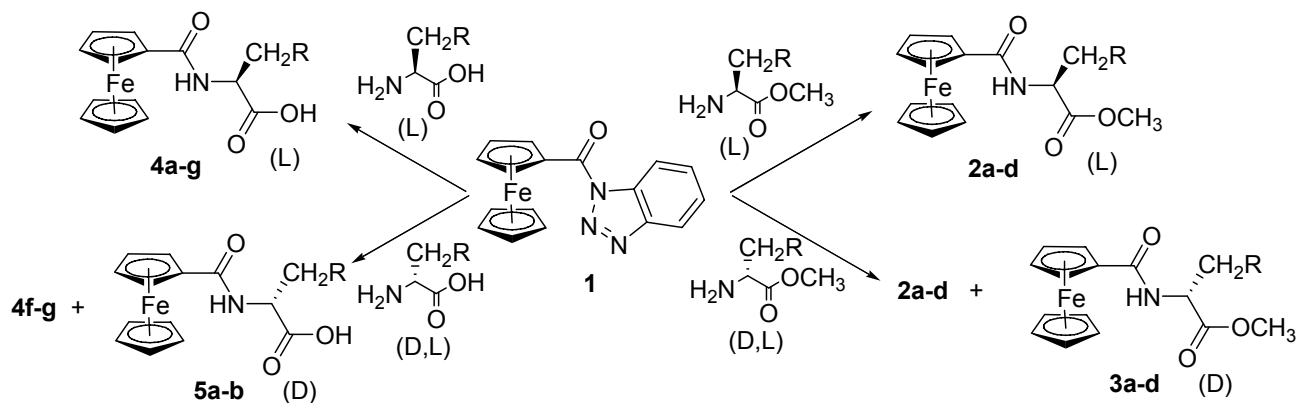
1 - Anadolu University, Department of Chemistry, Eskisehir, Turkey

2 - Eskisehir Osmangazi University, Department of Chemistry, Eskisehir, Turkey
sfekti@anadolu.edu.tr

Ferrocene chemistry has aroused interest of many researcher as a result of its ability synthesizing a large number of derivatives and to be applicated in many field. It has been used in electron transfer process of amino acids and peptides because of its very favorable electrochemical properties. Its redox potential makes ferrocene important biomarker redox device by conjugation with biomolecules such as aminoacids, peptides, nucleic acids [1] and carbohydrates [2].

Ferrocene amino acids [3] and peptides [4], which are the important ferrocene derivatives, have found a great number of uses in many application such as binding or caging structures for metal ions [5].

In present work crystalline and chirally stable carboxyl-protected and novel unprotected *N*-ferrocenoyl amino acid derivatives of Ser, Cys, Ala, Phe, Trp, Asp and Asn have been prepared. These amino acids undergo substitution reaction with 1-(ferrocenylcarbonyl)-1*H*-benzotriazole in partially aqueous media under microwave irradiation.



References:

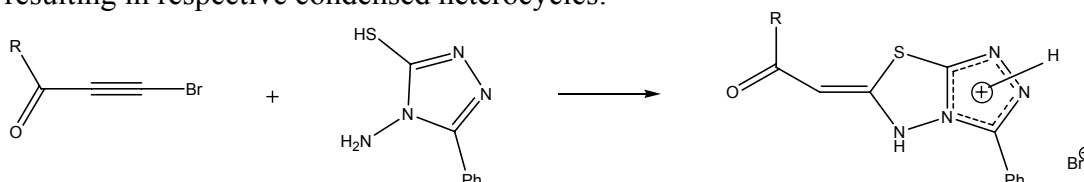
- [1] H.-B. Kraatz, Journal of Inorganic and Organometallic Polymers and Materials 15, 1 (2005) 83–106.
- [2] M. Chahma, J. S. Lee, H.B. Kraatz, J. Organomet. Chem., 648 (2002) 81-86.
- [3] J. Tauchman, P. Stepnicka, Inorg. Chem. Commun., 13 (2010) 149-152.
- [4] C. C. G. Scully, P. J. Rutledge, Tetrahedron, 66 (2010) 5653–5659.
- [5] F. E. Appoh, T. C. Sutherland, H.-B. Kraatz, J. Organomet. Chem. 690 (2005) 1209–1217.

PHOSPHORYLATED THIAZOLO[3,2-*b*][1,2,4]TRIAZOL-7-YLIUM CHLORIDES

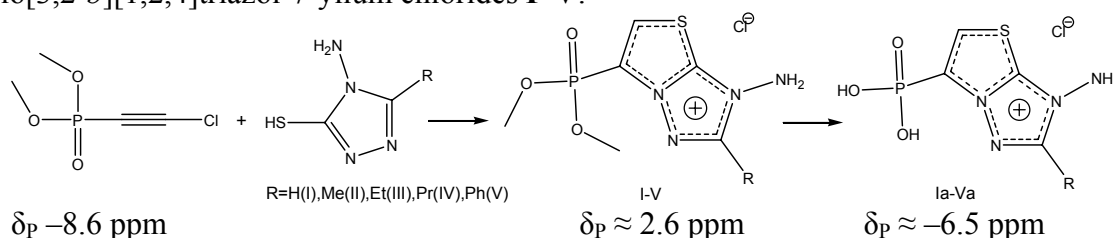
E.B. Erkhitueva
A.V. Dogadina
A.V. Khranchikhin
B.I. Ionin

Saint-Petersburg State Institute of Technology (Technical University),
Department of Organic Chemistry, Saint-Petersburg, Russia
erhitouevae@yandex.ru

A number of condensed heterocyclic compounds containing triazole ring are known to possess diverse pharmacological properties, including painkilling, anti-inflammatory, anticancer, antibacterial and radioprotecting [1]. To date, the phosphorus-containing compounds of such structure are unknown, although they are promising ones as they combine condensed heterocycles and phosphonate groups in one molecule that may lead to even greater variety of valuable biological properties. In [2] was shown that reactions of 4-amino-3-mercapto-5-phenyl-1,2,4-triazoles with 1-bromo-2-acylacetylenes proceed as a condensation involving amino- and mercapto groups resulting in respective condensed heterocycles:



We found that the reaction of dimethyl chloroacetylenephosphonate with 4-amino-3-mercapto-5-alkyl(aryl)-1,2,4-triazoles proceeds readily in acetonitrile medium at room temperature at the mixing equivalent amounts of the starting reagents, to form condensed heterocyclic compounds of unusual structures, namely 3-amino-6-(dimethoxyphosphoryl)-2-alkyl(aryl)-3*H*-thiazolo[3,2-*b*][1,2,4]triazol-7-ylum chlorides **I–V**:



Similar compound is formed in the reaction of 4-methyl-3-mercapto-1,2,4-triazole with chloroacetylenephosphonate. The compounds **I–V** are crystalline substances, poorly soluble in organic solvents, well soluble in water. When heated in concentrated hydrochloric acid, they are transformed into the corresponding phosphonic acids **Ia–Va**. The structure of the compounds **I–V**, **Ia–Va** was proved using ^1H , ^{13}C , and ^{31}P NMR spectroscopy. For example, in the ^1H NMR spectrum of compound **II** there is a doublet signal of the methoxy groups at the phosphorus, δ 3.94, J_{HP} 11.6 Hz, the methyl group in 2 position induces a singlet δ 2.72. Olefinic proton resonates in a weak field, δ 8.53, J_{HP} 4.4 Hz. The ^{13}C NMR spectrum of the compound contains the following signals (ppm): δ_{C} 10.12 (CH_3), δ_{C} 55.66 (OCH_3), δ_{C} 119.62, J_{CP} 195.7 Hz (CH=), δ_{C} 132.28, J_{CP} 17.3 Hz ($=\text{CNH}$), δ_{C} 154.92 ($=\text{CCH}_3$), δ_{C} 161.39 (SC=N). Formation of the compounds **I–V** with aromatic structure is proved unambiguously by the data of X-ray diffraction and mass-spectrometry.

References:

- [1] M. M. Ghorab and A. Y. Hassan, Phosphorus, Sulfur, and Silicon, 1998, 141, 251-260.
- [2] T.E. Glotova, A. Nakhmanovich, and M.V. Sigalov, – Russian Journal of Organic Chemistry, vol. 24, 10, (1988), p. 1941-1945.

THE FIRST EXAMPLES OF LIPOPHILIC AROMATIC DIAZONIUM SALTS: PREPARATION AND PROPERTIES

V.D. Filimonov
M.E. Trusova
P.S. Postnikov
K.V. Kutonova

National Research Tomsk Polytechnic University, Department of
Biotechnology and Organic Chemistry, Tomsk, Russia
filimonov@tpu.ru

Arendiazonium dodecylbenzenesulfonates ($\text{ArN}_2^+ \text{p-C}_{12}\text{H}_{25}\text{C}_6\text{H}_5\text{SO}_3^-$) (ADBS) as the first example of aromatic diazonium salts with strongly pronounced lipophilic nature were obtained by diazotization of aromatic amines in the presence of *p*-dodecylbenzene sulfonic acid. The diazotization was carried out at room temperature in the presence of the polymer-supported nitrite in acetic acid or *tert*-butyl nitrite in ether, providing almost quantitative yields of ADBS. It was shown that ADBS are oily and relatively stable substances at room temperature, exothermic decomposed at 115-120 ° C with release of the energy about 200 J/g (DSC data) that is explosion safe substances.

ADBS are unlimited soluble in nonpolar organic solvents (benzene, hexane, CCl_4 , etc.), which sharply distinguishes them from known aromatic diazonium salts. It was shown that ADBS have typical diazonium nature, giving in high yields the products of azo-coupling, aryl iodides by the reaction with KI, products of arylation with benzene and pyridine. At the same time they are also showing new and unprecedented properties for conventional diazonium salts. So ADBS form with quantitative yields arenes (hydro-dediazotization reaction) in hexane or chloroform, and aryl chlorides at boiling in CCl_4 . In the presence of triethylamine or pyridine.

These reactions have free-radical nature, as evidenced by the detection of hexachloroethane in the reaction mixture with CCl_4 and CHCl_3 , and the benzyl radicals conversion products in the reaction with toluene.

Thus, lipophilic ADBS extend the known properties of aromatic diazonium salts, and open new possibilities for usage of diazonium compounds in organic synthesis.

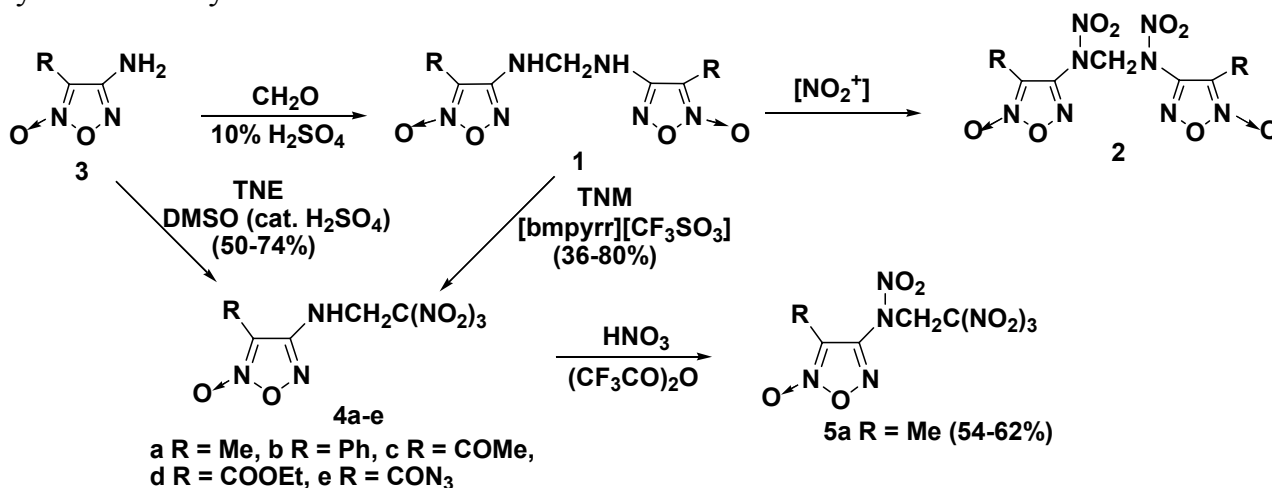
SYNTHESIS AND NITRATION OF 4-(2,2,2-TRINITROETHYLAMINO)-3-R-FUROXANS

A.O. Finogenov
M.A. Epishina
A.S. Kulikov
N.N. Makhova

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia
mn@ioc.ac.ru

Recently¹ we have synthesized methylenbis(aminofuroxans) **1** and their *N,N'*-dinitro derivatives **2** on the basis of Mannich reaction of aminofuroxans **3** with formaldehyde followed by nitration of products obtained.

To prepare 4-(2,2,2-trinitroethylamino)-3-R-furoxans **4** and their *N*-nitro derivatives **5** in this work an investigation of Mannich reaction of aminofuroxans **3** was continued. At first methylenbis(aminofuroxans) **1** were used as aminomethylating reagents in Mannich reaction with trinitromethane (TNM) in ionic liquids (ILs), which played a part of both reaction medium and acidic catalyst. The maximum yields (36-80%) of Mannich bases **4a-e** were obtained in IL [bmppyr][CF₃SO₃]. Then it was found that Mannich products **4a-e** were also formed at interaction of aminofuroxans **3a-e** with trinitroethanol (TNE). This reaction was carried out both in the same IL and in DMSO in the presence of catalytic amount of H₂SO₄. The best yields of compounds **4a-e** (50-74%) were obtained in DMSO. A nitration of compounds **4** was successfully performed both in IL [emim][HSO₄] and in DMSO with a mixture of HNO₃-TFAA by the example of compound **4a**, including *one-pot* variant without isolation of compound **4a**. 3-Methyl-4-(2,2,2-trinitroethynitramino)furoxan **5a** was synthesized in yields 54-62%.



References:

1. A.O. Finogenov, M.A. Epishina, A.C. Kulikov, I.A. Anan'ev, N.N. Makhova, V.A. Tartakovsky, *Russ. Chem. Bull., Int Ed.*, 2011, **59**, 2108-2113.

A.N. Galjautdinova

E.N. Klimovitskii

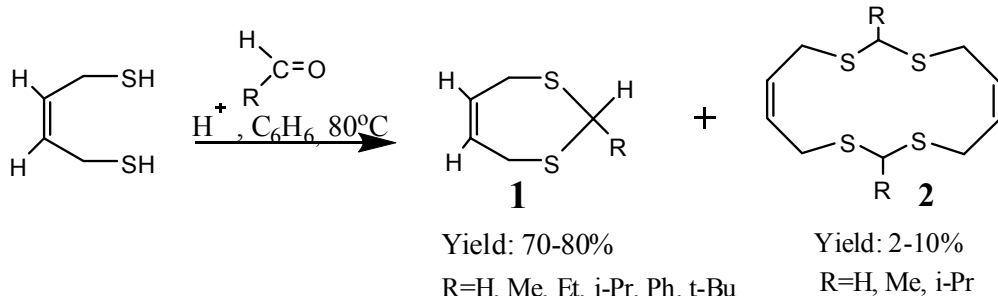
R.M. Vafina

E.A. Berdnikov

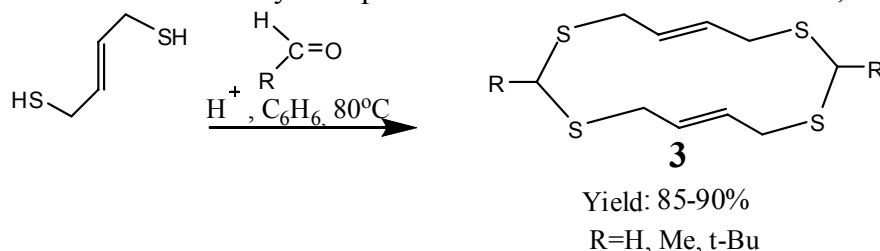
Yu.G. Shtyrilin

**CYCLIC SULFUR-CONTAINING DITHIOACETALES.
SYNTHESIS AND SPATIAL STRUCTURE**Kazan (Volga region) Federal University, A.M. Butlerov Chemical
Institute, Kazan, Russia
galj-albina@yandex.ru

Sulfur-containing cyclic dithioacetals are analogues of natural compounds and are of undoubted interest. In this study, the data on the synthesis of dithioacetals from *cis*-butene-2-dithiol-1,4 are systematized.



In order to obtain the products with *trans*-configuration of the butene fragment, the condensation reactions of the carbonyl compounds with *trans*-butene-2-dithiol-1,4 were conducted.



During condensation with acetaldehyde two products were found in the reaction mixture in a ratio of 10:1. Both products were isolated in a configurationally pure form, and the dominating product was the previously described as *trans*-2,9-dimethyl-(5*E*,12*E*)-1,3,8,10-tetrathiacyclotetradeca-5,12-diene with a *trans*-orientation of the substituents [1]. In view of the impossibility to obtain a seven-membered cycle, and the high melting temperature of the minor product, it was concluded, that the minor product was fourteen-membered bis-dithioacetal also, but it has a *cis*-orientation of the substituents. The condensation with the pivalic aldehyde was conducted as well. In the reaction mixture two products in a ratio of 2:1 were detected. According to the X-Ray analysis the minor product is the fourteen-membered bis-dithioacetal with *trans*-disposition of the substituents. The synthesis of formal leads to only one product in the reaction mixture, which was isolated in a configurationally pure form. Also the stereochemical study of the oxidation of cyclic seven-membered dithioacetals to the monosulfoxides and disulfoxides was carried out.

The structures of all synthesized compounds were proved by the methods of NMR ^1H and ^{13}C spectroscopy, elemental analysis, mass spectrometry, and X-ray analysis.

References:

1. E. N. Klimovitskii, A. N. Galyautdinova, A. B. Dobrynin, V. V. Gavrilov, S. G. Gnevashev, R. M. Vafina, I. A. Litvinov, and Yu. G. Shtyrilin, *Russ. J. Org. Chem.*, 45 (10), P. 1442.
2. A. N. Galyautdinova, R. M. Vafina, O. N. Kataeva, O. A. Lodochnikova, S. G. Gnevashev, O. I. Gnezdilov, V. V. Gavrilov, Yu. G. Shtyrilin, G. A. Chmutova, and E. N. Klimovitskii, *Russ. J. Org. Chem.*, 46 (2), P. 246.

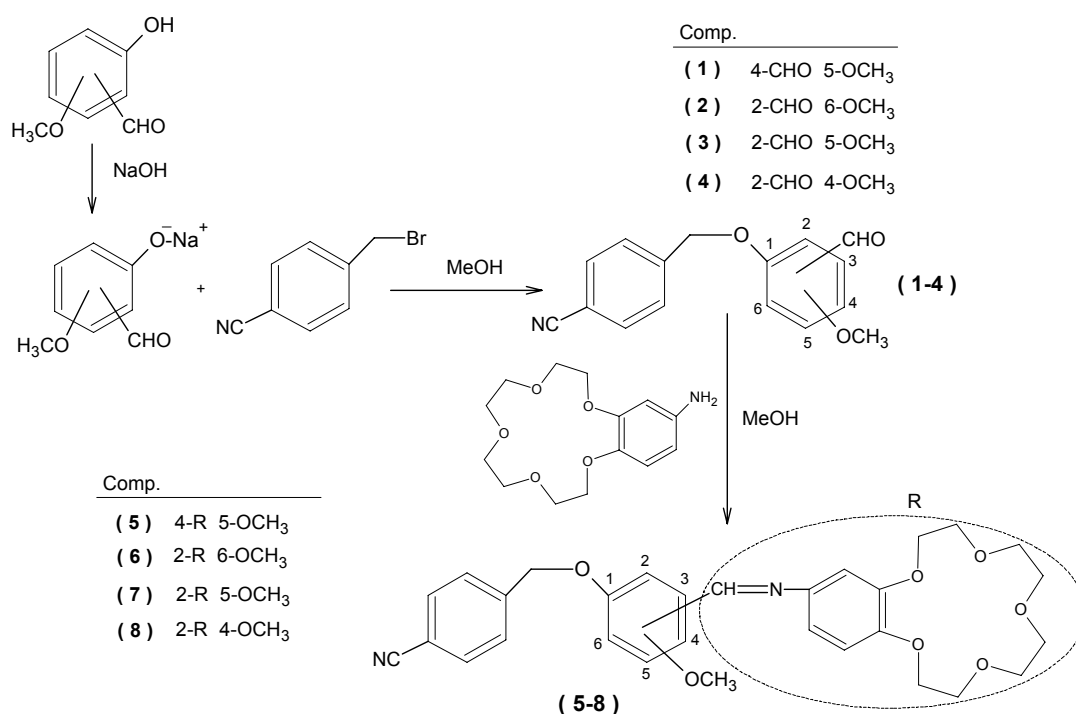
SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATIONS OF NEW SCHIFF BASES CONTAINING THE BENZO-15-CROWN-5 MOIETY

Z. Hayvali
H. Guler

Ankara University, Faculty of Science, Department of Chemistry,
Ankara, Turkey
zhayvali@science.ankara.edu.tr

Crown ethers have attracted great interest in the last three decades, not only from the synthetic and selectivity alkaline and alkaline earth metal cation complexation properties point of view, but also with respect to their unusual structural characteristics [1,2]. Crown ether containing Schiff bases are known to bind cations in the crown ether cavity in addition to the coordination of a transition metal centre through the NO donor atom.

A series of benzyloxybenzaldehyde derivatives (**1-4**) were synthesized by the reactions of 4-(bromomethyl)benzonitrile with 4-hydroxy-3-methoxybenzaldehyde (vanillin), 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin), 2-hydroxy-4-methoxybenzaldehyde and 2-hydroxy-5-methoxybenzaldehyde. Condensation reactions among the four benzaldehyde derivatives (**1-4**) with 4'-aminobenzo-15-crown-5 yielded the new Schiff base compounds (**5-8**). Compound structures have been characterized by the elemental analyses, FT-IR, ¹H-NMR, ¹³C-NMR and mass spectral data.



References:

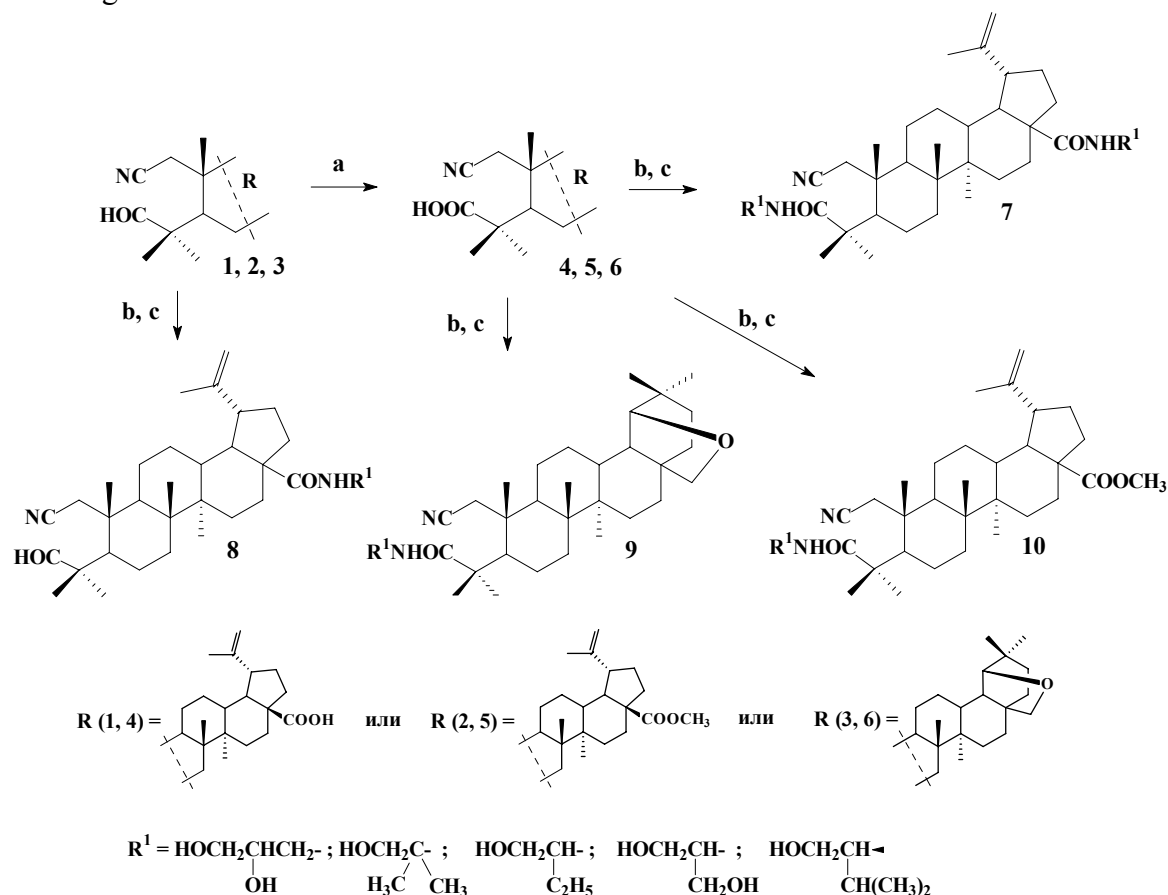
- [1] Beer, P.D., C.G., Crane, Drew, M.G.M. J. Chem. Soc., Dalton Trans 3235-3242 (1991).
[2] Hayvali, Z., Transition Met. Chem. **34**, 97-101 (2009).

SYNTHESIS OF 2, 3-SECOTRITERPENE MONO- AND DICONJUGATES WITH AMINO ALCOHOLS

E.V. Igosheva¹
 K.A. Prokashev²
 I.A. Tolmacheva¹
 V.V. Grishko¹

1 - Institute of Technical Chemistry, Biological Active Compounds,
 Perm, Russia
 2 - Perm State University, Perm, Russia
 ekig00@mail.ru

Mono- **1**, **5**, **6** and dicarboxylic 2,3-secotriterpene acids **4** [1, 2] were transformed *in situ* by reactions with amino alcohols into the corresponding amides **7-10**, promising as antiviral and anticancer agents.



Reagents and reaction conditions : (a) $Cr_2O_3/H_2SO_4/(CH_3)_2CO$; (b) $(COCl)_2/CH_2Cl_2$;
 (c) $R^1NH_2/CH_2Cl_2/(C_2H_5)_3N$

References:

1. Tolmacheva I.A., Nazarov A.V., Maiorova O.A., Grishko V.V. Synthesis of lupane and 19 β , 28-epoxy-18 α -oleanane 2, 3-secoderivatives based on betulin // Chem. Nat. Compd. 2008. V. 44 (5). P. 606-611.
2. Tolmacheva I.A., Grishko V.V., Boreko E.I., Savinova O.V., Pavlova N.I. Synthesis and antiviral activity of 2, 3-secoderivatives of betulonic acid // Chem. Nat. Compd. 2009. V. 45 (5). P. 673-676.

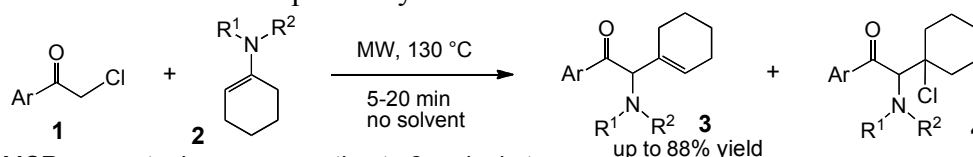
The work was supported by the RAS Presidium Program Development of Methods for Preparing Chemical Compounds and Creating New Materials, the Targeted Program of Interdisciplinary Collaborative Projects Between Scientists of the Ural and Siberian Branches of the RAS, and RFBR Grant No. 10-03-96044-r ural a.

MICROWAVE-ASSISTED MULTICOMPONENT REACTION FOR SYNTHESIS OF β -AMINOKETONES

T. Inokuchi
L.-J. Ma
Y. Zhang

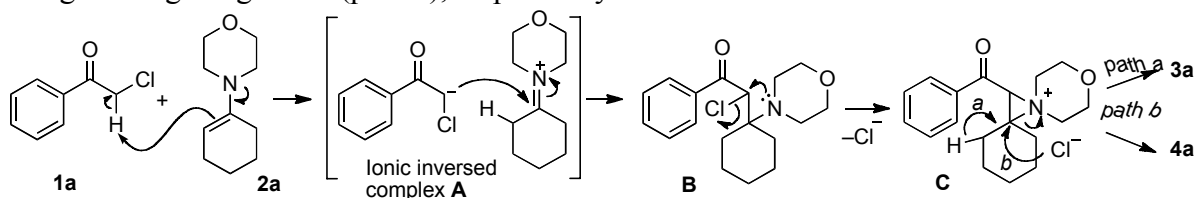
Okayama University, Department of Medicinal and Bioengineering
Science, Okayama, Japan
inokuchi@cc.okayama-u.ac.jp

We examined a three-component reaction by employing enamine as a source of ketone and amine to combine with 2-haloacetophenone, although the reactions of enamines and 2-bromo- or 2-iodoacetophenones are prone to undergo S_N2 alkylation. In order to avoid the S_N2 process and induce the participation of amine moiety to the products, we attempted to activate the haloketones and enamines to the ionic inversed complexes by microwave irradiation.



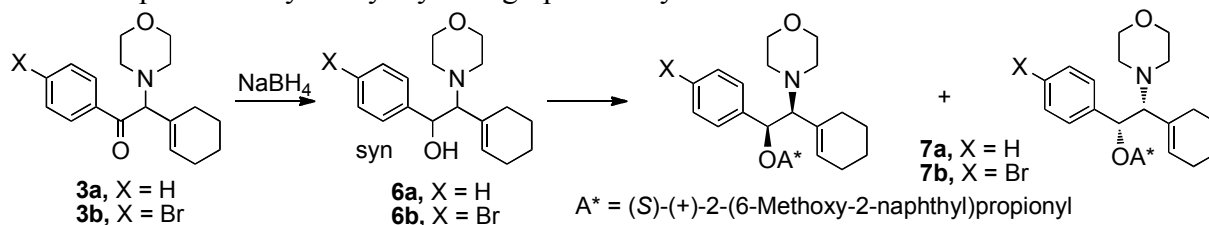
Scheme 1 MCR concept microwave reaction to 2-aminoketones

This multicomponent reaction (MCR) of enamines and chloroacetylarenes can be explained as follows (Scheme 2). Thus, upon MW-irradiation, the chloroketone and enamine would be activated so as to facilitate proton abstraction from the chloroketone with enamine base, forming the ionic inversed complex **A**. The resulting enolate and iminium complex **A** should induce aza-Darzens reaction through Mannich-type addition reaction followed by cyclization of the resulting α -chloro- β -aminoketones **B**. Subsequently, the resulting ammonium **C** can undergo either the spontaneous Hofmann elimination to give **3a** (path *a*) or substitution with chloride ion accompanied with ring cleavage to give **4a** (path *b*), respectively.



Scheme 2 Mechanistic assumption for MCR of **1a** and **2a**

Reduction of these aminoketones to the corresponding β -aminoalcohols **6** as pseudoephedrine analogues was examined. We found that the 2-aminoketones **3** underwent hydride attack *via* Felkin-Ahn-controlled manner instead of the chelation-controlled one, giving the corresponding syn- β -aminoalcohols **6**, exclusively. The structure was unambiguously determined with the compound **6b** by X-ray crystallographic analysis.



References:

L.-J. Ma, T. Inokuchi, *Chem. Commun.*, 7037–7039 (2010).

THE THREE-COMPONENT REACTION OF ISONITRILES WITH THIOPHENOLS AND GEM- DIACTIVATED OLEFINS

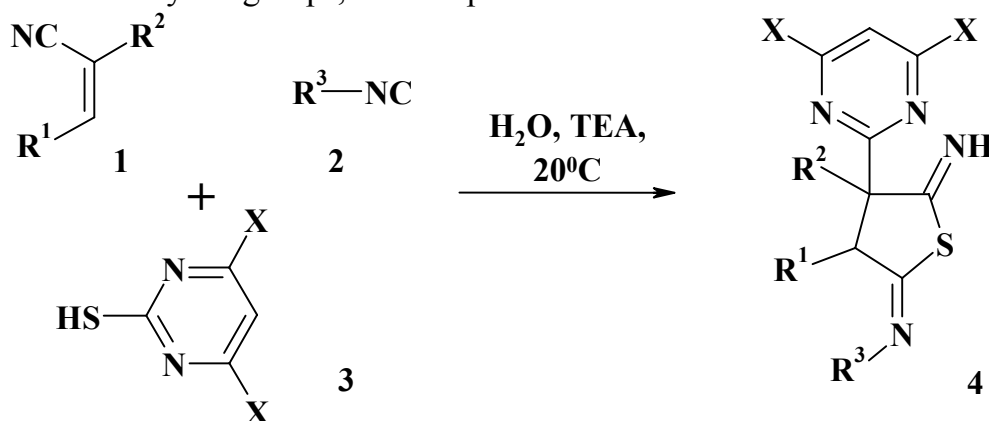
M.N. Ivantsova
M.A. Mironov
V.S. Mokrushin

Ural Federal University named after the First President of Russia
B.N. Yeltsin, Chemical Technology Department, Ekaterinburg, Russia
mivantsova@mail.ru

Sulphur-containing heterocyclic compounds are of special interest as potential biologically active substances. At the same time these compounds can show interesting physical and chemical properties.

During our works on research of three-component reaction based on isonitriles with olefins and phenols [1,2] we have elaborated a synthesis method of substituted tetrahydrothiophenes by the modification of given reaction with heterocyclic thiophenols.

So we have carried out reaction based on aliphatic isonitriles **2** with olefins **1**, activated one or two cyano groups, and thiophenols **3**.



$R^1 = \text{Alk, Ar} \quad R^2 = \text{CN, COOEt} \quad R^3 = \text{Alk}$

$X = \text{H, CH}_3$

As a result of these researches we have received various derivatives of tetrahydrothiophene **4**. The structure of all products is identified on the detailed analysis of ^1H , ^{13}C spectra and mass spectrometry.

References:

- [1] M.A. Mironov, M.N. Ivantsova, V.S. Mokrushin, *Synlett*. **2006**, 4, 615-617
- [2] A.N. Kolontsova, M.N. Ivantsova, M.I., Tokareva, M.A. Mironov, *Molecular Diversity*. **2010**, 14, 543-550

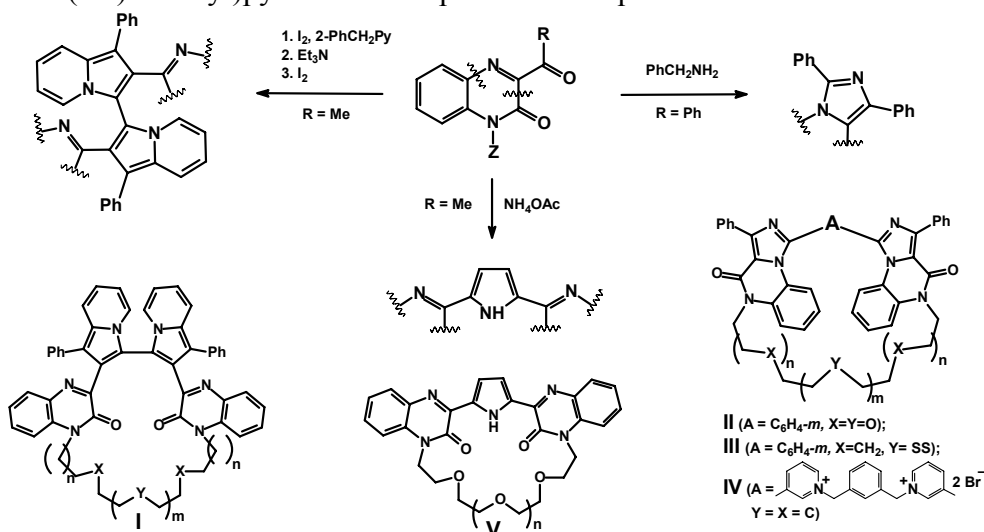
A.A. Kalinin
N.V. Nastapova
A.I. Samigullina
I.Kh. Rizvanov
A.V. Chernova
A.T. Gubaidullin
V.V. Yanilkin
I.A. Litvinov
V.A. Mamedov

NEW APPROACHES FOR SYNTHESIZING MACROCYCLES WITH QUINOXALINE FRAGMENTS

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
kalinin@iopc.ru

The continued interest in designing new macrocyclic ligands mainly stems from their use as models of protein-metal binding sites in biological systems, as synthetic ionophores, as therapeutic reagents in chelate therapy, as cyclic antibiotics, to study host-guest interactions and in catalysis. Heterocyclic fragments provide rigidity and are able in some cases, to participate, in complexation through their soft donor atoms. Although many macrocyclic compounds with heterocycles such as pyridine, bipyridine, pyrimidine, triazole, pyrazole, imidazole and thiophene have been synthesized and studied, very little is known about using benzoheterocycles as a subunit of macrocyclic compounds.

Here we report on the synthesis of novel macrocyclic ligands, which are fused to the quinoxaline units in combination with various heterocyclic systems and spacers between them. To this end, we aimed at synthesizing bi- and two types of tricyclic heteroaryl systems, with the quinoxaline moiety based on the three new methods developed by us starting from 3-acetyl- and 3-benzoylquinoxalinones. The key stages of these methods involve the forward conversion of quinoxalinones to the 3-indolizin-2-ylquinoxalinone, imidazo[1,5-*a*]quinoxalinone and 2,5-bis(quinoxalin-2(1*H*)-on-3-yl)pyrrole with at position 3 of quinoxalinones.



The report discusses the spectral characteristics and the peculiarities of the behavior of the synthesized heterocyclophanes and their complexes with some metal cations in redox conditions.

References:

1. Mamedov V.A., Kalinin A.A., Balandina A.A., Rizvanov I.Kh., Latypov S.K. *Tetrahedron*, **2009**, 65, 9412
2. Mamedov V.A., Kalinin A.A., Rizvanov I.Kh., Bauer I., Habicher V.D. *Rus. Chem. Bull.*, **2009**, 1493
3. Kalinin A.A., Mamedov V.A., Yanilkin V.V., Nastapova N.V., Rizvanov I.Kh., Morozov V.I. *Rus. Chem. Bull.*, **2009**, 1484

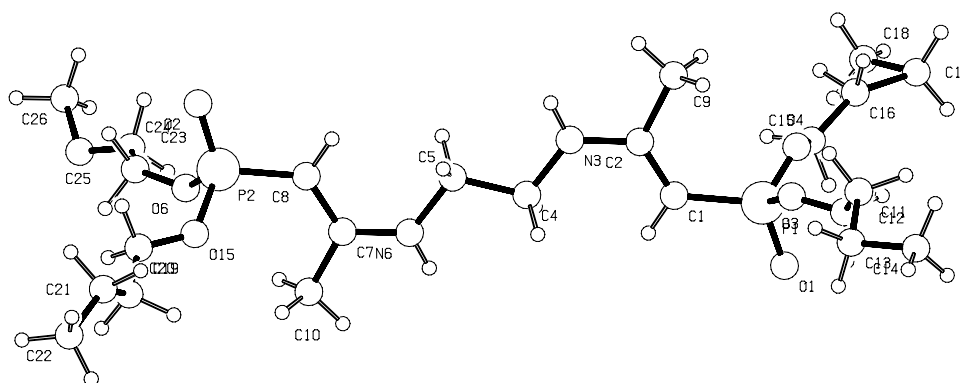
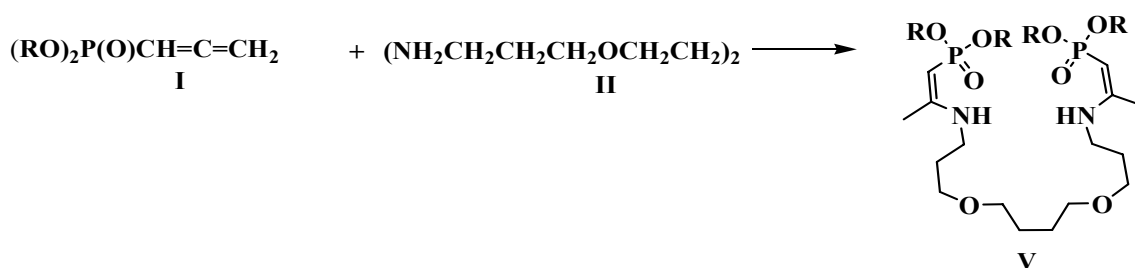
The investigations considered herein were supported by the Russian Foundation for Basic Research (grants №10-03-00413-a, 09-03-99011-r-ofi) and by the Federal Agency of Science and Innovation (the state contract № 02.740.11.0633).

INTERACTION OF 1,2-PROPADIENYL-PHOSPHONATE WITH DIAMINES

N.G. Khusainova¹
E.A. Berdnikov¹
S.M. Rybakov¹
D.V. Krivolapov²

1 - A.M. Butlerov Chemistry Institute of Kazan Federal University,
 Kazan, Russia
 2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
 Russia
narkis.khusainova@ksu.ru

Derivatives of alkenyl- and alkylphosphonic acids having nitrogen-containing groups in the β -position attract interest as potential biologically active compounds with a broad spectrum of action. We investigated a reactions of O,O-dibutyl-1,2-propadienylphosphonate (I) with 4,9-dioxa-1,12-dodecanediamine (II), 4,7,10,-trioxa-1,13-tridecanediamine (III) and 1,2-diaminoethane (IV). The mixing of the two divisible abundance of phosphonate (I) with diamine (II-IV) leads to products of additions (V-VII). It is found that the central C atom of the allene system is attacked by the N-atom of the diamine. The structure of the compound (V-VII) was investigated by IR, ^1H and ^{31}P spectroscopy and by X-ray diffraction analyses. Thus, the ^1H NMR spectra of the adduct of phosphonate (I) with diamine (II) contain the signals at δ_{H} 3.53 ppm ($^2J_{\text{PH}}$ 10.6 Hz) for the $\text{P}-\text{CH}=\text{}$ proton and δ_{H} 1.97 ppm ($^4J_{\text{PH}}$ 1.4 Hz) for the $\text{CH}_3\text{C}=\text{}$ proton. The absence of the signal of the $\text{P}-\text{CH}_2\text{-}$ protons can be attributed to the compound (V) of the enamine structure. The ^{31}P NMR spectra contain a intensive single signal δ_{P} 28 ppm. The interaction of the phosphonate (I) with diamines (III) and (IV) take place by analogy with the formation of adducts (VI-VII) with enamine structure. The adducts show fungicide activity



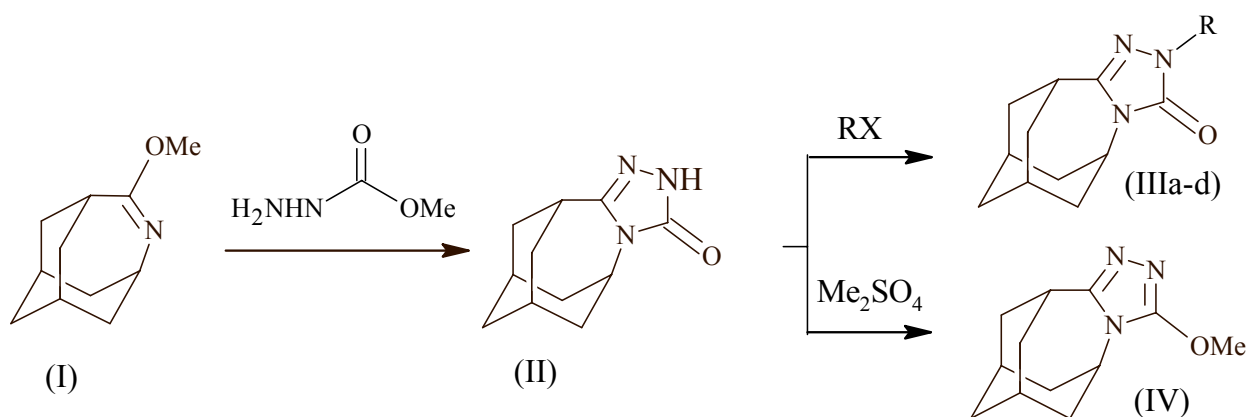
FUNCTIONIALIZATION OF 5-METHOXY-4-AZATRICYCLO[4.3.1.1^{3,8}]UNDEC-4-ENE

E.A. Knyazeva
Yu.N. Klimochkin

Samara State Technical University, Chemical-Technological
Department, Samara, Russia
katerina_knyazev@mail.ru

Some compounds based on 4-azahomoadamantane core show outstanding biological properties such as antiviral and antitumor activity [1]. 5-Methoxy-4-azatricyclo[4.3.1.1^{3,8}]undec-4-ene lets easy to obtain 4-azahomoadamantane annulated with different heterocycles [1, 2].

6,7,8,9,10,11-Hexahydro-5H-5,9:7,11-dimethano[1,2,4]triazolo[4,3-a]azocin -3-one was obtained by reaction of (I) with methyl hydrazinecarboxylate. Alkylation of (II) with soft alkylation agents in presence of K_2CO_3 leads to N-alkyltriazolones (IIIa-d). The preparation of N-adamantyltriazolone (III d) was carried out in conc sulfuric acid with 1-adamantanole. Reaction with dimethyl sulphate as hard alkylation agent leads to O-methyltriazole (IV).



R=Me, X=I (a); R=Bn, X=Cl (b); R=CH₂C₆H₄CF₃, X=Cl (c); R=Ad, X=OH (d).

References:

- [1] V. G. Keizer, J. G. Korsloot, *J. Med. Chem.*, **1971**, 5, 411-415
 [2] E. A. Knyazeva, M. Yu. Skomorohov, Yu. N. Klimochkin, *Chem. Het. Comp.*, **2011**, 11, 1407-1408

O.I. Koifman
C.A. Semeikina
C.A. Syrbu
T.A. Ageeva
A.S. Semeikin

NITRATION OF TETRAARYLPORPHYRINS

Ivanovo State University of Chemistry and Technology, Ivanovo,
Russia
koifman@isuct.ru

Electrophilic substitution reactions to porphyrins represent certain interest as show their aromatic character, relative reactivity of various positions of porphyrin macroheterocycle. This reaction allow to receive porphyrin derivatives inaccessible by another method. We investigated electrophilic nitration of 5,10,15,20-tetraarylporphyrins, having electrodonor substituents in various positions of phenylic rings by various nitrating agents.

In the process of investigations it has been positioned, that nitration goes exclusively in aryl substituents, not mentioning β -positions of porphyrin cycle. Nitrogroup position in phenyl ring is defined by electrodonor substituent present at it. No more than one nitrogroup enters into everyone aryl substituent, and depth of replacement (mono-, di-, three-, tetra-) is defined as donor ability of present group, the applied nitrating agent, its quantity and nitration time. Separation of nitroderivatives of porphyrins is manufactured by a method of column chromatography on alumina.

The received compounds are characterised by data electronic, ^1H NMR, IR- and mass spectroscopy, their cleanliness and individuality is proved by data of preparative layer chromatography.

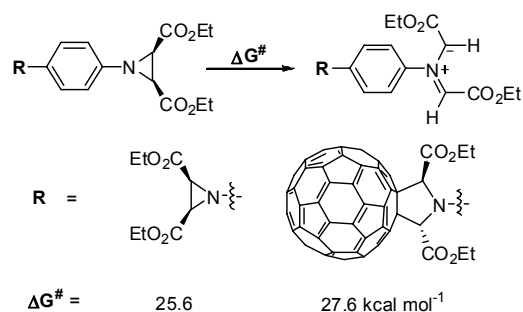
BISAZIRIDINES: EFFICIENT TOOL FOR CONSTRUCTION OF C₆₀-FULLERENE DYADS AND TRIADS

A.S. Konev
A.F. Khlebnikov

Saint-Petersburg State University, Chemistry Department,
 St. Petersburg, Russia
 alxon@rambler.ru

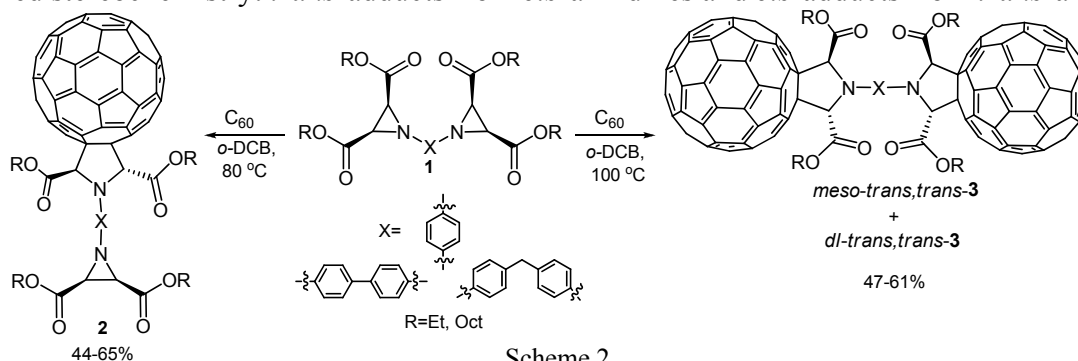
Donor-acceptor dyads containing fullerene C₆₀ core as electron-acceptor unit are broadly investigated for applications in the construction of photovoltaic devices.¹ Dumbbell-like C₆₀-linker-C₆₀ triads have recently received significant attention in molecular electronics applications.^{2,3} One of the most exploited methods to incorporate C₆₀ into organic molecule consists in 1,3-dipolar cycloaddition of azomethine ylides across [6,6]-juncture of the fullerene core, known as Prato reaction.¹ Based on this reaction, we envisage bis-aziridines **1** as convenient building blocks for construction of both fullerene containing dyads and triads.

According to our calculations at DFT B3LYP/6-31G(d) level (ONIOM B3LYP/6-31G(d): B3LYP/STO-3G for fullerene-containing compounds), activation barrier for the ylide formation rises from 25.6 kcal·mol⁻¹ to 27.6 kcal·mol⁻¹ after reaction of one of the aziridine rings with C₆₀ (Scheme 1). This implies that by a careful choice of the reaction temperature it is possible to selectively react either one or both aziridine rings with C₆₀, leading to C₆₀ dyads and triads respectively.



Scheme 1

Indeed, performing the reaction of aziridines **1** with C₆₀ at 80 °C resulted in predominant formation of mono-adducts **2** in 44-65% yield, while increasing the reaction temperature up to 100 °C allowed to obtain bis-adducts **3** in 47-61% yield. The reaction is stereospecific and allows the construction of mono- or bis-fulleropyrrolidines with predefined stereochemistry: *trans*-adducts from *cis*-aziridines and *cis*-adducts from *trans*-aziridines.



References:

- 1) P.A. Troshin, A.S. Peregodov, S.I. Troyanov, and R.N. Lyubovskaya. *Russ. Chem. Bull.* **2008** 57, 887-912.
- 2) C.A. Martin, D. Ding, J.K. Sørensen, T. Bjørnholm, J.M. van Ruitenbeek, H.S.J. van der Zant. *J. Am. Chem. Soc.* **2008**, 130, 13198-13199.
- 3) J.K. Sørensen, J. Fock, A.H. Pedersen, K. Jennum, K. Bechgaard, K. Kilså, V. Geskin, J. Cornil, T. Bjørnholm, M. Brønsted Nielsen. *J. Org. Chem.* **2011**, 76, 245-263.

We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (project 11-03-00186), Council for Grants of the President of Russian Federation (grant no. MK-3112.2010.3), and Federal Grant-in-Aid Program «Human Capital for Science and Education in Innovative Russia» (Governmental Contract no. 16.740.11.0442).

SYNTHESIS AND FLUORESCENCE OF ALKOXYSYLIL DERIVATIVES OF DIBENZOYLMETHANATE OF BORON DIFLUORIDE

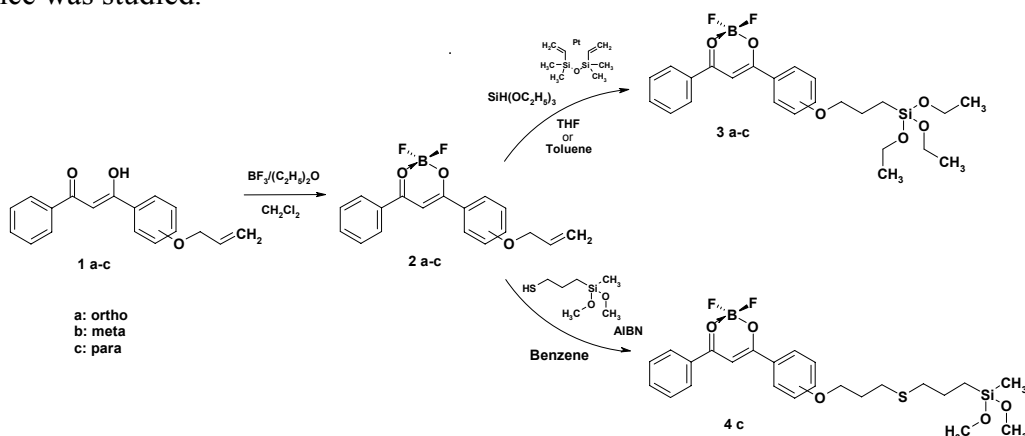
Y.N. Kononevich¹
I.B. Meshkov¹
N.V. Voronina¹
N.M. Surin²
A.M. Muzafarov¹

1 - N.S. Enikolopov Institute of Synthetic Polymer Materials of RAS,
Laboratory of the Synthesis of Organoelement Polymers, Moscow,
Russia

2 - N.S. Enikolopov Institute of Synthetic Polymer Materials of RAS,
Laboratory of Thermostable Plastics, Moscow, Russia
kononevich.yuriy@gmail.com

It is well known, that β -diketonatoboron difluorides possess valuable photophysical and photochemical properties. Thus, these compounds exhibit large extinction coefficients and two-photon absorption cross section, and show intense fluorescence with high quantum yields [1].

In order to immobilize derivatives of dibenzoylmethanate of boron difluoride on polymer matrix alkoxyaryl derivatives of dibenzoylmethanate of boron difluoride were synthesized and their fluorescence was studied.



Compounds **3 a-c** were obtained by the hydrosilylation of O-allylic derivatives **2 a-c** with triethoxysilane in the presence of 1,3 divinyl-1,1,3,3-tetramethyl-disiloxane-platinum(0) in tetrahydrofuran or toluene. Compounds **4 c** were obtained by free radical addition of 3-mercaptopropylmethyl-dimethoxysilane to compound **2 c**. β -Diketonatoboron difluorides **2 a-c** in turn were obtained by the reaction between boron trifluoride/diethyl ether and the corresponding 1,3-diketones **1 a-c** in dichloromethane at room temperature.

Fluorescence of β -diketonatoboron difluorides **3 a-c** were investigated in tetrahydrofuran solutions. Absorption and emission spectra for the **3 a-c** shown on fig. 1. Quantum yields for **3 c** (83%) are higher than for **3 a** (24%) and **3 b** (23%) under similar conditions. Structure of synthesized compounds was confirmed by ¹H, ¹³C, ¹⁹F, ²⁹Si NMR, IR and mass-spectra (ESI) methods.

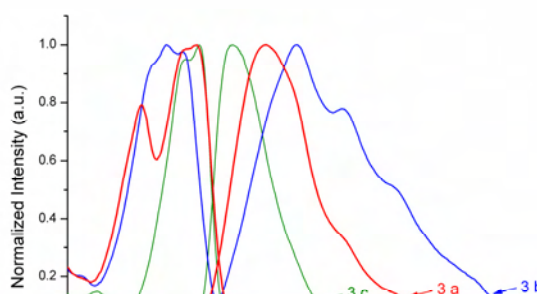


Fig. 1 Absorption and fluorescence emission spectrum **3 a-c** in THF

References:

[1] E. Cogne-Laage, J.-F. Allemand, O. Ruel, et. al. *Chem.- Eur. J.*, **2004**, *10*, 1445–1455.

This work was supported by the Russian Ministry for Science and Education (contract no. 02.527.11.0009).

A SYNTHETIC APPROACH TO SULFUR-CONTAINING DERIVATIVES OF 3-PYRROLIN-2-ONE

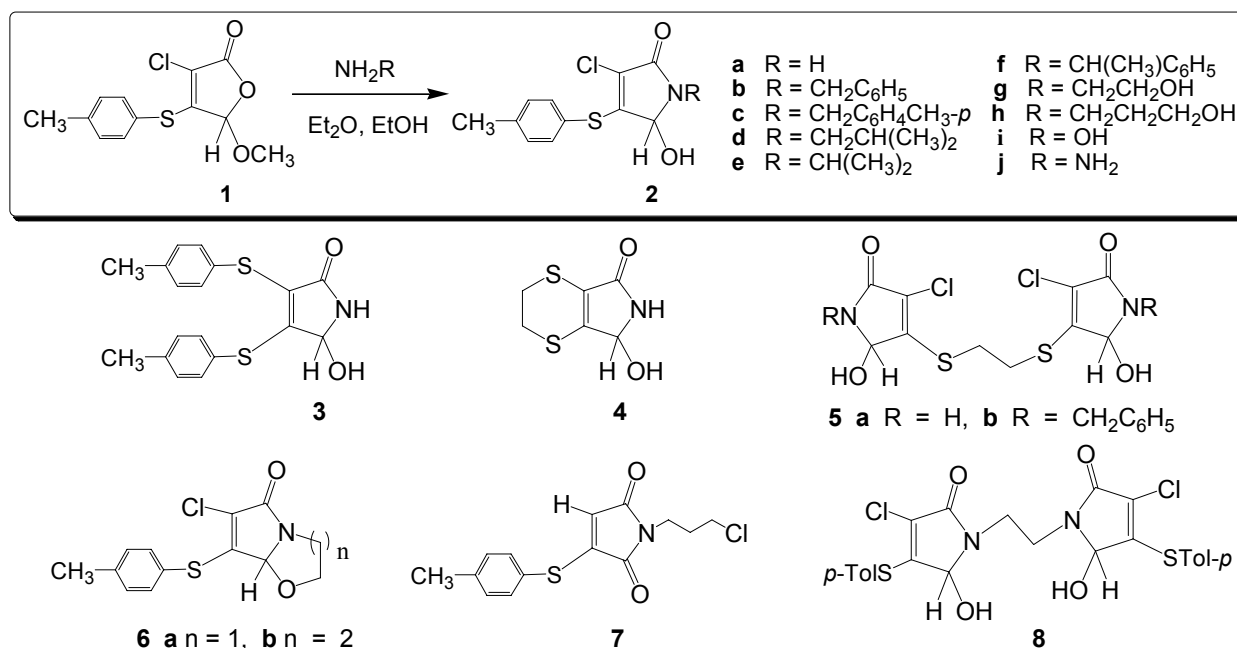
L.S. Kosolapova¹
 M.F. Valiev¹
 A.R. Kurbangalieva¹
 O.A. Lodochnikova²
 E.A. Berdnikov¹
 G.A. Chmutova¹

1 - A.M. Butlerov Chemical Institute at Kazan Federal University, Kazan, Russia

2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia

Almira.Kurbangalieva@ksu.ru

A convenient and efficient approach to the synthesis of various sulfur-containing derivatives of 5-hydroxy-3-pyrrolin-2-one **2-8** was developed via reactions of corresponding thioethers of 5-alkoxy-2(5*H*)-furanones **1** with different nitrogen-containing mono- and binucleophilic reagents. *Bis*-thioethers with -SCH₂CH₂S- chain, connecting two lactam units **5** were obtained from the reaction of corresponding 5-methoxyderivatives of 2(5*H*)-furanone with ammonia and benzylamine. Products of the reactions with aminoalcohols **2g**, **2h** under acidic conditions undergo an intramolecular dehydration to give novel fused bicyclic compounds **6**. The utilization of *N,N*-binucleophilic reagents in amination reactions allowed us to obtain novel heterocyclic compounds of different structural types, e.g. *bis*-pyrrolinone **8** that combines -CH₂CH₂- moiety and two lactam fragments bridged through their nitrogen atoms. Novel compounds of the 3-pyrrolin-2-one series have been characterized in detail by NMR spectroscopy and single crystal X-ray diffraction.



The financial support from the Ministry of Science and Education of Russian Federation within FTP "Scientific and scientific-pedagogical personnel of the innovative Russia" (Governmental Contract No 14.740.11.1040) is gratefully acknowledged.

SYNTHESIS AND PROPERTIES OF COMPOUNDS ON THE BASIS OF 5-ARYL-3-ARYLIMINO-3H-FURAN-2-ONES

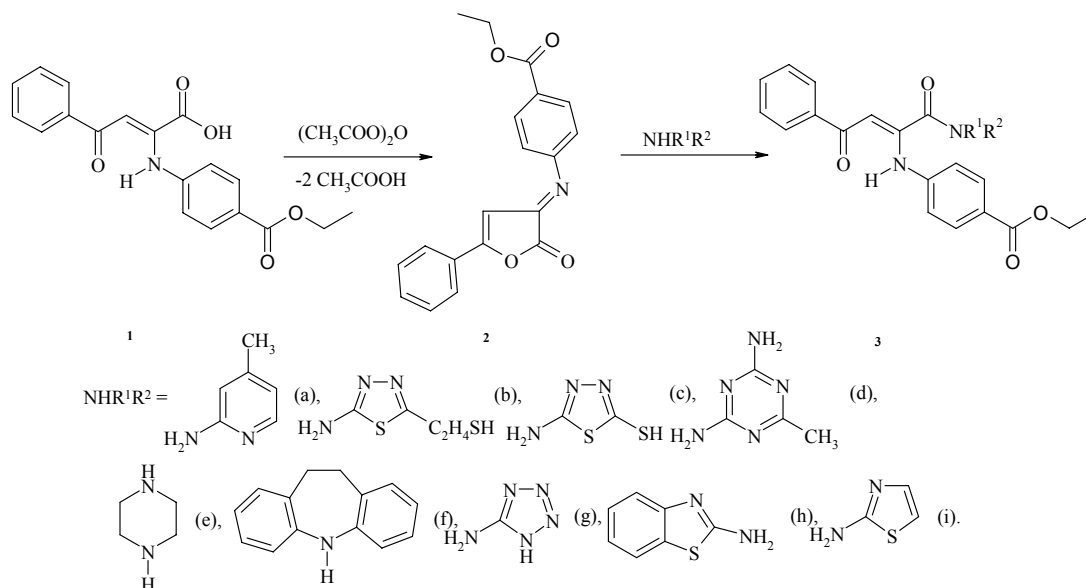
V.J. Kozhukhar¹
N.A. Pulina¹
A.E. Rubtsov²

1 - Perm State Pharmaceutical Academy, Perm, Russia
2 - Perm State University, Perm, Russia
slavaperm@inbox.ru

One of the fundamental problems of preparative organic chemistry is the synthesis of new compounds that have a practical application as biologically active compounds or building blocks for the construction of new compounds. For this purpose, there is a significant interest in 5-aryl-3-arylino-3H-furan-2-ones. Analysis of published data demonstrates that iminofuranones represent a promising class of furan derivatives, as their structure determines rich synthetic possibilities.

Initially, (Z)-2-((4-(ethoxycarbonyl)phenyl)amino)-4-oxo-4-phenylbut-2-enoic acid (1) was obtained by the known method [1]. On the 2nd stage it was converted into (E)-3-((4-(1-ethoxycarbonyl)phenyl)imino)-5-phenylfuran-2(3H)-one (2) under the action of acetic anhydride.

Heterylamides of N-substituted 2-amino-4-aryl-4-oxobut-2-enoate acids (3) were obtained by interaction of iminofuranones (2) with a number of heteryl amines:



The structure of iminofuranone 2 and decyclized derivatives 3a-i proved by IR, ¹H NMR spectroscopy, mass spectrometry and is in good agreement with published data for related structures.

References:

1. Zalesov, V.V. Synthesis, structure and chemical properties of N-substituted 2(3)-amino-2,3-dihydrofuran-3(2)-ones (review) / V.V. Zalesov, A.E. Rubtsov // Chemistry of Heterocyclic Compounds.- 2004.- №2.- Pp. 163-186.

This work is supported by RFBR (project № 11-03-00882).

REACTIVITY OF FLUORENES IN THE REACTION OF CYANINE CONDENSATION

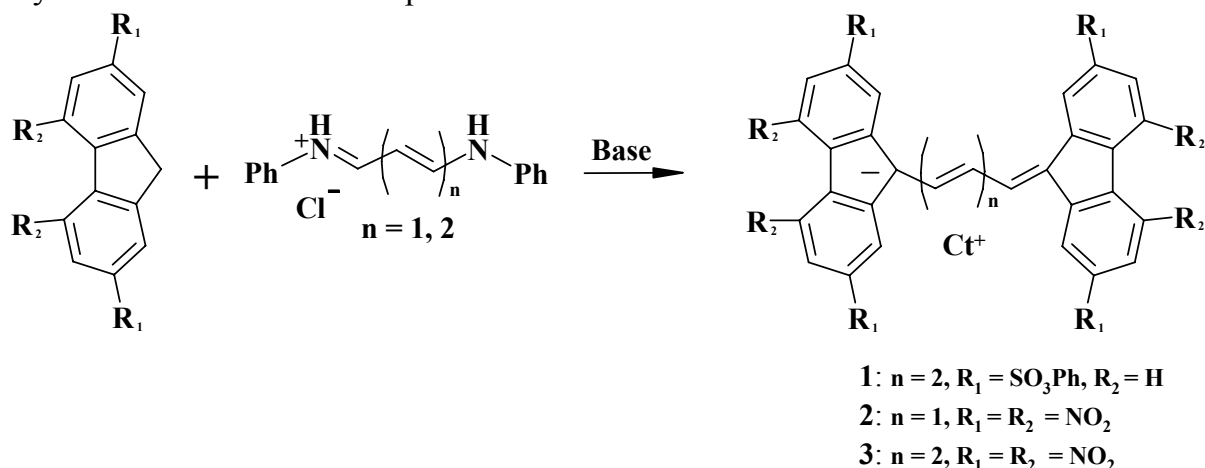
I.V. Kurdyukova¹
N.A. Derevyanko¹
A.A. Ishchenko¹
D.D. Mysyk²

1 - Institute of Organic Chemistry National Academy of Sciences of Ukraine, Colour and Structure of Organic Compounds Department, Kiev, Ukraine
 2 - Donetsk National Technical University, Physical and Organic Chemistry Department, Donetsk, Ukraine
Iryna_Kurdiukova@ukr.net

Fluorene has extended π -system, high electronic symmetry, and the methylene group potentially capable, due to conjugation with two benzene nuclei, to be active in the reaction of cyanine condensation. Therefore, the carbocyclic fluorene core is a promising terminal group of polymethine dyes. However, unsubstituted fluorene does not enter into this reaction even in the presence of such strong organic bases as sodium ethoxide, potassium tert-butoxide, DBU and "proton sponge" (N,N,N',N'-tetramethylnaphthalene-1,8-diamine).

DFT//B3LYP/6-31G(d,p) quantum chemical calculations of fluorene anion showed that the electron density increases on excitation mainly in the positions 2, 4, 5 and 7. Therefore, the acceptor substituents in these positions will have the largest influence on the dye colour. The fluorene acidity and the methylene group activity in the cyanine condensation increases with such substitution.

Really, even acceptors of medium strength in the positions 2 and 7 (see scheme) allowed to carry out the condensation in the presence of DBU. 2,7-Dinitrofluorene also reacts when DBU is used as a condensing agent. And only with 2,4,5,7-tetranitrofluorene the cyanine condensation takes place under its standard conditions.



A novel deeply coloured anionic polymethine dyes **1-3** containing only carbocycles as terminal groups have been synthesized by this method.

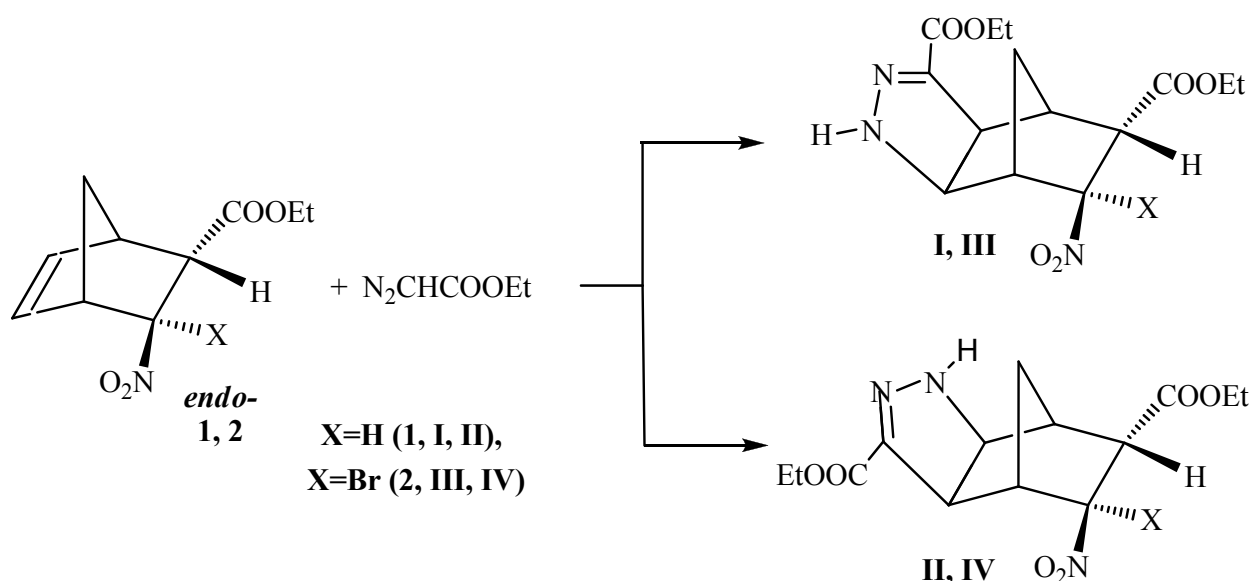
NITRONORBORNENE DERIVATIVES IN THE REACTION OF 1,3-DIPOLAR CYCLOADDITION ETHYL DIAZOACETATE

A.A. Kuzhaeva¹
N.A. Anisimova²

1 - St. Petersburg State Mining University, St. Petersburg, Russia
2 - Saint-Petersburg State Technological University of Plant
Polymers, St. Petersburg, Russia
kaarlo@mail.ru

It is known that the C = C bond of bicycle bridge compounds can initiate polymerization and addition reactions, keeping bicycle skeleton. This property of unsaturated alicycle used to produce a polymer frame and fused carbo- and heterocyclic systems with perspective properties.

We are the first investigators who have studied the interaction between *endo*-nitronorbornenes (**1**, **2**) with ethyl diazoacetate. The reaction of norbornene (**1**) with alkyldiazoacetate proceeded at room temperature, while the geminal bromnitronorbornene (**2**) with the noticed diazo- compound reacted in the severe condition (80 °C, C₆H₆, 3 hours). In both cases, the process was ended with the formation of a complex mixture of products, from those by the column chromatography isolated regioisomeric adducts of 1,3-dipolar cycloaddition of (**I-IV**).



The structure of the resulting adducts (**I-IV**) is evaluated using IR and ¹H NMR spectroscopy.

SYNTHESIS AND STRUCTURE OF A NOVEL 2(5H)-FURANONE BASED SULFONES AND SULFOXIDES

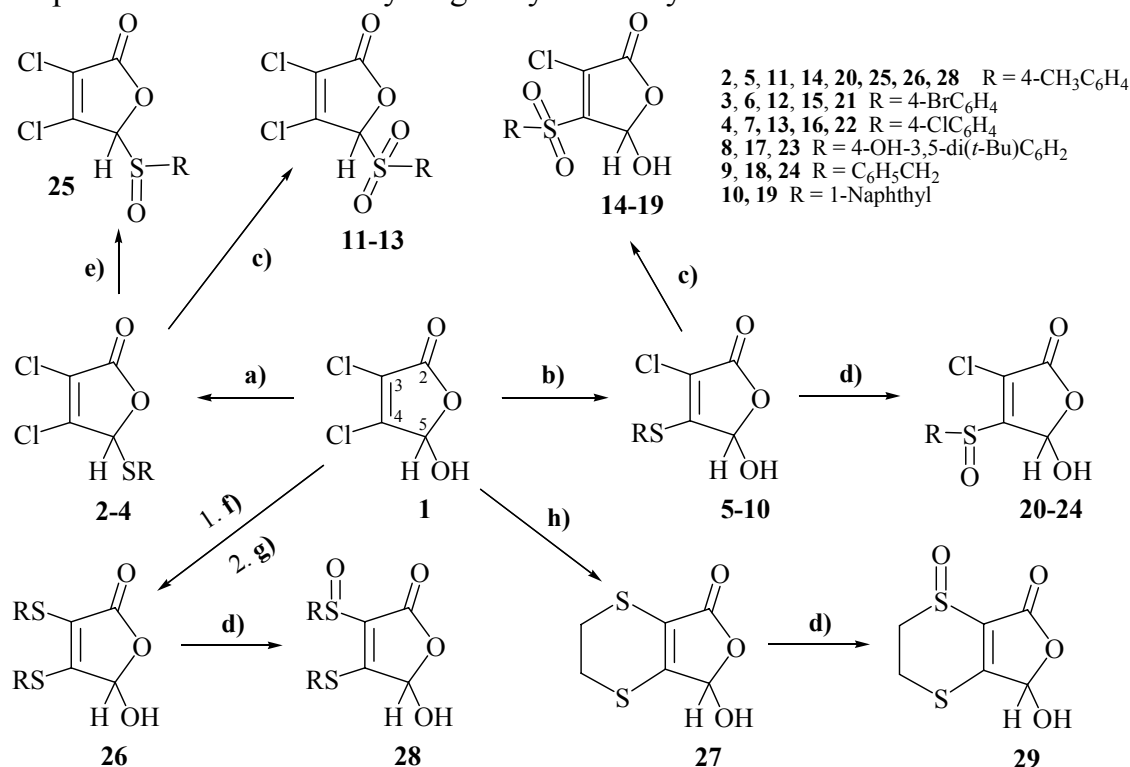
L.Z. Latypova¹
A.R. Kurbangalieva¹
E.Sh. Saigitbatalova¹
O.A. Lodochnikova²
E.A. Berdnikov¹
G.A. Chmutova¹

1 - A.M. Butlerov Chemical Institute at Kazan Federal University, Kazan, Russia

2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia

Almira.Kurbangalieva@ksu.ru

The 2(5H)-furanone subunit is found in several bioactive natural products and a number of drugs with diverse biological activities. A variety of thioethers of the 2(5H)-furanone series **2-10** obtained from mucochloric acid **1** were selectively oxidized to their corresponding sulfones **11-19** or sulfoxides **20-25** in good yields. The reaction of 3,4-dithiosubstituted derivatives **26** and **27** with *m*-chloroperbenzoic acid provides a method to functionalise selectively the sulfur atom bonded to carbon atom C³ of the lactone ring, leading to novel monosulfoxides **28** and **29**. The molecular and crystal structure of several oxidation products were studied by single crystal X-ray diffraction.



(a) RSH (1 eq.), conc. H₂SO₄ (10 mol %), C₆H₆, 3 h, t^o; (b) RSH (1 eq.), Et₃N (1 eq.), Et₂O, 2 h, r.t.; (c) H₂O₂ (excess), CH₃COOH, r.t.; (d) 3-ClC₆H₄CO₃H (1.2 eq.), Et₂O, -12°C; (e) Oxone (1.2 eq.), Me₂O, H₂O, 1.5 h, r.t.; (f) RSH (3.4 eq.), KOH (4.1 eq.), H₂O; (g) HCl; (h) HSCH₂CH₂SH (1 eq.), Et₃N (1 eq.), Me₂CO, 6 h, t^o.

The financial support from the Ministry of Science and Education of Russian Federation within FTP "Scientific and scientific-pedagogical personnel of the innovative Russia" (Governmental Contract No 14.740.11.1040) is gratefully acknowledged.

N.Yu. Lisovenko
A.A. Merkushev
V.N. Krivonogich
E.A. Romanova
Yu.A. Simonova

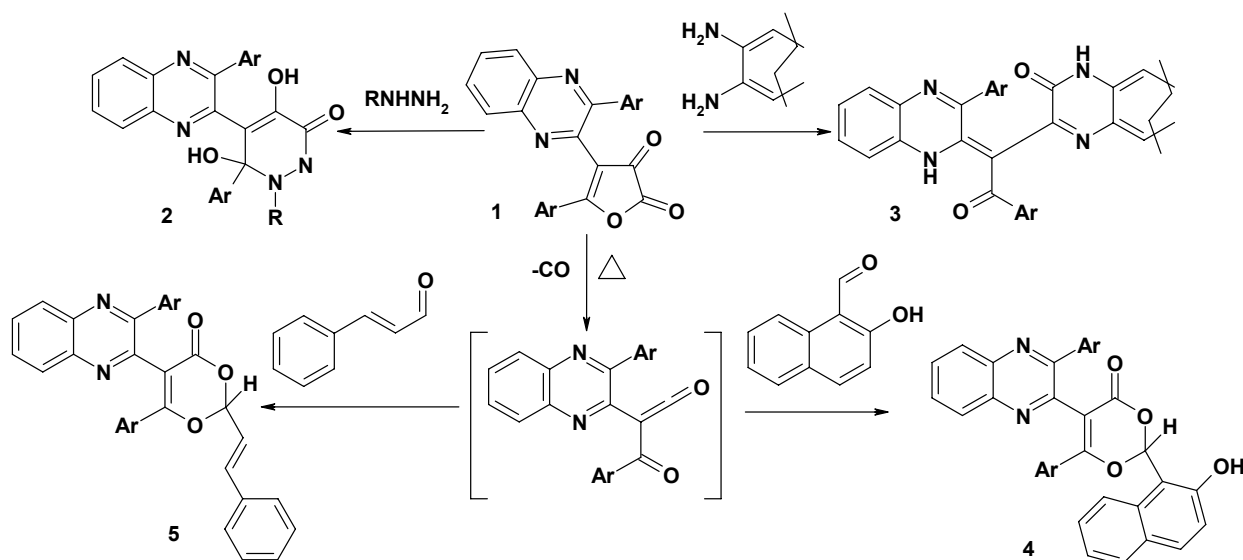
NEW HETEROCYCLIC SYSTEMS ON A BASIS 5-ARYL-4-QUINOXALINYLFURAN-2,3-DIONES

Perm State University, Perm, Russia
lisovn@mail.ru

5-Aryl-4-hetarylfuran-2,3-diones are accessible and convenient subjects for the creation of various acyclic and heterocyclic structures [1].

We established that 5-aryl-4-quinoxalinylfuran-2,3-diones **1** undergo recyclization under the influence bi-NH-nucleophiles to the substituted pyridazin-3-ones **2** or substituted quinoxalinones **3**.

Thermolysis of 5-aryl-4-quinoxalinylfuran-2,3-diones in the presence of the aldehydes contains several of reactivity centers in their molecules, as a result in one of a possible product substituted dioxin-4-ones **4,5**.



References:

1. Nekrasov D.D., Maslivets A.N., Lisovenko N.Yu., Zalesov V.V., Pulina N.A., Rubtsov A.E. / Five-Membered Heterocycles with Vicinal Oxo Groups. Perm: Perm. Univ., 2004, p. 183

SYNTHESIS AND TRANSFORMATIONS OF POLYBROMOCONTAINING SPIROBICYCLIC ISOXAZOLES

A.M. Maharramov¹
G.Kh. Veliyeva²
A.M. Mustafayev³
S.N. Javadova³

1 - Baku State University, Baku, Azerbaijan

2 - Institute of Polymer Materials of Azerbaijan National Academy of Sciences, Sumgayit, Azerbaijan

3 - Sumgayit State University, Sumgayit, Azerbaijan
 vgulya@mail.ru

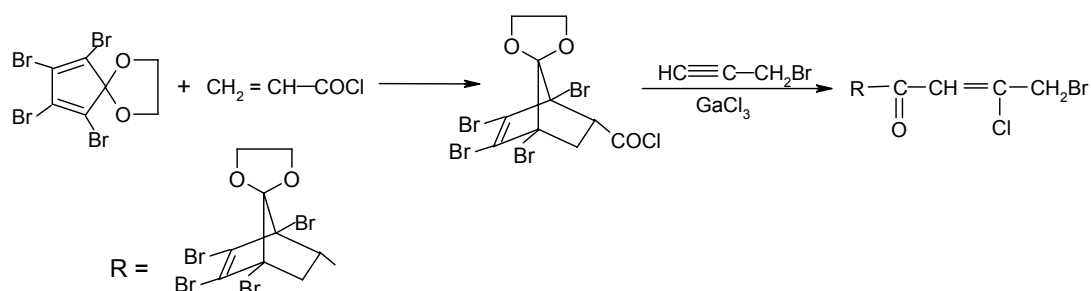
One of the most actual problems of synthetic organic chemistry is the elaboration of synthetic method of new heterocyclic compounds with high-performance biologically active properties.

In continuation of our systematic investigations in this paper were presented the results of the synthesis and investigations of new polybromocontaining spirobicyclic isoxazoles.

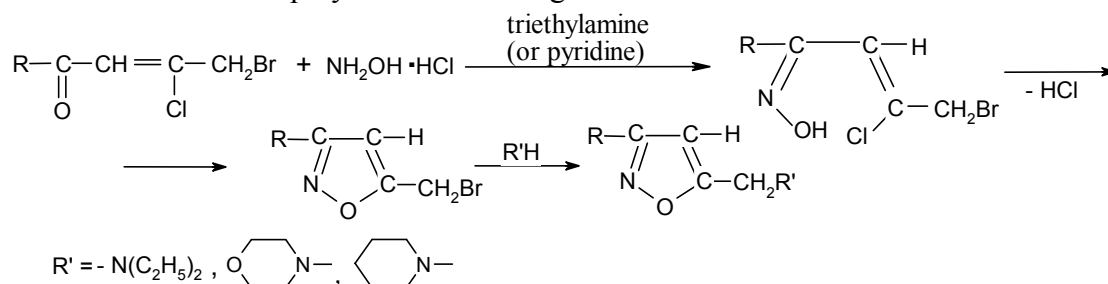
The chloranhydrides of polybromonorbonenic acid were obtained from the reaction of 5,5-ethylenedioxy-1,2,3,3-tetrabromo-1,3-cyclopentadiene with chloranhydride of acrylic acid.

Next by interaction between propargyle bromide in presence of GaCl₃ was synthesized the corresponding dihalogencontained unsaturated ketone of bicyclic structure. Also it has been established that synthesized bicyclic unsaturated ketone easily reacted with muriatic hydroxylamine.

As a result the isoxazole derivative with bicyclic fragments in molecule was formed on scheme:



At first the muriatic hydroxylamine associated to the ketone group. Then it undergone to cyclization and obtained the polybromocontaining isoxazole.



By interaction of diethylamine, morpholine and piperidine with the synthesized polybromocontaining spirobicyclic isoxazole have been obtained its corresponding derivatives. Also the optimal conditions of synthesis and biology activity of the synthesized isoxazoles have been determined. The structure of the synthesized compounds has been confirmed by IR-, ¹H and ¹³C NMR-spectroscopy, but purity and composition by TLC and elemental analysis.

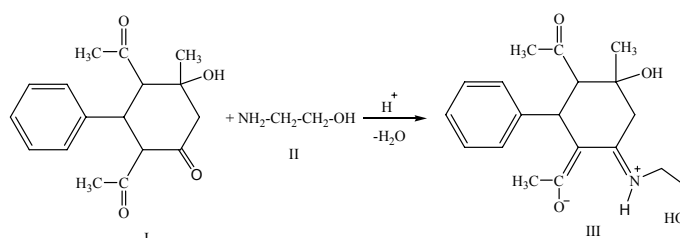
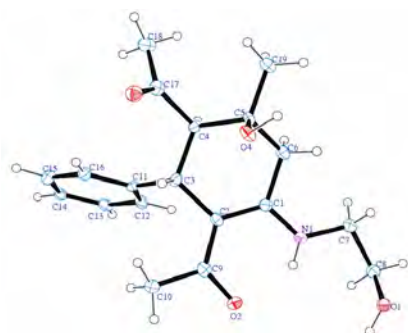
ACID CATALYSIS IN THE REACTION OF DIACETYL SUBSTITUTED HYDROXYCYCLOHEXANONE WITH MONOETHANOL AMINE

A.M. Maharramov
A.I. Ismiyev

Baku State University, Baku, Azerbaijan
vgulya@mail.ru

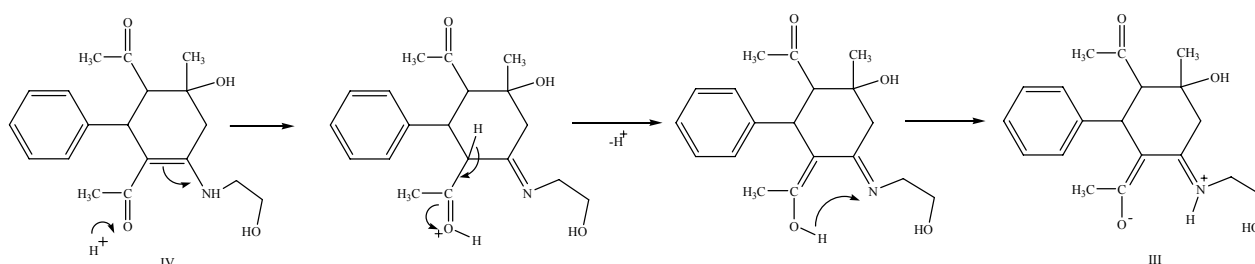
At the interaction of dicarbonyl substituted hydroxycyclohexanones with nitric nucleophiles the mineral acids catalyze the amine condensation by alicycles carbonyl groups and provides also a dehydration in cyclohexanes ring [1].

In the present work the new reaction of 2,4-diacetyl-5-hydroxy-5-methyl-3-phenylcyclohexanone (I) with monoethanol amine (II) in the presence of H_2SO_4 has been investigated. Structure of the obtained compound (III) (yield 63 %) has been determined by X-ray structure analysis.



Molecular crystal structure of synthesized compound III

Since the lack of H_2SO_4 the enamine (IV) is the product of this reaction, the formation of the compound (III) could be explained by future prototropic enamine transformations as the following:



A.M. Maharramov
A.I. Ismiyev
M.A. Allakhverdiyev
Sh.I. Nazarov

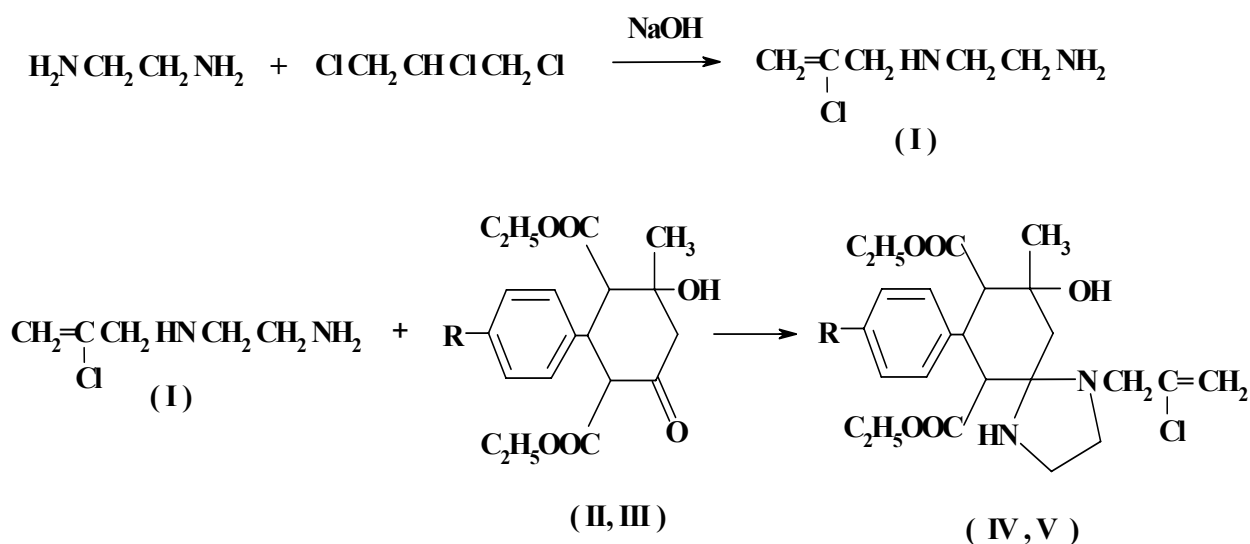
SYNTHESIS OF NEW DIAZOSPIROCYCLIC SKELETON CONTAINING COMPOUNDS

Baku State University, Baku, Azerbaijan
vgulya@mail.ru

By now chemistry of polycarbonyl substituted cyclohexanolones and particularly their reactions with nucleophylic reagents has been widely studied [1]. Unstudied or by-way of learning are the questions of constructions on their basis spirocyclic systems and also their interactions with diamines.

We assumed that N-R-ethylene diamines have the positive synthetic perspectives in direction of spirocycles synthesis if they have been used as initial compounds in the reactions with 4-hydroxy-6-oxocyclohexan-1,3- dicarboxylates.

In present work has been found that N(2-chlorprop-2-en-1-yl) ethylenediamine (I) in soft conditions easy subjected to cyclization with cyclohexanolones (II,III) and brings to obtaining unknown compounds (IV,V) containing diazospirocyclic skeleton.



Structure of the obtained compound (IV,V) has been confirmed by IR-, NMR- and X-ray structure analysis.

References:

1. V.L. Gein, N.V. Nosova, K.D. Potemkin, Z.G. Aliev, A.P. Krivenko *Russ. J. Org Chem.*, **2005**, 45, 1039.

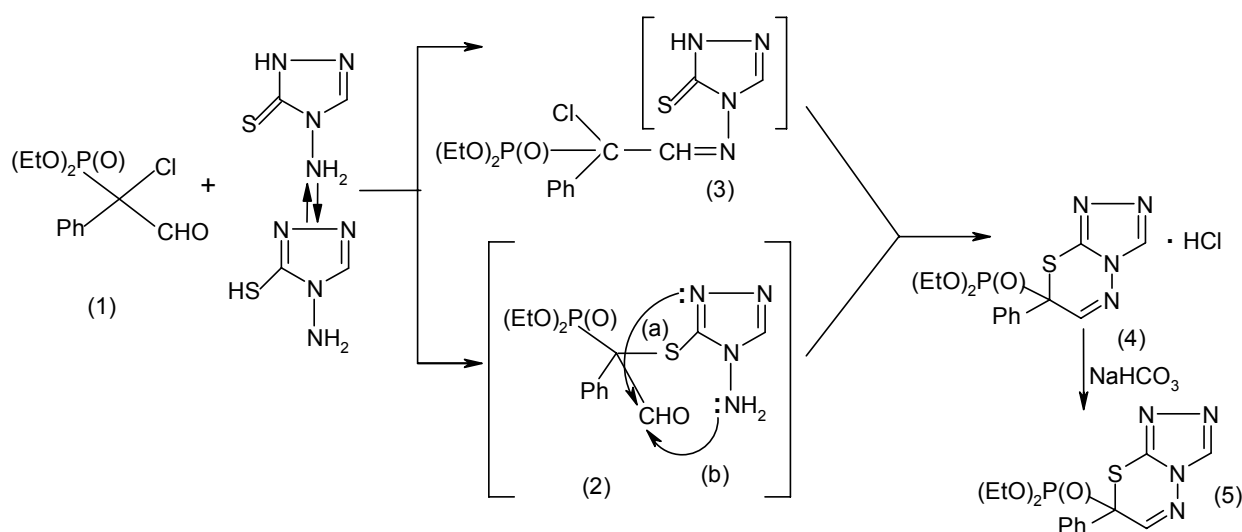
PHOSPHORYLATED α -PHENYL- α -CHLOROACETALDEHYDE IN REACTION WITH 4-AMINO-1,2,4-TRIAZOLE-5-THIONE

Kh.A. Asadov¹
 R.N. Burangulova²
 G.Kh. Veliyeva¹
 F.I. Guseynov²
 A.M. Maharramov¹

1-Baku State University, Baku, Azerbaijan
 2-Kazan State Technological University, Kazan, Russia
 vgulya@mail.ru

Aminotriazoles – are highly active bifunctional monomers, building blocks and semi-products for new organic compounds. The combination in one molecule a few nitrogen atoms, a fundamentally different on nucleophilic ability and reactivity, creates almost unlimited opportunities for using these compounds in fine organic synthesis.

In this paper, we investigated the condensation of phosphorylated α -chloro-aldehyde (1) with 4-amino-1,2,4-triazole-5-thione, in which the thiourea fragment is responsible for the formation of the five-membered heterocyclic systems, was blocked in such a way that after the first stage the obtained intermediate (2) can not be stabilized as a result of nucleophilic attack of nitrogen on the carbonyl carbon atom (path a) failing the proton at the attacked nitrogen atom. At the same time the stabilization through the intramolecular Schiff's reaction with participation of amine group (path b) has been possible, more so that the presence the HCl in the reaction mass in the salt form should accelerate this reaction.



We also can't excluded the possibility of the formation of thiadiazine through an intermediate α -chlorothiosemicarbon (3), which was easily undergo to intramolecular nucleophilic substitution, can produced a final product (5) – 6-diethoxyphosphoryl-6-phenyl-1,2,4-thiazolo[3,4-b]-1,3,4-thiaziazine.

The structure of the synthesized compounds has been proved by IR, ^1H , ^{13}C , ^{31}P NMR and mass-spectroscopy, but the composition has been confirmed by elemental analysis.

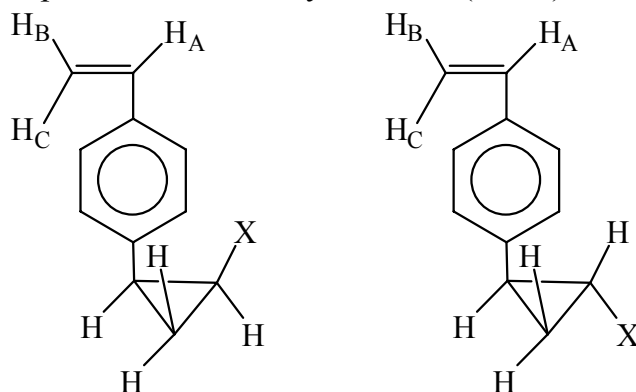
STEREISOMER 2-SUBSTITUTED CYCLOPROPYLSTYRENES

S.B. Mamedli
K.G. Guliyev
A.M. Guliyev

Institute of Polymer Materials of Azerbaijan National Academy of
Sciences, Sumgait, Azerbaijan
ipoma@science.az

Hydrocarbons of a series of phenylcyclopropane due to specific properties of three-membered cycle are of large interest, their activity, mainly, depends on structure of these compounds.

For study of this question we have synthesized a number of stereoisomer trans- and cis-2-ethoxycarbinol- (I), 2-carboxy- (II) 2-hydroxymethylparacyclo-propylstyrenes. These compounds have been prepared as a result of condensation of divinylbenzene with ethyldiazoacetate with the subsequent isolation of stereoisomers from methanol solution by the method of low-temperature crystallization. It has been established that in all synthesized compounds trans-isomers prevail considerably over cis- (70:30)



X = –CO₂Et (I), –COOH (II), CH₂OH (III)

It has been revealed at analysis of the IR-spectra of stereoisomer trans- and cis-isomers of compounds I-III that there are a number of absorption bands characteristic only for trans- or cis-isomers independently of type of substituent in them. Some of these absorption bands with various intensity are simultaneously appeared in the spectrum of both isomers.

According to the data of the PMR-spectra a substitution of electron-donor substituents for electron-acceptor ones leads to a change of chemical shift of H_B-proton of vinyl group, the chemical shifts of the protons of H_A, H_B, H_C are appeared in more weak field in comparison with such ones in styrene.

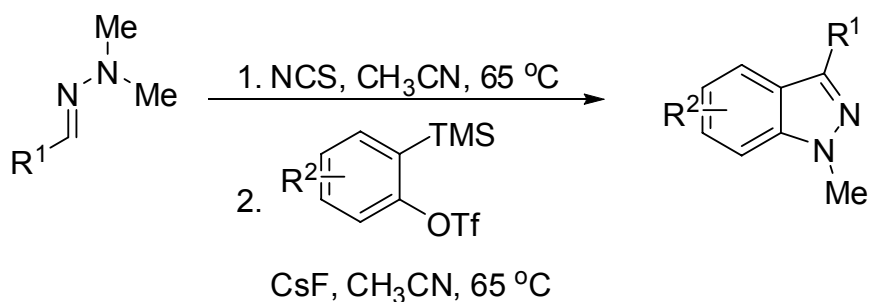
It has been shown that the resonance signals of the protons of vinyl group in stereoisomers are differed. It has been determined that the protons of H_A, H_B, H_C in trans-isomers are shifted to more weak field in comparison with the protons of cis-isomers. This fact is explained by the configuration structure of isomer compounds and electron influence of substituent through cyclopropane ring on vinyl group.

**ONE-POT SYNTHESIS OF 1-ALKYLINDAZOLES
FROM *N,N*-DIALKYLHYDRAZONES, NCS, AND
ARYNES**

N.A. Markina
A.V. Dubrovskiy
R.C. Larock

Iowa State University, Department of Chemistry, Ames, IA, USA
nataliya.markina@gmail.com

Indazoles represent an important class of heterocyclic compounds widely used in the pharmaceutical industry. A novel one-pot approach to 1-alkylindazoles has recently been discovered, which involves the NCS chlorination of *N,N*-dialkylhydrazones, followed by reaction with commercially available *o*-(trimethylsilyl)aryl triflates and CsF. The scope, possible applications of this methodology, and the mechanism of this process will be discussed.



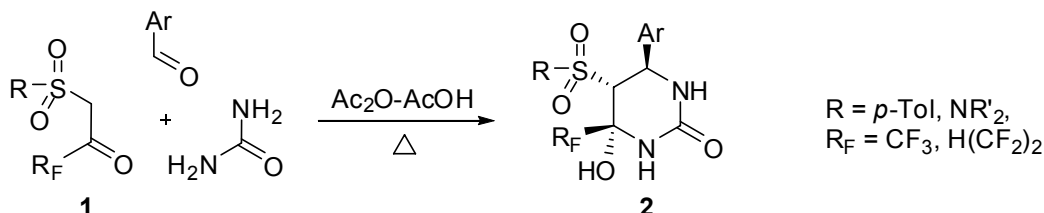
FIRST OBSERVATION OF “RETRO-BIGINELLI” REACTION FOR 5-SULFONYL TETRAHYDROPYRIMIDINONES

Yu.N. Markitanov
V.M. Timoshenko
Yu.G. Shermolovich

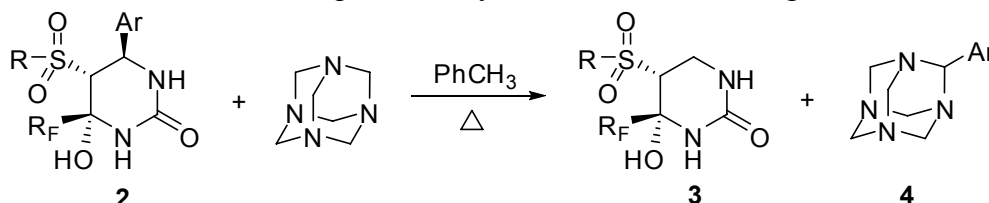
Institute of Organic Chemistry, NAS of Ukraine, Kiev, Ukraine
markitanov@ioch.kiev.ua

The Biginelli reaction belongs to the most widely utilized preparative methods to obtain pyrimidine derivatives, important class of heterocycles in the field of drug discovery. Biginelli condensation has been extensively investigated and various combinations of structurally diverse substrates have been used, including fluorine-containing β -dicarbonyl compounds.

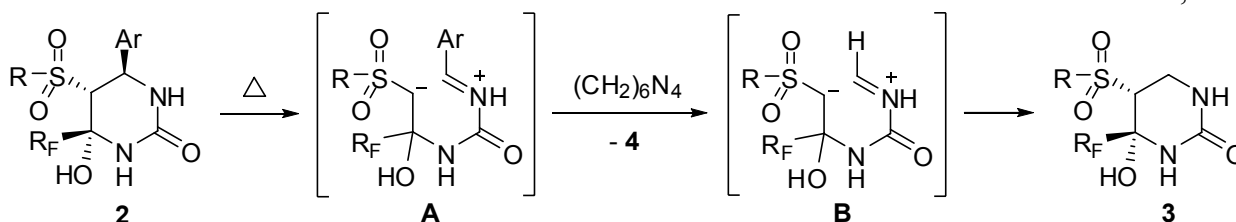
We have demonstrated that 1,1-dihydro-2-oxo-2-fluoroalkyl-sulfones and -sulfamides **1** as methylene components also react with aryl aldehydes and urea under the Biginelli reaction conditions furnishing fluoroalkyl tetrahydropyrimidinones (THPM's) **2** with sulfonyl moiety.



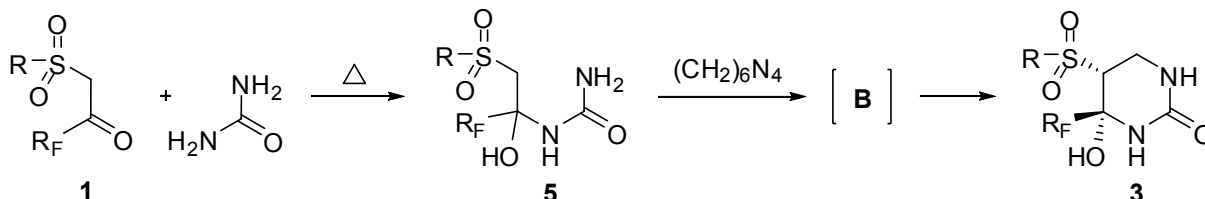
When examining the chemical properties of the pyrimidinones **2** we have revealed the unprecedented reaction with hexamethylenetetramine (HMTA). Heating **2** with HMTA in toluene yielded pyrimidinones **3**, lacking aryl substituent at the heterocyclic framework. The described reaction can be formally considered as replacement of aryl group in **2** on the hydrogen atom donated by HMTA. Thus the overall process may be named as “retro-Biginelli” reaction.



We assume that the reaction outcome is attributed to the formation of intermediates **A**, **B**:



In order to support this hypothesis the adduct **5** ($R = p\text{-Tol}$, $R_F = \text{CF}_3$) was synthesized. The latter reacted with HMTA to give pyrimidinone **3** ($R = p\text{-Tol}$, $R_F = \text{CF}_3$).



Stereochemistry of the compounds **2** and **3** ($R = p\text{-Tol}$, $R_F = \text{CF}_3$, $\text{Ar} = \text{Ph}$) was established by the single crystal X-ray analysis.

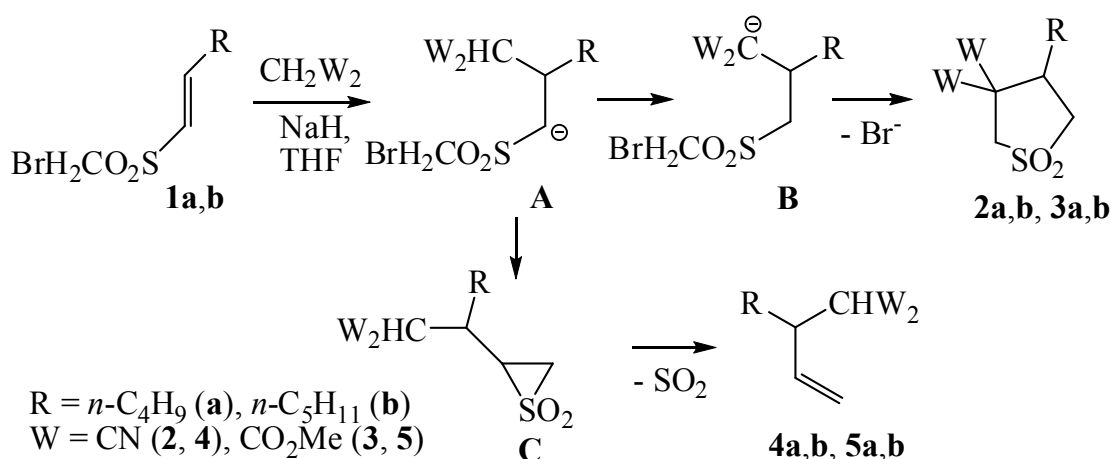
ABOUT PRODUCTS OF THE MICHAEL INDUCED ADDITION REACTION OF BROMMETHYL 1-ALKENYL SULFONES WITH MALONIC ACID DERIVATIVES

Yu.Yu. Masterova
I.Yu. Bolusheva
V.A. Vasin

Mordovian State University, Department of Chemistry, Saransk,
 Russia
 orgchem@mrsu.ru

As we have stated earlier, brommethyl (*E*)- β -styryl sulfone upon interaction with the «hard» base–nucleophile – sodium methylate, undergoes a Michael induced Ramberg–Bäcklund (MIRB) addition reaction with the formation of olefinic compound and upon interaction with the «soft» bases–nucleophiles – sodium enolates prepared from dimethyl malonate, malononitrile and methyl acetoacetate, give products of the Michael induced ring closure reaction – tetrahydrothiophene-S,S-dioxide derivatives. In contrast to brommethyl (*E*)- β -styryl sulfones acyclic and cyclic brommethyl sulfones containing the labile H atoms in the γ -position to sulfonyl group if treated with the «hard» bases–nucleophiles – alkali metals alcoholates, form the products of a vinylogous Ramberg–Bäcklund reaction – conjugated dienes.

We have found that brommethyl alkenyl sulfones **1a,b** upon interaction with the sodium enolates prepared from dimethyl malonate and malononitrile give tetrahydrothiophene-S,S-dioxide derivatives **2a,b**, **3a,b** as the main products. Simultaneously, allylmalonic acid derivatives **4a,b**, **5a,b** are obtained in the amount 10 – 20 % in the cases of the malonate and malononitrile, respectively, as a result of the competitive MIRB addition reaction.



Seemingly, the products ratio is determined by the relative reaction rates of the isomerization of initially formed carbanion **A** into more stable carbanion **B** and its transformation into episulfone **C**.

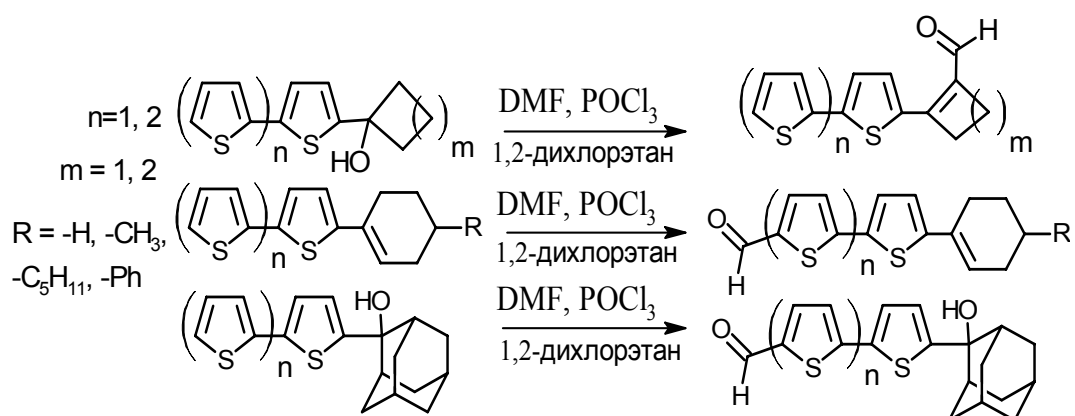
CYCLOALKYL- AND HETEROCYCLOALKYL-2,2'-BITHIOPHENES IN THE VILSMEIER-HAACK REACTION

V.V. Meshkovaya
A.V. Yudashkin

Samara State Technical University, Department of Organic Chemistry,
Samara, Russia
ayudashkin@mail.ru

Derivatives of 2,2'-bithiophenes have fluorescent and semiconducting properties.¹ Grignard reaction of 2-thienyl- and 5-bithienyl-2,2'-magnesium bromides with cyclobutanone and cyclopentanone leads to the formation of stable tertiary alcohols (1,2). However reaction with cyclohexanones, accompanied by water elimination at decomposition of magnesium alkoxides, leads to corresponding cycloalkenyl derivatives (3-6).

Tertiary alcohols (1) and (2) in the reaction with POCl₃-DMF mixture are dehydrated to cycloolefins, which formed corresponding α,β -unsaturated aldehydes (8,9). At the same time formylation of cyclohexenyl-2,2'-bithiophenes (3,4) passes into 2''-position (13,14), but also into 5' position (10-12) of heterocycle unit. In the case of heteroalicyclic compounds (6,7) formylation passes only into 2,2'-bithiophene moiety (15,16).



The research work focused on the development of new organic luminophores allowed us to convert the aldehyde group into carbonitrile and dicyanoethylene moieties. The obtained compounds (1-16) have luminescence properties in the wavelength range from 400 to 550 nm with quantum yield up to 0,5.

References:

1. Herbivo C. et all. Tetrahedron, 2009, 65, 2079-2086.

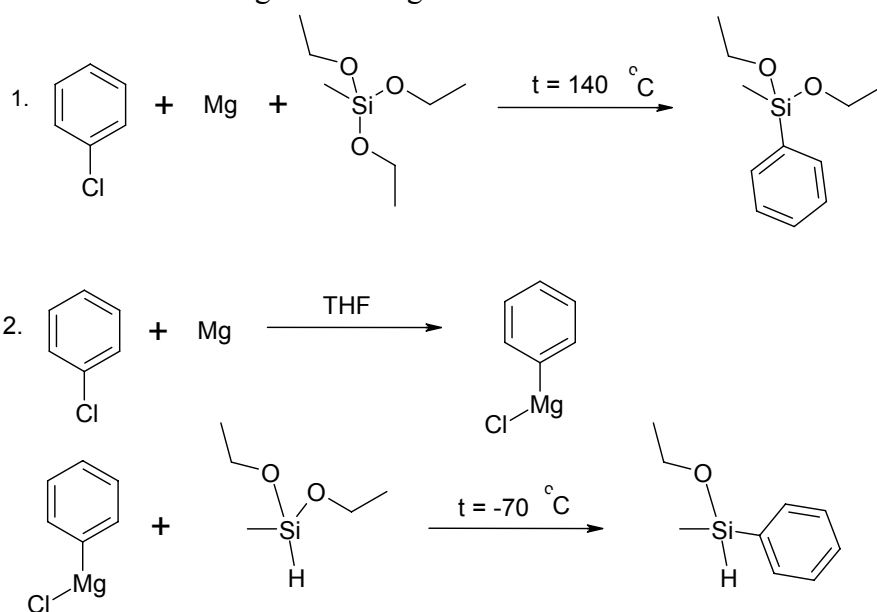
SYNTHESIS OF ALKYL-, ARYL- ALKOXYSILANES IN ETHER MEDIUM AND WITHOUT ETHER

S.A. Milenin
N.A. Sheremetyeva
A.M. Musafarov

Enikolopov Institute of Synthetic Polymer Materials, Russian
 Academy of Sciences, Laboratory of the Synthesis of Organoelement
 Polymers, Moscow, Russia
CepHe@mail.ru

Alkyl-, aryl-alkoxysilanes with various substituents and substitution extent of alkoxy-groups are the basis for obtaining a wide range of oligomers and polymers with various structure.¹ Such substituted alkoxysilanes can be obtained by several methods, and the basic method is etherification of chlorosilanes with alcohols and with organomagnesium compounds.

As of today there is a tendency of non-chlorine production of substituted alkoxysilanes. So, organomagnesium synthesis of these compounds, which is known for a long time, goes through the second birth. Therefore it can be regarded as a good alternative to obtain them.



In this study, we compared the methods of substituted alkoxysilane obtaining in the solvent medium, and without solvent. The reactivity of different alkoxy-groups was analyzed as well.

The results obtained point that the method of substituted alkoxysilane obtaining through organomagnesium synthesis is universal. It means that you can easily choose conditions, namely the solvent and process temperature, depending on structure of required product, in order to obtain it with a good yield. So, in given study phenyl(hydride)alkoxysilanes were obtained for the first time through the organomagnesium synthesis.

References:

1. Amy S. Manoso, Chuljin Ahn,[†] Arash Soheili, Christopher J. Handy, Reuben Correia, W. Michael Segenish, and Philip DeShong, *J. Org. Chem.* **2004**, 69, 8305-8314
2. Andrianov K. A. , Gribanova O. I. Org. Him. , 8, 558, (1938)

This work was financially supported by GK № 02.740.11.0259 and grant IIII 4342.2010.3 . This work was financially supported by the Grant of President of Russian Federation MK-2212.2010.3.

A REEXAMINATION OF THE REACTION OF 2-ETHOXYCARBONYLMETHYLENE-1,2-DIHYDROQUINOXALIN-3(4H)-ONE WITH VILSMAYER REAGENT: REVISION OF A STRUCTURAL ASSIGNMENT

A.M. Murtazina
S.V. Kharlamov
D.I. Adgamova
S.K. Latypov
V.A. Mamedov

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia
mamedov@iopc.ru

2-Ethoxycarbonylmethylene-1,2-dihydroquinoxalin-3(4H)-one **1** has been reported to react with the Vilsmeier reagent [$\text{DMF}(N,N\text{-dimethylformamide})\text{-POCl}_3$] with the formation of 3- N,N -dimethylaminocarbonylfuro[2,3- b]quinoxaline hydrochloride **2** as an end product instead of the expected formylated compound **3** [1]. The structure of the latter as has been established and reported on the basis of its IR [$\nu(\text{C}=\text{O})$ 1755 cm^{-1}], NMR [^1H ($\text{DMSO}-d_6$): 7.93-7.43 (4H, m, aromatic), 7.90 (1H, s, H2), 4.02 (3H, s, NMe), 3.50 (3H, s, NMe)], mass spectral, elemental analytical data and besides on the basis of its reaction products with hydrazines [1,2], *ortho*-phenylenediamine [3,4] and 2-aminepyridine [2,4].

Herein we describe our results on the reexamination of the reaction of 2-ethoxycarbonylmethylene-1,2-dihydroquinoxalin-3(4H)-one **1** with the Vilsmeier reagent under the reaction conditions which are given in the above paper [1]. In fact the same product with almost identical spectral (IR and ^1H NMR) parameters was obtained under the same reaction conditions [1].

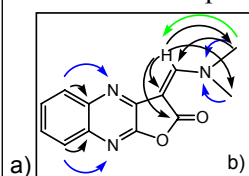
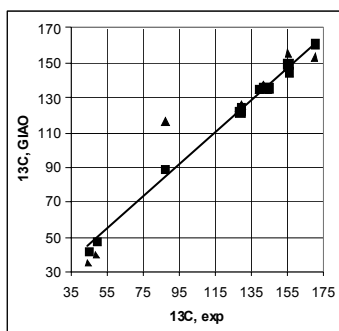
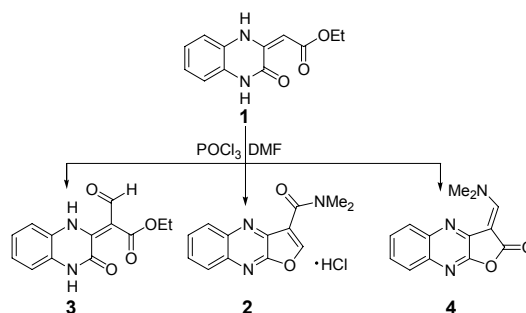


Figure 1. a) Correlation of calculated (GIAO B3LYP/6-31G(d)) versus experimental ^{13}C NMR CSs (■ – for **4**, ▲ – for **2**), **b)** Schematic representation of observed NMR correlations for **4**.

However, with a variety of NMR correlation methods (2D ^1H - ^1H COSY, DEPT, ^1H - ^{13}C HSQC, ^1H - $^{15}\text{N}/^{13}\text{C}$ HMBC, 1D DPFGNOE) used we concluded that the product of the investigated reaction is 1- N,N -dimethylaminomethylene-2-oxo-1,2-dihydrofuro[2,3- b]quinoxaline **4** and neither compound **2** nor compound **3**. First, structure **3** can be easily omitted because there are neither quinoxaline NH (non aromatic) nitrogens nor OEt carbons. As to the hypothesis **2** and **4** although the NMR correlations of quinoxaline moiety can well correspond to both structures the NMR connectivities of $\text{Me}_2\text{N}-\text{CH}=\text{C}-$

$\text{C}(\text{O})-$ fragment (Fig. 1) can be attributed only to **4** and there are NMR correlations that could be ascribed to **2**.

A good correlation ($R^2=0.99$) of the calculated (GIAO DFT) versus experimental ^{13}C chemical shifts (Fig. 1a) for the “right” structure

(**4**) and no good one for the “wrong” (**2**) finally proves the above conclusions.

As can be seen from the structures of compounds **2**, **3** and **4**, each one of them when interacting with the above nucleophilic reagents might give one and the same product. Therefore, on the basis of the results of these reactions it is impossible to unambiguously differentiate between the structures **2**, **3** and **4**.

References:

1. Y. Kurasawa, A. Takada *Heterocycles* **1980**, 14, 281; 2. Y. Kurasawa, A. Takada *Heterocycles* **1980**, 14, 611; 3. Y. Kurasawa, Y. Okamoto, K. Ogura, A. Takada *J. Heterocyclic Chem.* **1985**, 22, 661; 4. Y. Kurasawa, J. Satoh, M. Ogura, Y. Okamoto, A. Takada *Heterocycles* **1984**, 22, 1531.

Acknowledgement. We thank the Russian Foundation for Basic Research (Grant No. 10-03-00413) for financial support.

COPPER-CATALYZED ARYLATION OF TETRAZOL-5-TIONES UNDER CONVENTIONAL HEATING AND MICROWAVE ACTIVATION

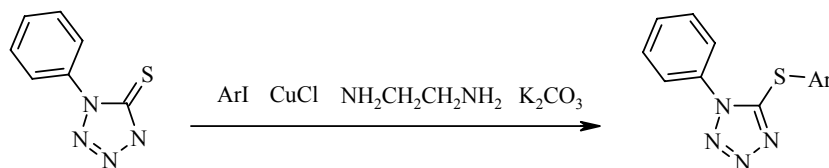
U.N. Dmitrieva
S.M. Ramsh
Y.E. Zevatskiy
T.V. Artamonova
L.V. Myznikov

Saint-Petersburg State Institute of Technology, Department of
 Chemical Technology of Organic Dyes and Phototropic Compounds,
 Saint-Petersburg, Russia
Myznikov_lv@mail.ru

5-Thioaryltetrazoles have been mainly prepared by the direct arylation with fluoro(chloro)nitrobenzenes [1], by the electrochemical reaction with dihydroxybenzenes [2] or by reaction of 5-Tosyltetrazoles with thiophenols [3]. However, all of these methods require a specific reaction conditions and have a limitations for an applications thereof. Recently it has been reported an arylation of 1-Methyltetrazol-5-thione with benzene iodide in a presence of CuI as a catalyst and 1,10-Phenanthroline as a ligand at 120°C [4].

Proceeding our research in a tetrazoles functionalisation we have investigated an arylation of 1-Phenyltetrazol-5-thione with variety of aryl iodides under a convectional heating and a microwave activation.

It was found that reaction of 1-Phenyltetrazol-5-thione with aryl iodides in a presence of 20 mol. % CuCl and ethylenediamine in DMF at 85°C yielded a 1-Phenyl-5-thioaryltetrazoles.



Ar = 2,4,6-Me₃C₆H₂ (1); 4-CH₃C₆H₄ (2) 4-CH₃OC₆H₄ (3); 4-NO₂C₆H₄ (4), Ph (5).

Yields of 1-Phenyl-5-thioaryltetrazoles are not noticeably changed by using of 1,10-phenanthroline instead of ethylenediamine as ligand.

The arylation reaction can be promoted by microwave activation. Microwave activation leads to increasing yields at the same reaction time. Duration of reactions and yields are presented in a Table.

Compound	T, h	Yields, %	
		Convectional heating	Microwave activation
1	2	52	76
2	1,5	60	98
3	2,5	38	90
4	2	36	95
5	1,5	42	80

In conclusion an arylation of 1-Tetrazol-5-thiones in the presence of copper (I) in the microwave activation conditions is the most convenient method of preparation 5-thioaryltetrazoles.

References:

1. М. А. Гольцберг, Г. И. Колдобский. *ЖОрХ*, **32**, 1238 (1996).
2. М. М. Khodaei, A. Alizadeh, N. Pakravan. *J. Org. Chem.* **73**, 2527 (2008).
3. Z. P. Demko, K. B. Sharpless. *Angew. Chem, Int. Ed.* **41**, 2110 (2002).
4. Liang-Feng Niu, Yan Cai, Chao Liang, Xin-Ping Hui, Peng-Fei Xu *Tetrahedron* **67**, 2878 (2011).

**OLEFINS, ALCOHOLS, ALDEHYDES AND
POLYOLS OF PETROCHEMICAL AND
RENEWABLE WOOD RAW MATERIALS IN
PHOSPHORYLATION AND
THIOPHOSPHORILATION REACTIONS**

I.S. Nizamov
R.R. Shamilov
I.D. Nizamov
R.A. Cherkasov

Kazan (Volga region) Federal University, Kazan, Russia
isnizamov@mail.ru

There is a considerable interest in tetracoordinated phosphorus organic acids and thioacids and their derivatives due to their great variety of useful applications. These substances may be prepared on the basis of petrochemical and renewable wood raw materials. Thus, industrial fractions C₁₆-C₁₈, C₂₀-C₂₆ and C₂₈-C₄₀ are waste materials of oligomerization of ethylene, where as natural isoprenoides as aldehydes and alcohols in pyrophosphate forms seem to be renewable wood raw materials for phosphorylation. Hyperbranched aliphatic polyols have found an expanding application as additives thermoplastic resins and crosslinked thermosetting resins, rheology modifiers for thermoplastics, resins for coatings etc.

The reactions of higher monoolefins of industrial fractions C₁₆-C₁₈, C₂₀-C₂₆ and C₂₈-C₄₀ with dialkyl phosphites in the presence of benzoyl peroxide were studied. On the basis of these studies, the technological method of synthesizing o,o-dialkyl esters of mixed long-chain alkylphosphonic acids was developed. O,O-Dialkyl alkylphosphonates obtained were used as intermediates for the synthesis of corresponding higher alkylphosphonic acids and their potassium salts. Higher alkylphosphonous and dialkylphosphinic acids were obtained by the reactions of water solution of hypophosphorous acid with olefins of fractions C₁₆-C₁₈, C₂₀-C₂₆ and C₂₈-C₄₀ in the presence of benzoyl peroxide and sulfuric acid. Addition reactions of O,O-dialkyl dithiophosphoric and bisaryldithiophosphonic acids with olefins of industrial fractions of C₁₆-C₁₈ and C₂₀-C₂₆ were performed in the presence of anhydrous of ZnCl₂ with the formation of the mixture of adducts. The model reactions of O,O-diethyl dithiophosphoric acid with individual octene-1, hexadecane-1 and octadecene-1 as α -olefins of linear structure and with 2-methylpentene-1 as an isomeric vinylidene α -olefin results in the formation of adducts in accordance with Markovnikow's rule. Long chain alkylphosphonic, alkylphosphonous and dialkylphosphinic acids, their esters and salts, S-alkyl esters and diesters of dithiophosphoric and bisdithiophosphonic acids possess high anticorrosion activities toward steel hand-make goods in the condition of aggressive carbonaceous medium.

Substitution reactions of geraniol, nerol and racemic linalool with amido- and chlorophosphites, Kabachnik-Fields reaction of citral with dialkyl phosphites in the presence alkyl amines, imine formation reaction of *E,Z*-citral, *R,S*-citronellal and (*R*)-(-)-myrtenal with primary amines and Pudovik reactions of prenyl imines obtained with dialkyl phosphites or with O,O-dialkyl trimethylsilylphosphites were studied. On the basis of these studies, new dienyl diprenoid phosphite esters, unsaturated prenyl imines and α -aminophosphonates were prepared.

We have developed convenient method for the thiophosphorylation of aliphatic polyesters of Boltorn H20, H30 and H40 containing 16, 32 and 64 hydroxyl groups respectively by the reactions with 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides to give oligomeric dithiophosphonic acids. Their ammonium salts were also obtained. The reactions of hyperbranched polyols with cyclic amidophosphites were performed with the formation of the corresponding phosphite derivatives and the elimination of diethylamine. The hyperbranched polyols were found to react with pyrocatechol chlorophosphite in the presence of triethylamine to give 1,3,2-dioxaphospholane derivatives. Dialkyl phosphate derivatives of Boltorn H20, H30 and H40 were prepared by use of ultrasonic irradiation in the substitution reactions of the polyesterpolyols with dialkyl chlorophosphates. Unsaturated polyacrylates obtained by the reactions of Boltorn H20, H30 and H40 with acryloyl and methacryloyl chlorides reacts with O,O-dialkyl dithiophosphoric acids to form the corresponding dithiophosphates.

INVESTIGATION OF CHEMICAL MODIFICATION OF 2-AMINO-4-DIETHYLPHOSPHONOTHIAZOLE

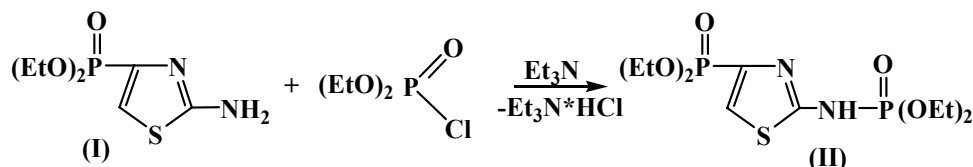
L.K. Salkeyeva
M.T. Nurmaganbetova
Y.V. Minayeva
A.K. Shibayeva
E.K. Tayshibekova

Academician E.A. Buketov Karaganda State University, Faculty of Chemistry, Department of Organic Chemistry and Polymers, Karaganda, Kazakhstan
ritunur@mail.ru

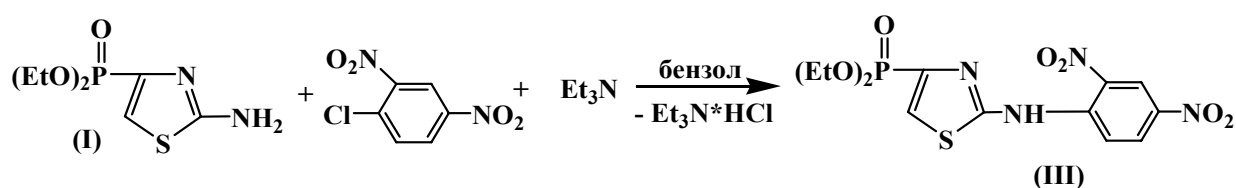
Interest in organophosphorous compounds was defined by their variety and unique set of features making these substances valuable objects of theoretical research and significant for practical use.

Previously, we developed a convenient method for the synthesis of phosphorylated thiazole (I) according to the scheme of classical Hantzsch reaction based on diethylketophosphonate and thiourea [1].

Chemical modification of the synthesized phosphorus-containing amino-thiazole (I) can be implemented with the participation of the free amino group, which has a sufficiently high nucleophilicity. Using this feature of the structure allows receiving a variety of derivatives based on nucleophilic substitution reactions. We carried out the reaction of 2-amino-4-diethylphosphonothiazole (I) with diethylphosphite in the presence of base, as a result of which 2 - (N-diethylphosphonamino)-4-diethylphosphonothiazole (II) was obtained.



In our opinion, easily accessible and reactive 2,4-dinitrochlorobenzene is interesting nucleophilic agent in chemical modification reactions of the (I). The reaction of 2-amino-4-diethylphosphonothiazole (I) with 2,4 - dinitrochlorobenzene was carried out in the presence of triethylamine in benzene.



The resulting 2 - (N-2,4-dinitrophenylamino)-4-diethylphosphonothiazole (III) is a valuable reagent for further chemical modifications.

References:

1. Salkeyeva L.K., Minayeva, E.V., Mantel, A.I., Nurmaganbetova M.T. Synthesis and chemical modification of the phosphorus-containing derivatives of 2-aminothiazole /Proceedings of the 6th Beremzhanov's Congress on Chemistry and Chemical Engineering. Karaganda: Karaganda State University, 2008. - P. 365-368.

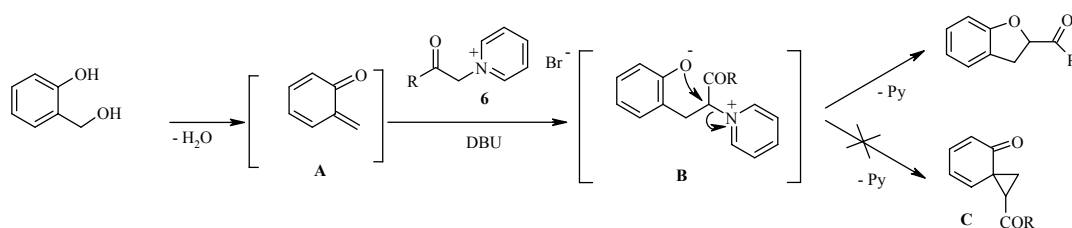
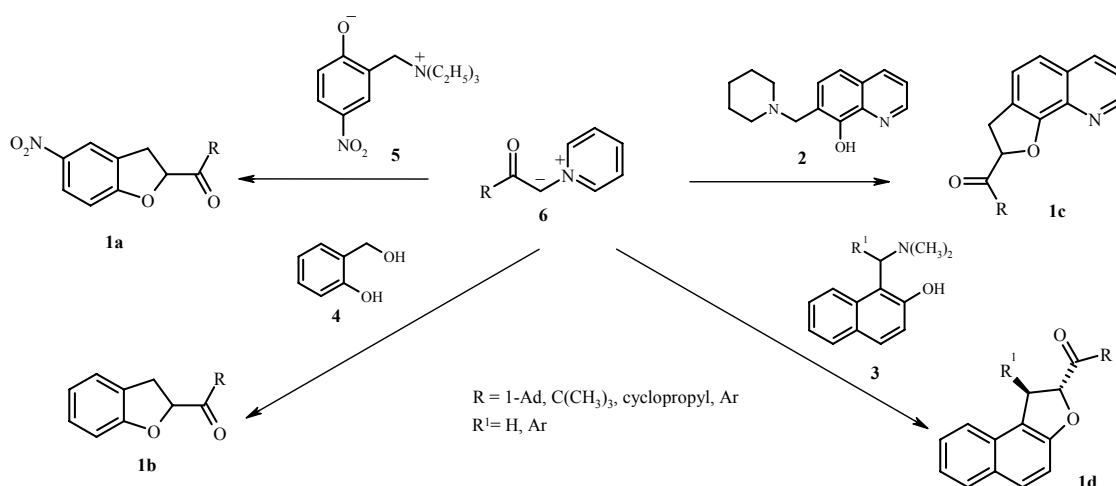
PYRIDINIUM YLIDES IN THE SYNTHESIS OF 2-ACYL-SUBSTITUTED CONDENSED DIHYDROFURANS

V.A. Osyanin
D.V. Osipov
Y.N. Klimochkin

Samara State Technical University, Organic Chemistry, Samara,
Russia
vosyanin@mail.ru

Arene ring-fused dihydrofurans have attracted widespread interest in view of their presence in natural products, and their pharmacological activities. Extended arenofurans have potential applications as fluorescent dyes, organic light-emitting diodes, two-photon absorption materials etc.

We have developed a simple, general route to the condensed dihydrofurans (**1a-d**), substituted in position 2 by an acyl group, starting from phenolic Mannich bases (**2,3**), salicylic alcohol (**4**), *ortho*-triethylammoniomethylphenolate (**5**) and the carbonyl-stabilised pyridinium ylides (**6**):



Some of the prepared products may be useful intermediates for the preparation of highly functionalized arenofurans.

This work was supported by the Council on Grants of the President of the Russian Federation (the program of state support of young Russian scientists, grant MK-3368.2011.3) and using the equipment CCU "Investigation of physical and chemical properties of substances and materials".

SYNTHESIS OF OXAZOLIDINES BASIS ON VICINAL AMINO ALCOHOL SULFOLANE SERIES

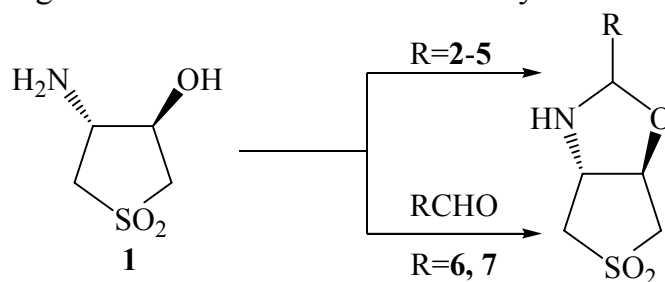
V.A. Palchikov¹
I.S. Prishlyak¹
S.V. Tretyakov¹
P.G. Dulnev²

1 - Dnepropetrovsk National University
2 - Scientific Center "AKSO" NAS of Ukraine
palchikoff@mail.ru

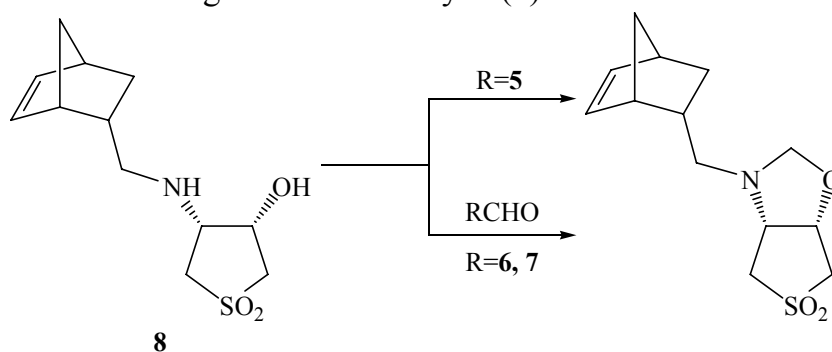
Compounds including vicinal amino alcohol and sulfolane fragments as well as substances containing naturally widespread oxazolidine cycle possess distinct and various biological activities. Since few compounds containing both fused sulfolane and oxazolidine fragments are currently described, we have developed the appropriate synthesis route.

It was considered the possibility of formation novel heterocycles from amino alcohol (1) and aldehydes (2-7, R = p-NO₂C₆H₄ (2), p-BrC₆H₄ (3), p-FC₆H₄ (4), H (5), Ph (6), C₃H₇ (7)) having different electronic pattern of substituents. The reactions were carried out by refluxing equimolar quantities of precursors in benzene with p-toluenesulphoacid (5-10 mol.%) using a Dean-Stark trap.

All the reactions gave desired heterocycles in moderate yields (30-65%) except for the interaction involving electron-enriched aromatic aldehyde.



In addition, *cis*-amino alcohol (8) containing both norbornene and sulfolane fragments turned out to be inactive towards aromatic aldehydes but it easily underwent heterocyclization when treating with formaldehyde (5).



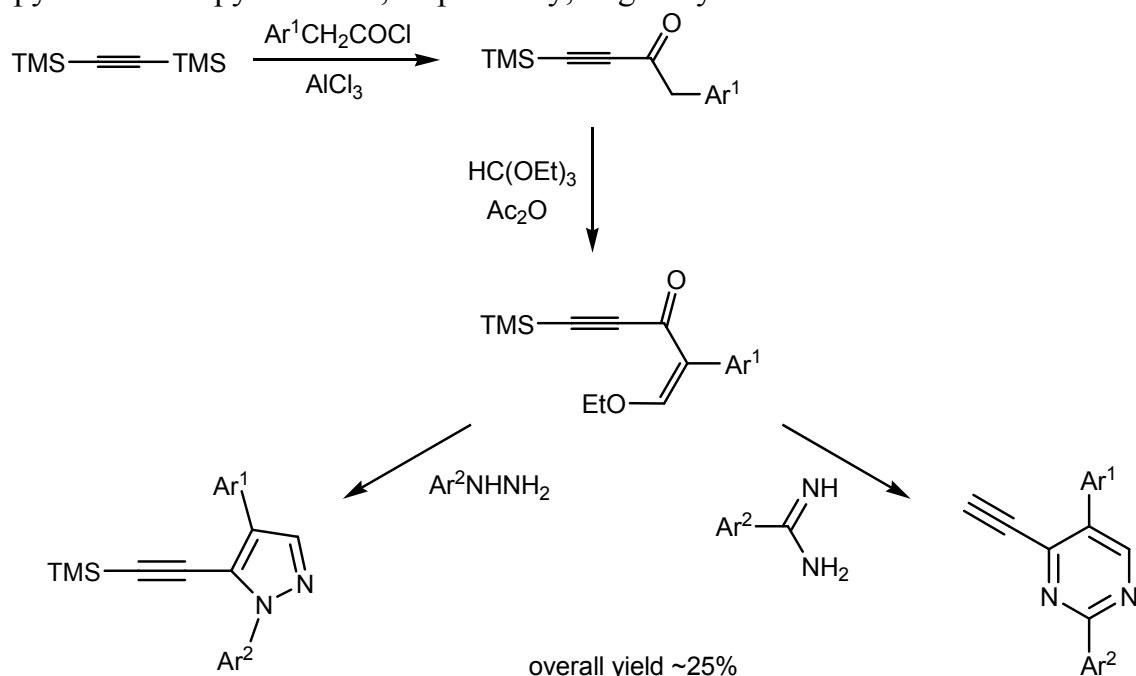
The structures of the products were proven by NMR ¹H and IR methods.

TRANSFORMATION OF BIS(TRIMETHYLSILYL)ACETYLENE TO ALKYNYL SUBSTITUTED NITROGEN HETEROCYCLES

A.S. Pankova
P.R. Golubev

Saint-Petersburg State University, Chemistry Department,
Saint-Petersburg, Russia
pank-alena@yandex.ru

We suggest a convenient three-stage synthetic method to prepare 5-alkynylpyrazoles and 4-alkynylpyrimidines from easily available starting compounds. Friedel-Crafts acylation of bis(trimethylsilyl)acetylene with arylacetyl chlorides followed by ethoxymethylation of the products leads to acetylenic ketones with several electrophilic centers. Their condensation with such dinucleophiles as arylhydrazines and arylamidines gives pyrazoles and pyrimidines, respectively, in good yields.



The regioselectivity of the processes matches the different activities of the reaction centers of the ketone molecule. The resulted heterocycles possess a triple bond in a side chain, but while in the pyrazoles the TMS group remains at the terminal position, a basicity of amidines appears to be enough to remove it in pyrimidines under reaction conditions. In addition, these pyrazoles and pyrimidines contain such combinations of substituents which make them hard to obtain by other methods.

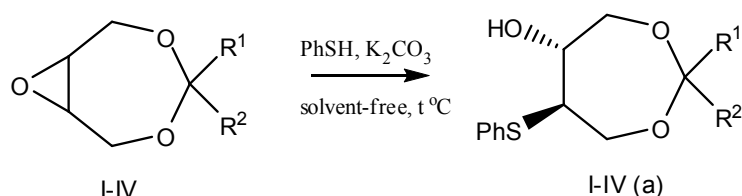
This work was supported by Saint-Petersburg State University (research grant №12.38.16.2011).

SYNTHESIS OF HYDROXYSULFIDES BASED ON 3,5,8-TRIOXABICYCLO[5.1.0]OCTANES

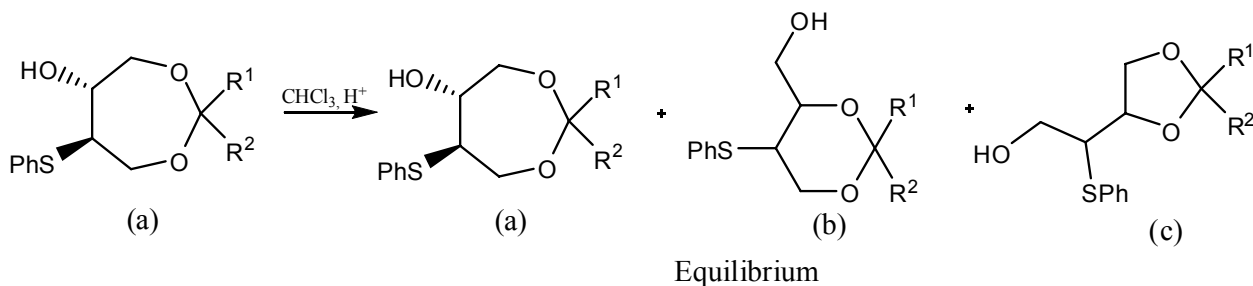
R.S. Pavelyev¹
S.G. Gnevashev¹
R.M. Vafina¹
L.E. Nikitina²
Yu.G. Shtyrilin¹
E.N. Klimovitskii¹

1 - A.M. Butlerov Chemical Institute, Kazan Federal University,
Kazan, Russia
2 - Chemistry Department, Kazan State Medical University, Kazan,
Russia
pavelev.r.s@rambler.ru

Thiolysis of 3,5,8-trioxabicyclo[5.1.0]octanes I-IV by thiophenol was found to be pH-dependent and leads to the 5-7 – membered cyclic acetals. Only the seven-membered products (a) were formed under the basic conditions. In the acidic medium 1,3-dioxepane I-III (a) is isomerized to the less-membered cyclic acetals I-II (c) and III (b). This approach is very suitable for the preparation of five- and six-membered cycles. Unsubstituted at C² dioxepane IV (a) was established to remain intact in the presence of acid.



R¹ = R² = CH₃ (I); R¹ = R² = -(CH₂)₅- (II); R¹ = H, R² = Ph (exo, endo) (III); R¹ = R² = H (IV)



I and II:	9	:	< 1	:	90
III:	< 7	:	85	:	< 7

R¹ = R² = CH₃ (I); R¹ = R² = -(CH₂)₅- (II); R¹ = H, R² = Ph (III).

Hydroxysulfides including their acetates were oxidized to the corresponding sulfones.

The product structure was confirmed by 1D, 2D NMR, chromatography-mass spectrometry and single crystal X-ray diffraction.

ALKYLATION OF 1,4-DIHYDROXYNAPHTHALENE WITH TERTIARY ALCOHOLS AND SYNTHESIS OF NITROGEN-CONTAINING DERIVATIVES OF 2-(ADAMANTHYL-1)-TETRALIN-1,4-DIONE

I.V. Peterson¹
W.A. Sokolenko¹
N.M. Svirskaya¹
A.I. Rubailo²

1 - Institute of Chemistry and Chemical Technology SB RAS,
Krasnoyarsk, Russia

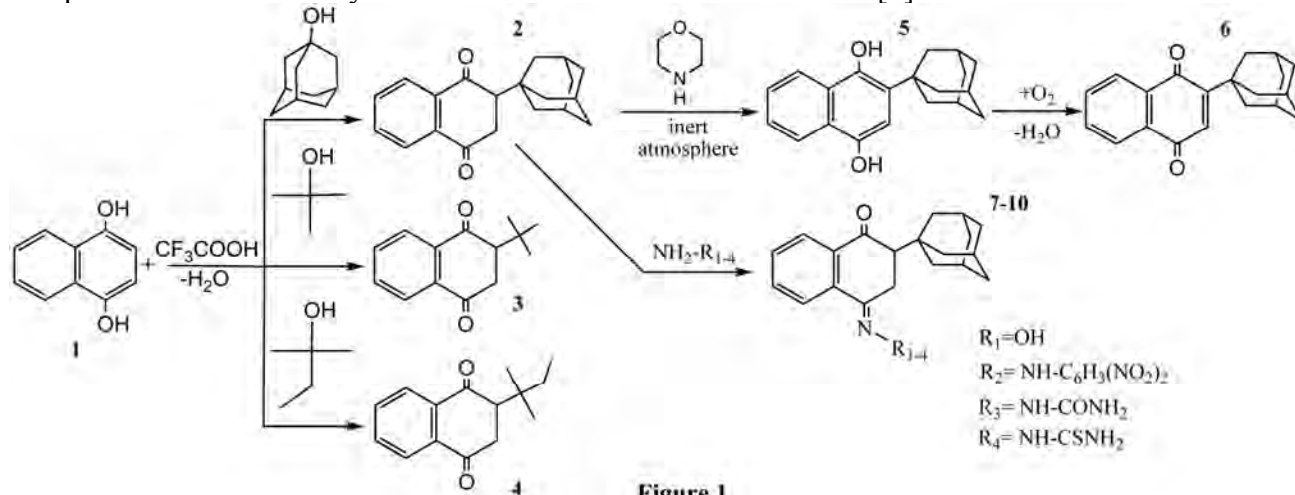
2 - Siberian Federal University, Krasnoyarsk, Russia
Defender200385@mail.ru

Conversion 1,4-dihydroxynaphthalene into its tautomer 1,2,3,4-tetrahydro-naphthalene-1,4-dione and chemistry of its derivatives was studied by the authors [1].

We studied 1,4-dihydroxynaphthalene (**1**) alkylation with adamantanol-1, *tert*-butyl and *tert*-amyl alcohols in trifluoroacetic acid. We found that compound **1** C-alkylation occurred in the position 2 with simultaneous keto-enol tautomerization and corresponding 1,4-dihydroxynaphthalenes were formed in diketone form. Diketones **2-4** were stable in usual conditions. Dienol form, 2-(adamantyl-1)-1,4-dihydroxynaphthalene (**5**), was received at 2-(adamantyl-1)-tetralin-1,4-dione (**2**) by interaction with morpholine under an argon atmosphere in the sealed NMR tube. After loss of sealing of NMR-tube, **5** quickly oxidized into 2-(adamantyl-1)-1,4-naphthoquinone (**6**).

It is well known that many nitrogen-containing adamantane derivatives are used in pharmacology (Rimantadine, Amantadine, Dopamantine, Bemantane and etc.) [2]. We studied diketone **2** reactions with the following nitrogen-containing compounds: hydroxylamine (R_1), 2,4-dinitrophenylhydrazine (R_2), semicarbazide (R_3) and thiosemicarbazide (R_4). The new synthesized compounds **7-10** could be interesting as compounds with potential biological activities and as the starting material for further organic synthesis.

General synthesis compounds **2-10** scheme is presented on figure 1. Physical data of compounds **2-6** and their synthesis methods are described in article [3].



References:

1. a). Pearson M. S., Jensky B.J. *J. Org. Chem.* **1978**, V.43, P.4617-4622. b). Laatsch H. *Liebigs Ann. Chem.* **1980**, V.1, P.140-157. c). Kundig E. P., Garcia A. E. *Angew. Chem. Int. Ed.* **2006**, V.45, P.98-101.
2. Morozov, I.S. *Pharmacology of adamantanes*. **2001**. Volgograd. – 320 p.
3. Peterson I.V., Sokolenko W.A., Svirskaya N.M., Rubailo A.I. *Journal of Siberian Federal University. Chemistry*. **2010**, V.3, №3, p. 253-259.

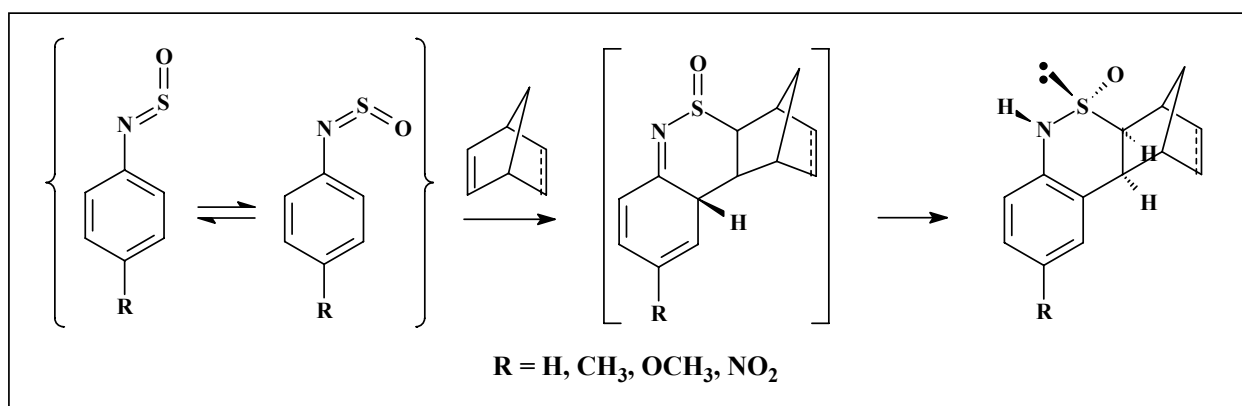
V.V. Plemenkov¹
 Ya.V. Veremeychik¹
 D.N. Shurpik¹
 I.A. Litvinov²
 O.A. Lodochnikova²
 D.B. Krivolapov²

THIONILANILINES AS DIENE STRUCTURES IN DIELS-ALDER REACTIONS

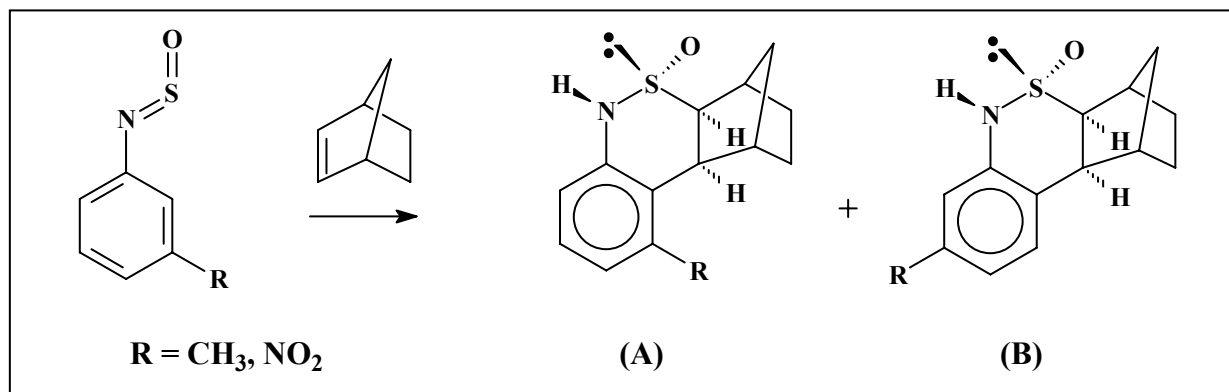
1 - Immanuel Kant Baltic Federal University, Kaliningrad, Russia

2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
 Academy of Sciences, Kazan, Russia
 plem-kant@yandex.ru

On basement of reactivity of aromatic N-sulfinilamines as heteroatom dienes in Diels-Alder reactions, adducts of substituted thionilanilines with norbornene and norbornodiene was obtained. Their molecular structure was determined using methods of X-ray diffraction, IR and NMR spectroscopy and considered to be benzo-ortho-thiazine. We clarified that addition of diene component to bicyclo[2.2.1]heptene structure in all cases is performing from the side of methylene bridge of last. Configuration of sulfoxide group corresponds to both *endo*-orientation of addends in case of *Z*-configuration of parent thionilanilines or *exo*-orientation in case of *E*-configuration of thionilanilines.



Reactions of meta-substituted thionilanilines lead to formation of two isomers (A and B). Proportion of isomers depends on the type of substitute and thermal conditions of reaction: with $R = NO_2$ and $t = 20\text{ }^\circ\text{C}$ ratio of A:B is 1:1 and with growing of temperature the part of isomer B significantly increases.

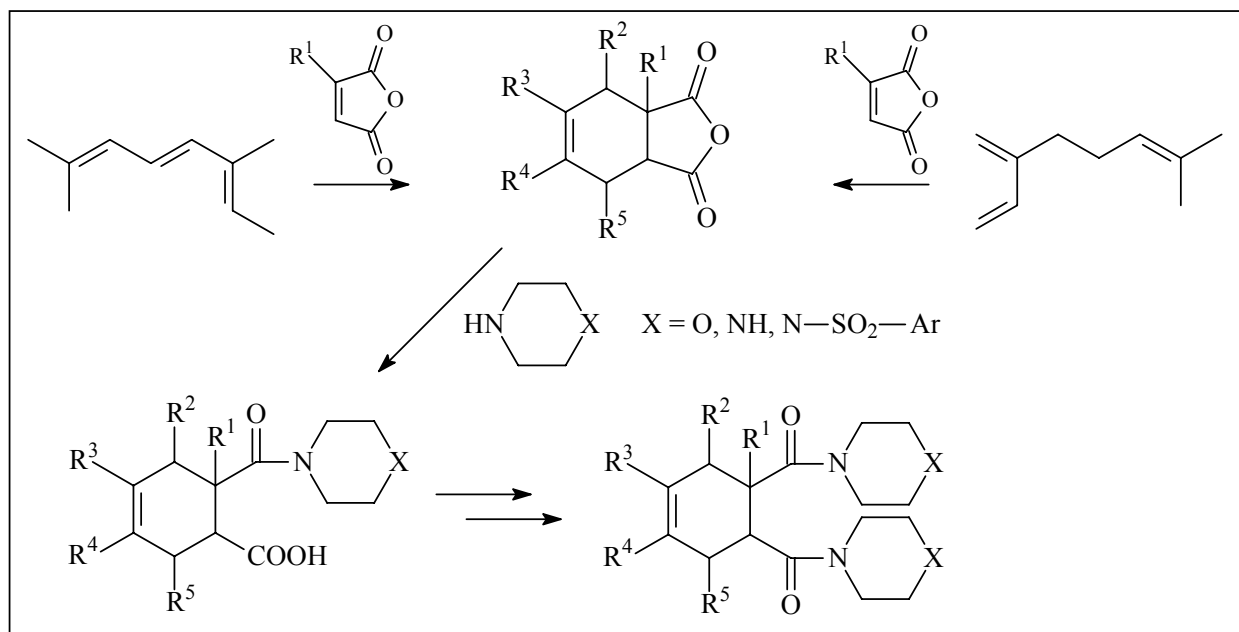


CHEMICAL MODIFICATION OF MONOTERPENES BY DIELS-ALDER REACTIONS

M.S. Dzyurkevich¹
V.V. Plemenkov¹
O.A. Lodochnikova²
D.B. Krivolapov²
I.A. Litvinov²
O.V. Kazimirchenko³

1 - Immanuel Kant Baltic Federal University, Kaliningrad, Russia
2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia
3 - Kaliningrad State Technical University, Kaliningrad, Russia
plem-kant@yandex.ru

By interaction of myrcene and alloocimene with maleic and citraconic anhydrides adducts of Diels-Alder reaction which is anhydrides of dicarboxylic acids of sesquiterpene class were obtained. By further modification of adducts using morpholine, piperazine and N-substituted piperazines corresponding mono- and bis- amides were obtained. The disclosure of cyclic anhydride fragment takes place preferably to one of two carbonyl groups as it shown in scheme.



Molecular structures of all compounds were determined using methods of X-ray diffraction, IR and NMR spectroscopy

The amides obtained were tested for biological activity. It was shown that number of compounds is demonstrating moderate and high activity against *Escherichia coli*, *Staphylococcus* sp. and *Aspergillus niger*.

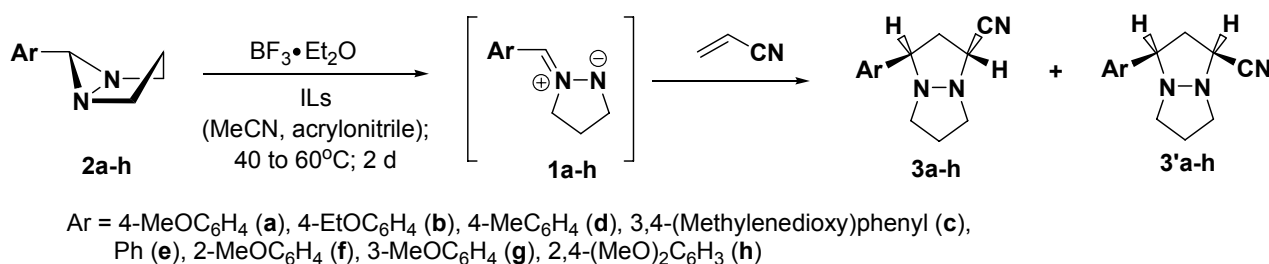
DIAZIRIDINE RING EXPANSION IN 6-ARYL-1,5-DIAZABICYCLO[3.1.0]HEXANES UNDER THE ACTION OF ACRYLONITRILE AT BORON TRIFLUORIDE ETHERATE CATALYSIS

M.I. Pleshchev
V. Yu. Petukhova
V.V. Kuznetsov
N.N. Makhova

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences (ZIOC RAS), Moscow, Russia
michele-chem@yandex.ru

Diaziridine ring expansion reactions in mono- and bicyclic diaziridines under the action of different dipolarophiles were widely studied in ZIOC RAS, in particular the [3+2]-cycloaddition reactions of CS₂, activated nitriles, 1,3-diphenylpropen-2-one, β-nitrosterenes to azomethine imines **1**, generated from 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **2** in ionic liquids (ILs) at BF₃·Et₂O catalysis.^{1,2} These reactions proceeded with high both regio- and stereoselectivity resulting in new methods for the synthesis of tetrahydro-1*H*,5*H*-pyrazoles annelated by 1,3,4-thiazolidine, 1,2,4-triazoline, pyrazolidine heterocycles.

In this work diaziridine ring expansion reactions in 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **2a-h** were performed with acrylonitrile both in ionic liquids ([bmim][BF₄] and [bmpyrr][NTf₂]) and in MeCN at BF₃·Et₂O catalysis. In both kinds of solvents reactions proceeded regiospecifically contrary to the Michael addition mechanism and with high diastereoselectivity resulting in the mixture of diastereomers 3-aryltetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazoles **3a-h** and **3'a-h** with predominance of diastereomers **3a-h** (¹H NMR) in ratio 2.5-4:1. Diastereomers **3b** and **3'b** were separated by column chromatography on SiO₂. The total yields of compounds synthesized were moderate. The best results (39%) were obtained in IL [bmpyrr][NTf₂] in excess of acrylonitrile.



References:

1. Yu.S. Syroeshkina, V.V. Kuznetsov, K.A. Lyssenko, N.N. Makhova, *Mendeleev Commun.*, 2008, **18**, 42-44, 207-208; 2009, **19**, 276-278.
2. Yu.S. Syroeshkina, V.V. Kuznetsov, L.L. Fershtat, N.N. Makhova, *Russ. Chem. Bull, Int Ed.*, 2009, **58**, 366-379; 2010, **59**, 1621-1630.

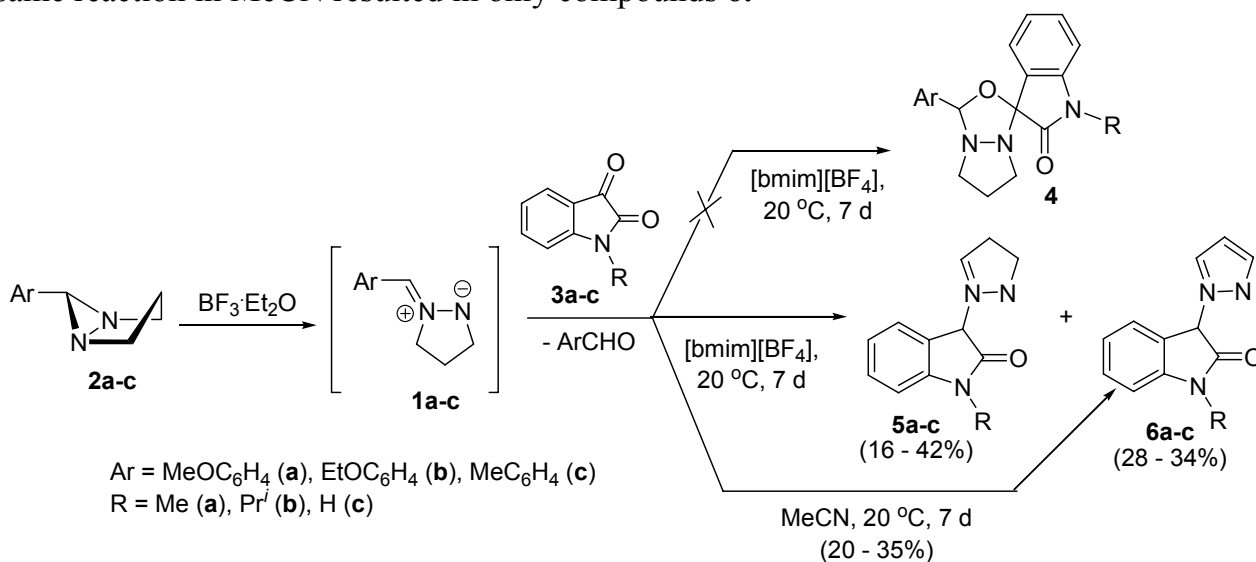
METATHESIS OF CARBONYL COMPOUNDS IN REACTION OF 6-ARYL-1,5-DIAZA- BICYCLO[3.1.0]HEXANES WITH ISATINS AT BORON TRIFLUORIDE ETHERATE CATALYSIS

M.I. Pleshchev
V.Yu. Petukhova
L.L. Fershtat
V.V. Kuznetsov
N.N. Makhova

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia
michele-chem@yandex.ru

Isatin and its derivatives are part of composition of many organic compounds displaying a wide spectrum of biological activity. And so a development of methods for the preparation of new compounds incorporating isatin fragment is till now of interest. One of the pathway of isatin fragment introduction in organic molecules is reactions on its 3-C=O group. Recently in laboratory of nitrogen-containing compounds of ZIOC RAS reaction of [3+2]-dipolar cycloaddition of different dipolarophyles to azomethine imines **1**, generated by catalytic opening of diaziridine ring in 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **2** in ionic liquids (ILs) at $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalysis was studied.¹

In this work reaction of azomethine imines **1** with isatins **3a-c** in IL [bmim][BF_4] was investigated at $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalysis. It could be expected that 3-C=O group of isatins entered in [3+2]-cycloaddition reaction with azomethine imines **1** with formation of spiro-articulated structures **4**. However instead of structures **4** a mixture of 1-substituted 3-(4,5-dihydro-1*H*-pyrazol-1-yl)indolin-2-ones **5** and 3-(1*H*-pyrazol-1-yl)indolin-2-ones **6** as well as aromatic aldehydes, which were used at the synthesis of compounds **2**, was obtained. Compounds **5** and **6** were separated by column chromatography on SiO_2 . The same reaction in MeCN resulted in only compounds **6**.



References:

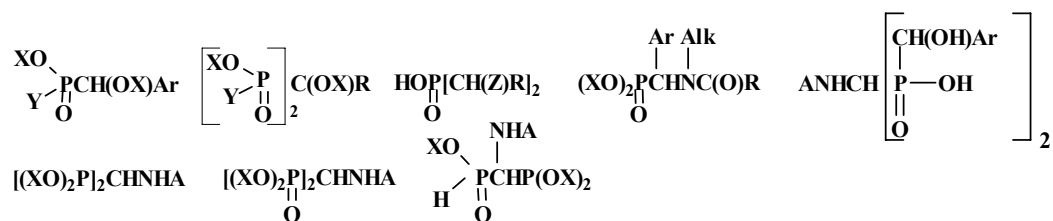
1. S. G. Zlotin, N. N. Makhova, *Russ. Chem. Rev.*, 2010, **79**, 543-583.

SYNTHESIS OF NEW FUNCTIONALIZED ORGANOPHOSPHORUS ACIDS WITH HETEROCYCLIC AND UNSATURATED FRAGMENTS AS PERSPECTIVE ANTIOXIDANTS AND LIGANDS

A.A. Prishchenko
M.V. Livantsov
O.P. Novikova
L.I. Livantsova
V.S. Petrosyan

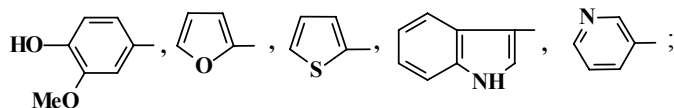
Department of Chemistry, M.V. Lomonosov Moscow University,
Moscow, Russia
aprishchenko@yandex.ru

Functionalized organophosphorus acids and their derivatives with heterocyclic and aromatic fragments are of great interest as effective chelating ligands and perspective bioactive substances with various properties. These acids are well-known analogs of hydroxyl(amino)carbonic acids and natural pyrophosphates. We have developed the convenient methods of synthesis of new functionalized organophosphorus acids and their derivatives including heterocyclic, aromatic and unsaturated fragments as well as hydroxyl, amino, and carboxyl groups using as starting compounds the trimethylsilyl esters of several trivalent phosphorus acids and functionalized alkenes, aldehydes, and carbonic acids^{1,2}. The obtained trimethylsilyl esters of functionalized organophosphorus acids easily react with methanol or sodium methylate in methanol yielding the new water soluble organophosphorus acids or their salts which are presented here.



R = MeCH=CH, Me(CH=CH)₂, PhCH=CH, Me(CH₂)₇CH=CH(CH₂)₇, Ph, 4-MeOC₆H₄, Py;

Ar = Ph, 4-FC₆H₄, 4-MeOC₆H₄, 4-Me₂NC₆H₄, 4-MeOCC₆H₄, 2-HOC₆H₄, 4-HOC₆H₄, 2-HOCC₆H₄,



X = H, Et, Me₃Si, Na; Y = H, OX, (CH₂)₂Ph, (CH₂)₂Py, (CH₂)₂COOX, (CH₂)_nN₂, n = 1, 2;

Z = OH, NHR, N(R)Ac, N(R)C(O)(CH₂)₇CH=CH(CH₂)₇Me; A = H, Me₃Si, Ar.

Antioxidative activity of organophosphorus derivatives of 2,6-di-*tert*-butyl-4-methylphenol was investigated on homogenates of rat liver, fish sperm (*Asipenser gueldenstaedti* B.), and rat liver mitochondria. It was shown these compounds are antioxidative scavengers for organotins in unsaturated acids peroxidation³. Also the influence of these compounds was studied on functional characteristics of rat liver mitochondria and on *tert*-BHP- and Fe^{m+}- induced toxicity in cerebellar granule cells of rats.

References:

- 1) Prishchenko A.A., Livantsov M.V., Novikova O.P., Livantsova L.I., Petrosyan V.S. *Heteroatom Chemistry*, **2008**, 19, 352; **2009**, 20, 319; **2010**, 21, 361.
- 2) Prishchenko A.A., Livantsov M.V., Novikova O.P., Livantsova L.I., Milaeva E.R., *Heteroat. Chem.*, **2008**, 19, 490, 562, 733; **2009**, 20, 70.
- 3) Tyurin V.Yu., Gracheva Yu.A., Milaeva E.R., Prishchenko A.A., Livantsov M.V., Novikova O.P., Livantsova L.I., Maryashkin A.V., Bubnov M.P., Kozhanov K.A., Cherkasov V.K., *Russ. Chem. Bull.*, **2007**, 744.

This work was supported by Russian Foundation for Basic Researches, grants 11-03-00402 and 11-03-00414.

A.E. Rubtsov¹
S.N. Shurov²
E.R. Nasibullina¹
A.S. Kuznetsov¹
N.N. Koryagina¹
S.S. Dubovik¹
O.A. Komarova¹
R.A. Bykov¹
D.V. Ivanov¹
N.M. Igidov³
N.A. Pulina³

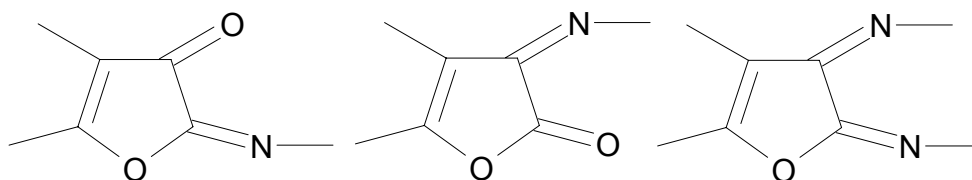
**SYNTHESIS, STRUCTURE AND CHEMICAL
PROPERTIES OF N-SUBSTITUTED 2(3)-IMINO-2,3-
DIHYDROFURAN-3(2)-ONES**

1 - Perm State University, Department of Natural and Biological
Active Compounds, Perm, Russia

2 - Perm State University, Department of Organic Chemistry, Perm,
Russia

3 - Perm State Pharmaceutical Academy, Perm, Russia
rubtsov@psu.ru

Iminofuranones and diiminofurans represent an interesting class of furan derivatives. Alternative methods of synthesis have been worked out for the iminofuranones and, this gives the researcher the opportunity to choose between one or other method according to task in hand.



The structure of iminofuranones gives rise to abundant synthetic potential. The presence of several electron-deficient centers in their molecules makes it possible to control the direction of attack by the nucleophilic reagent and the structure of the final reaction products by varying the substituents in the heterocycle and at the imino functions. A number of OH, SH, and NH nucleophiles have already been tested in reactions with iminofuranones. Broad synthetic possibilities are presented by the recyclization of iminofuranones and cyclization at the C=N bonds of iminofurans.

Thus, iminofuranones are accessible and convenient subjects for the creation of various acyclic and heterocyclic structures.

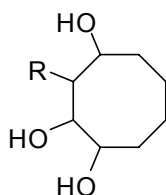
This study was performed under financial support by the Russian Foundation for Basic Research (project no. 11-03-00882)

DEVELOPMENT OF ALTERNATIVE METHODOLOGIES FOR THE SYNTHESIS OF CYCLITOLS CONTAINING EIGHT-MEMBERED RING AS GLYCOSIDASE INHIBITORS

E. Salamci¹
K. Ecer¹
M. Senturk²

1 - Department of Chemistry, Science Faculty Ataturk University,
 Erzurum, Turkey
 2 - Agri Ibrahim Cecen Univ, Dept Chem, Sci & Arts Fac, Agri,
 Turkey
 esalamci@atauni.edu.tr

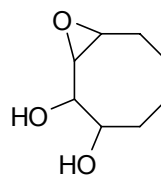
Cyclitol is a generic term used to describe polyhydroxycycloalkanes. Many biologically important molecules and natural products contain polyhydroxylated carbocycles [1,2]. Cyclooctanetetrols and aminocyclooctanetriol analogues form a class of polyhydroxylated cyclooctanoids. Several cyclitols have been used as sweeteners, antibiotics, antiviral, antidiabetes, and anticancer agents. Cyclooctanetetrol and derivatives are generally important intermediates in the synthesis of supramolecules and natural products. Diaminocyclooctandiols are core units in various bioactive compounds, e.g. aminoglycoside antibiotics and antiviral nucleosides [3,4].



R= OH, Cyclooctanetetrol

R= NH₂, 3-Aminocyclooctanetriol

R= Cl, 3-Chlorocyclooctanetriol



Epoxycyclooctane-3,4-diol

The aim of this research is to develop new synthetic methodologies for cyclooctanetetrols and their derivatives. Starting from cis,cis-1,3-cyclooctadiene and cyclooctene epoxide, the corresponding endoperoxide and azido alcohol were synthesized. Then, these compounds would be used for the synthesis of various new cyclooctanetetrols and their derivatives such as two isomeric cyclooctanetetrols, 3-aminocyclooctanetriol, 3-chlorocyclooctanetriol and epoxycyclooctane-3,4-diol. All of the synthesized cyclitols exhibited strong enzyme-specific inhibition against α -glycosidase.

References:

- 1) Salamci, E., *Tetrahedron*, **2010**, 66(23), 4010-4015.
- 2) (a) Gultekin, M. S., Celik, M., Balci, M. *Curr. Org. Chem.* **2004**, 8, 1159-1186. (b) Salamci, E., Seçen, H., Sütbeyaz, Y., Balci, M., *J. Org. Chem.* **1997**, 62, 2453-2457.
- 3) Grabowski, S., Armbruster, J., Prinzbach, H. *Tetrahedron Let.* **1997**, 38, 5485-5488.
- 4) Gypser, A., Michel, D., Nirschi, D. S., Sharpless, K. B. *J. Org. Chem.* **1998**, 63, 7322-7327.

Acknowledgment: The authors are indebted to TUBITAK (Scientific and Technological Research Council of Turkey) for their financial support of this work (Grant No: **110T208** and **106T647**).

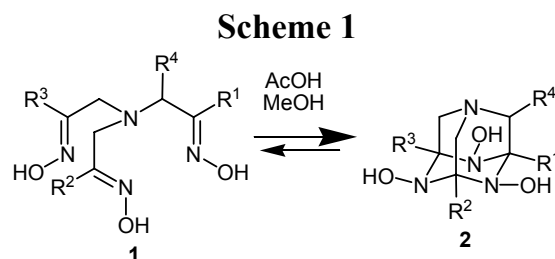
A.N. Semakin
A.Yu. Sukhorukov
S.L. Ioffe
V.A. Tartakovsky

REDUCTION OF 4,6,10-TRIHIDROXY-1,4,6,10-TETRAAZAADAMANTANES. FIRST SYNTHESIS OF ISOMER OF UROTROPIN

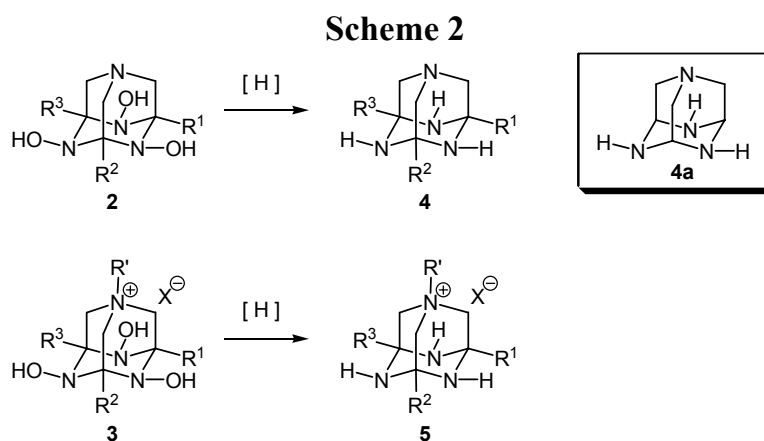
N.D. Zelinsky IOC RAS, Laboratory 42, Moskow, Russia
artyomsemakin@mail.ru

Azaadamantanes are supposed as perspective compounds for application in different areas such as medicinal chemistry and design of energetic compositions.

Recently we have discovered an unusual heterocyclotrimerization of oximino groups in tris(β -oximinoalkyl)amines leading to 4,6,10-trihydroxy-1,4,6,10-tetraazaadamantanes (Scheme 1). Since 1,4,6,10-tetraazaadamantanes are a novel type of heterocage compounds a detail investigation of their chemistry is reasonable.



The present report deals with reduction of hydroxylamino groups in 4,6,10-trihydroxy-1,4,6,10-tetraazaadamantanes and their quaternary ammonium salts into secondary amino groups. A number of 4,6,10-NH adamantanes has been synthesized including isomer of urotropin – unsubstituted 1,4,6,10-tetraazaadamantane **4a** (Scheme 2).



References:

1. A. N. Semakin, A. Yu. Sukhorukov, A. V. Lesiv, S. L. Ioffe, K. A. Lyssenko, Yu. V. Nelyubina, V. A. Tartakovsky *Organic Letters* **2009**, 11(18), 4072.

We are grateful for the financial support from RFBR (grant 09-03- 00676-a).

NEW PHOSPHORYLATED PHENOLS, POLYPHENOLS, CONTAINING STERICALLY HINDERED FRAGMENTS

T.R. Shaekhov¹
E.M. Gibadullina¹
D.B. Krivolapov²
J.K. Voronina²
D.R. Sharafutdinova³
A.R. Burilov¹

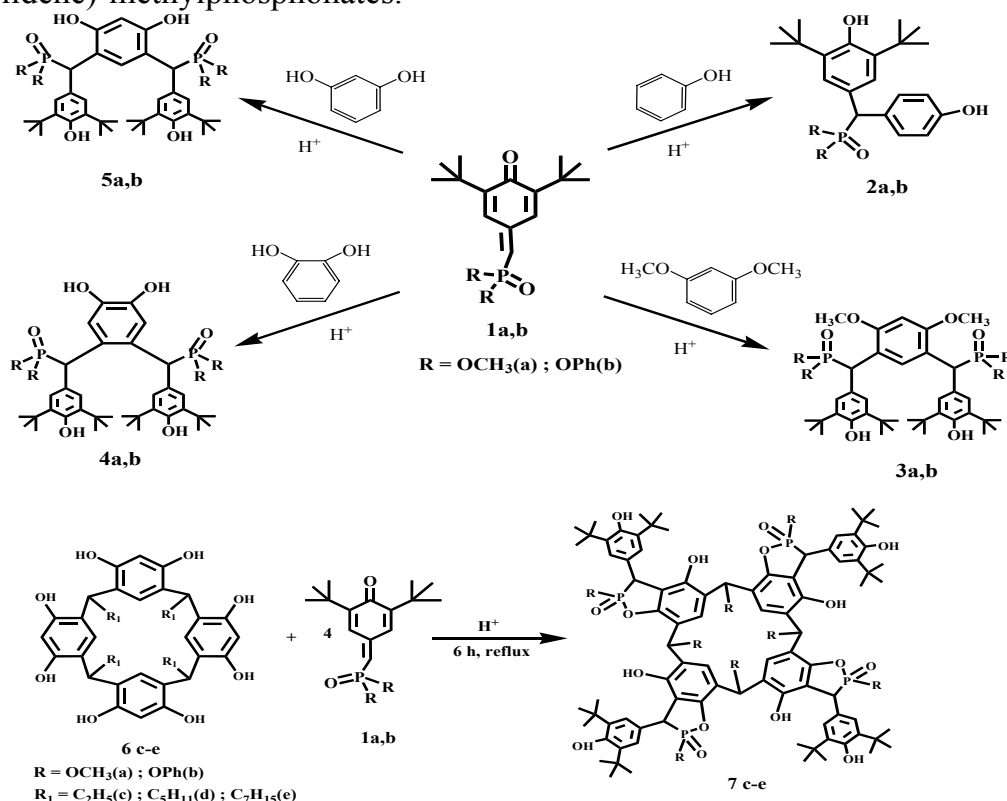
1 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Laboratory of Organoelemental Synthesis, Kazan, Russia

2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Laboratory of Diffraction Research Methods, Kazan, Russia

3 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Laboratory of Physical-Chemical Analysis, Kazan, Russia

shaekhov@iopc.ru

Important property of the polyphenolic compounds that define use *in vivo* and synthetic materials is high antioxidant activity and ability to form stable radicals. This property is most full shown in sterically hindered phenols many of which are used in industry for production of polymeric materials and also in synthesis of drugs. We developed methods of synthesis of a wide range phosphorylated polyphenolic compounds containing sterically hindered fragments with use dimethyl(diphenyl)(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dienylidene)-methylphosphonates.



The structure of synthesized compounds was proved by NMR ^1H , ^{13}C , IR spectroscopy, mass-spectrometry (MALDI) and element analysis.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (grant no. 11-03-00416-a), and as part of the Federal Program State contract № II837.

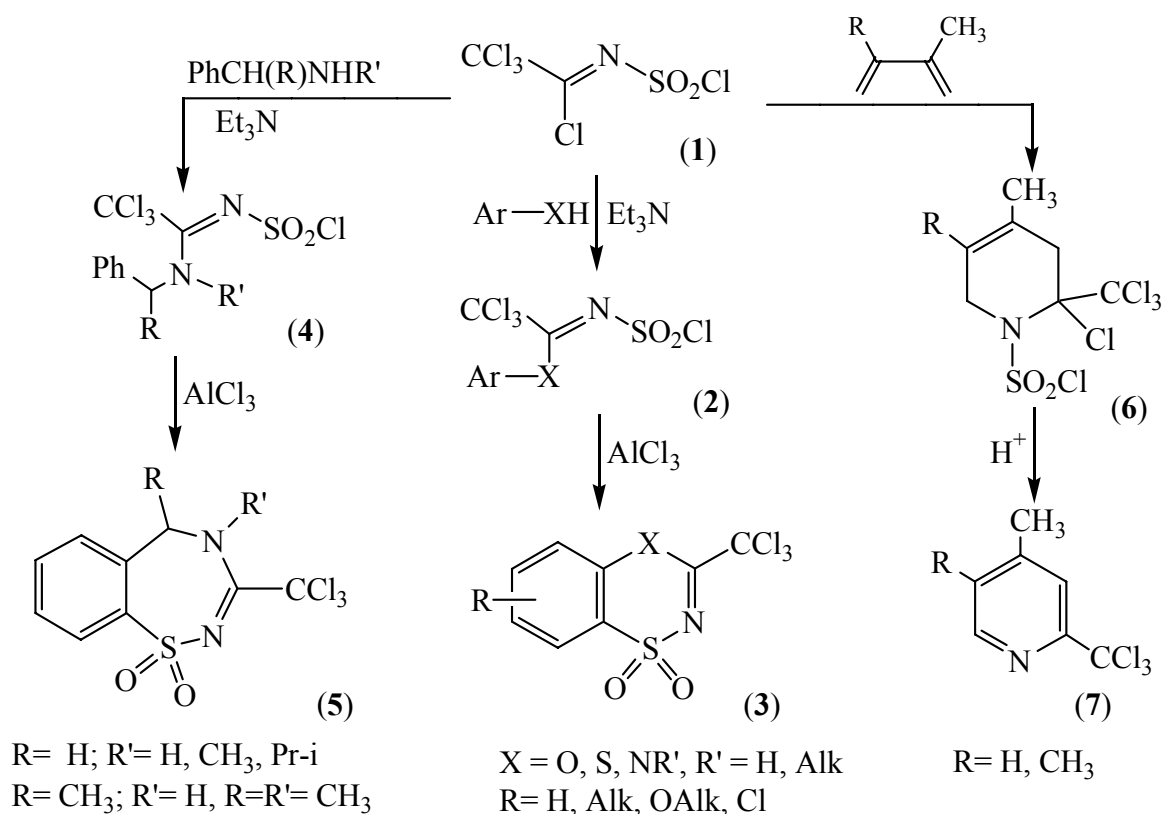
N-CHLOROSULFONYLTRICHLOROACETIMIDOYL CHLORIDE: NOVEL CONVENIENT REAGENT FOR HETEROCYCLIZATION

A.A. Shalimov
C.V. Lobanov
P.P. Onysko
A.D. Sinita

Institute of Organic Chemistry, NAS of Ukraine, Kyiv-94, Ukraine
ashal@ukr.net

Synthetic approach for N-chlorosulfonyltrichloroacetimidoyl chloride (**1**) was developed and potentialities of this novel 1,3-CNS-bielectrophilic reagent in construction of biologically promising six- and seven-membered heterocyclic systems were disclosed.

It was shown that (**1**) reacts regioselectively with phenols, thiophenols or aromatic amines to give 4,2,1-benzoxathiazines, 1,2,4-benzodithiazines and 1,2,4-benzothiadiazines (**3**) ($X = O, S, NR'$), respectively. The reaction involves initial nucleophilic substitution of imidoyl chlorine atom followed by intramolecular Friedel-Crafts cyclization of intermediates (**2**).



The reaction of (**1**) with benzylamines represents a novel convenient approach to difficultly accessible 1,2,4-benzothiadiazepines (**5**) by cyclization of amidines (**4**).

N-Chlorosulfonyltrichloroacetimidoyl chloride (**1**) reveals itself as reactive dienophile in the reactions with dienes. It was shown that [2+4] cycloaddition with substituted butadienes proceeds regioselectively and leads to tetrahydropyridines (**6**) which are readily transformed into 2-trichloromethylpyridines (**7**) under acidic conditions.

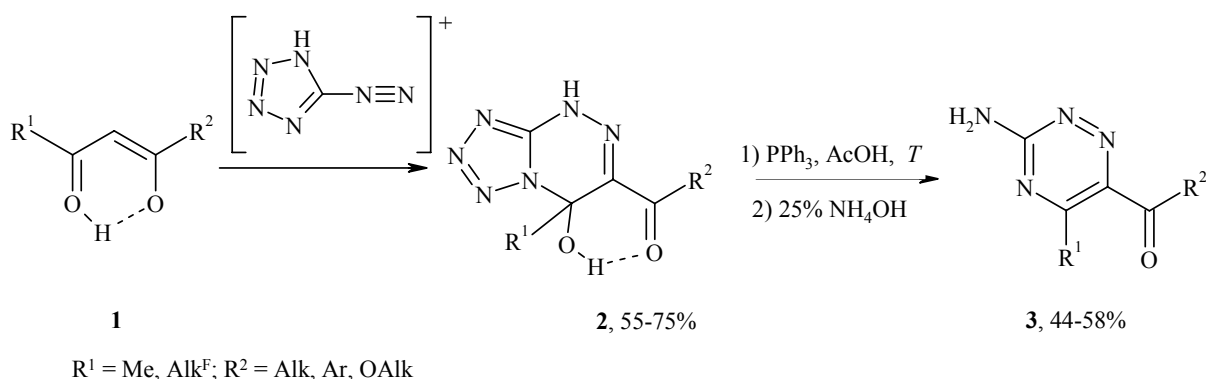
The structure of heterocycles synthesized was confirmed by ^1H , ^{13}C NMR, IR spectra and X-ray analysis.

SYNTHESIS OF 4-HYDROXY-4-ALKYL-4,7-DIHYDROTETRAZOLO[5,1-c][1,2,4]TRIAZINES AND THEIR TRANSFORMATIONS

E.V. Schegolkov
Ya.V. Burgart
V.I. Saloutin

Institute of Organic Synthesis UD RAS, Ekaterinburg, Russia
 schegolkov@ios.uran.ru

The interaction of both non-fluorinated and polyfluoroalkyl-containing 1,3-dicarbonyl compounds **1** with tetrazolyldiazonium salts yields the stable 4-hydroxy-4-(polyfluoro)alkyl-1,4-dihydrotetrazolo[5,1-c][1,2,4]triazines **2**. It is typical for azo coupling reactions of polyfluoroalkyl-containing 1,3-dicarbonyl compounds with hetaryldiazonium salts having the NH group in their α -position,¹⁻³ while such reactions of non-fluorinated 1,3-dicarbonyl compounds are revealed for the first time.



We have failed to achieve the dehydration effect of the fluoroalkyl-containing heterocycles **2**. However, we have found that the destruction of tetrazole ring occurs in boiling acetic acid in the presence of triphenylphosphine to result in the aromatized 3-amino-5-(polyfluoro)alkyl-6-acyl(benzoyl)-1,2,4-triazines **3**.

References:

1. Shchegol'kov, E.V.; Sadchikova, E.V.; Burgart, Ya.V.; Saloutin, V.I. *Russ. Chem. Bull., Int. Ed.* **2008**, 57, 612.
2. Shchegol'kov, E.V.; Sadchikova, E.V.; Burgart, Ya.V.; Saloutin, V.I. *Russ. J. Org. Chem.* **2009**, 45, 572.
3. Shchegol'kov, E.V.; Khudina, O.G.; Anikina, L.V.; Burgart, Ya.V.; Saloutin, V.I. *Pharmaceut. Chem. J.* **2006**, 40, 373.

This work was financed by the Russian Foundation for Basic Research (Project No. 09-03-00274a), the Ministry Education and Science of the Russian Federation (State Contract No. 02.740.11.260), the Project of the Program of UB RAS 09-P-3-2001, and the State Program for Support of Leading Scientific School (No. 65261.2010.3).

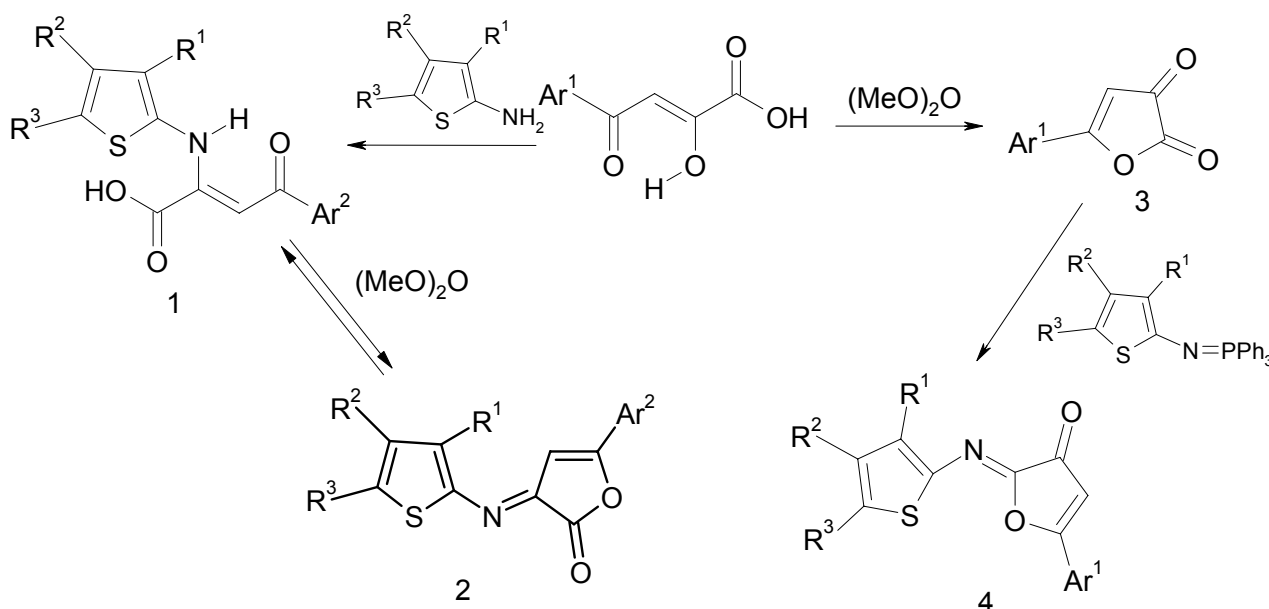
SYNTHESIS AND CHEMICAL TRANSFORMATION OF DERIVATIVES 2(3)-THIENYLIMINO-2(3)*H*-FURAN-3(2)-ONES

S.A. Shipilovskikh
A.O. Panchenko
A.E. Rubtsov

Perm State University, Natural and Biological Active Compounds,
Perm, Russia
Shipilovskikh@psu.ru

2(3)-Imino-2(3)*H*-furan-3(2)-ones are a class of highly reactive compounds, on the basis of which it is possible to obtain various heterocyclic and acyclic compounds [1]. From literature it is known, that derivatives of 2-aminothiophenes have a large range of biological activity [2].

With this information we have great interest in synthesis of derivatives 2(3)-iminofuran-3(2)-ons with thiophene substituent. For this purpose we have synthesized compounds 2,4.



$\text{Ar}^1 = \text{Ph}$, 4- MeC_6H_4 ; 4- MeOC_6H_4 ; 4,2- $(\text{MeO})_2\text{C}_6\text{H}_4$; 4- BrC_6H_4 ; 4- ClC_6H_4 ; 4- EtOC_6H_4 ; 4- $\text{C}_5\text{H}_5\text{O}$; 4- FC_6H_4 . $\text{R}^1 = \text{COOEt}$; CN . $\text{R}^2 + \text{R}^3 = (\text{CH}_2)_4$; $(\text{CH}_2)_3$; CH_3 , CH_3 ; CH_3 , Ph ; Ph , CH_3 ; H , Ph ; Ph , H ; Ph , Ph ; Ph , PhCH_2 .

References:

1. Sabnis, R. W. *Sulfur Reports*, **16** (1), 1-17 (1994).
2. Zalesov, V.V., Rubtsov, A.E. *Chem. of Heterocyclic Compounds*, **40**(2), 133-153 (2004).

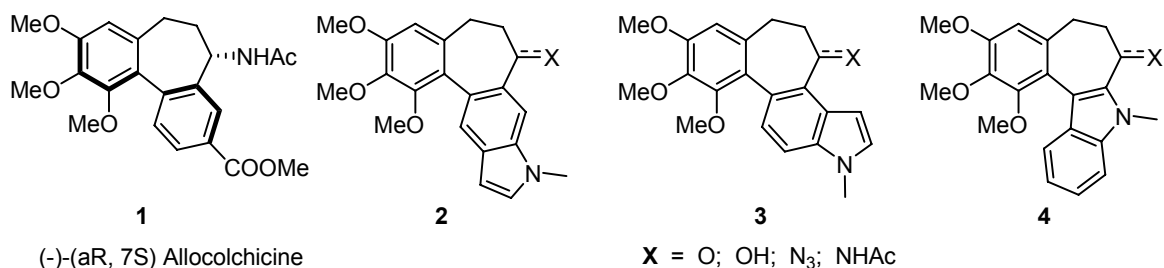
This study was performed under financial support by the Russian Foundation for Basic Research (project no. 11-03-00882)

SYNTHESIS AND BIOLOGICAL EVALUATION OF INDOLE-CONTAINING ALLOCOLCHICINOIDS

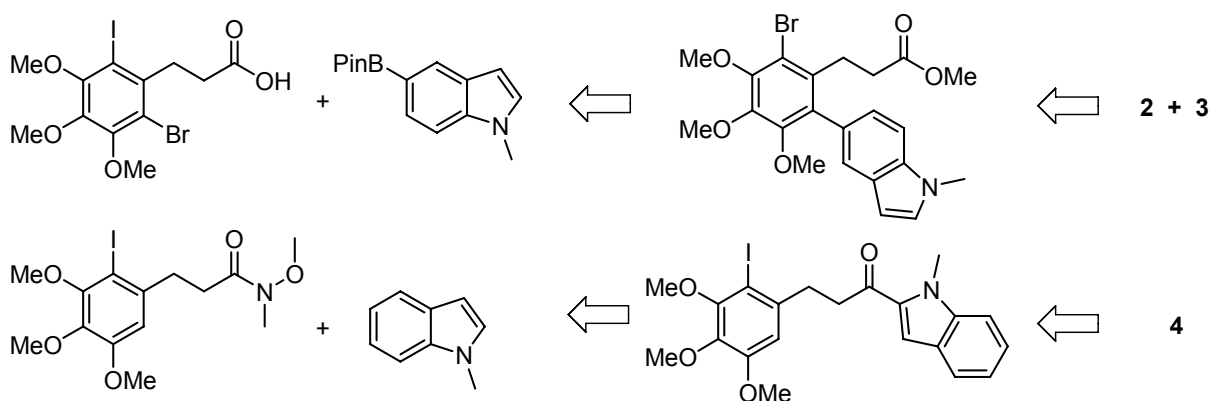
N.S. Sitnikov¹
 J. Velder²
 A. Prokop³
 A.Yu. Fedorov¹
 H.-G. Schmalz²

1 - N.I. Lobachevsky Nizhny Novgorod State University, Organic Chemistry Department, Nizhny Novgorod, Russia
 2 - University of Cologne, Organic Chemistry Department, Cologne, Germany
 3 - Children's Hospital Cologne, Department of Paediatric Oncology, Cologne, Germany
 nikolaj-sitnikov@ya.ru

(-)-Colchicine [1], the major alkaloid from *Colchicum autumnale*, is known for decades as an efficient antimitotic agent able to inhibit microtubule formation (tubulin polymerization) in living cells, thus causing mitosis arrest in the metaphase. While high toxicity has prevented its use as an antitumor agent, colchicine still represents an important lead structure for drug discovery [2]. Allocolchicine (**1**) [1] is a constitutional isomer of colchicine bearing a six membered aromatic C-ring instead of the tropolone moiety. Allocolchicine itself as well as its analogues show promising biological activities similar to colchicines. Herein we report the synthesis of a series of novel allocolchicine analogs **2-4** containing 1-methyl-1*H*-indolyl fragment.



The fused four-membered carbocyclic skeleton in compounds **2**, **3** was constructed via Suzuki – Miyaura cross-coupling reaction and subsequent Friedel – Crafts annulation. In turn, Weinreb ketone synthesis and subsequent direct intramolecular C-H arylation reaction gave access to compounds of type **4**.



Preliminary biological screening of compounds **2**, **3** on BJAB tumor cell line revealed high antimitotic and apoptose-inducing activity (nanomolar or subnanomolar concentration range) along with particularly low unspecific cytotoxicity as determined by LDH-release assay.

	colchicine	2 (X = O)	3 (X = O)	2 (X = OH)	3 (X = OH)	2 (X = NHAc)	3 (X = NHAc)
IC ₅₀ [μ M]	0.02	0.0025	< 0.001	0.03	0.008	0.08	0.03
AC ₅₀ [μ M]	0.03	0.005	< 0.001	0.1	0.01	0.5	0.05

References:

- [1] O. Boye, A. Brossi in *The Alkaloids* (Eds.: A. Brossi, J. A.Cordell), Academic Press, New York, **1992**, 41, 125.
 [2] G A. Dorlans, B.Gigant, R. B. G. Ravelli et al., *Proc. Natl. Acad.Sci. USA*, **2009**, 106, 13775

Acknowledgements - this work was supported by Russian Foundation for Basic Research (09-03-00647-a), German Academic Exchange Service (DAAD № A/08/79551), Council for grants under the President of Russia (МД-5606.2010.3).

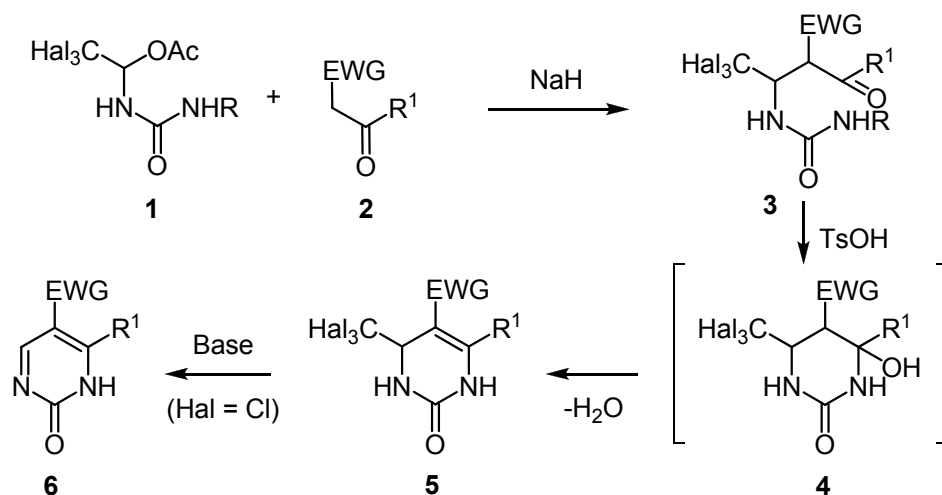
SYNTHESIS OF 5-FUNCTIONALIZED 4-TRIHALOMETHYL-1,2,3,4-TETRAHYDRO- PYRIMIDIN-2-ONES

P.A. Solovyev
A.A. Fesenko
A.D. Shutalev

Moscow State Academy of Fine Chemical Technology, Department of
Organic Chemistry, Moscow, Russia
paulnighti@gmail.com

4-Trihalomethyl-1,2,3,4-tetrahydropyrimidin-2-ones are of great interest as potentially biologically active compounds and starting materials for the synthesis of various heterocycles. However no methods for the preparations of the above-mentioned compounds exist so far. In continuation of our studies on synthesis of hydrogenated nitrogen-containing heterocycles we report here a general approach to 4-trichloromethyl- and 4-trifluoromethyl-1,2,3,4-tetrahydropyrimidin-2-ones.

N[(1-Acetoxy-2,2,2-trihalo)ethyl]ureas **1** obtained in two steps from chloral hydrate or fluoral hydrate and urea were used as starting materials. Reaction of **1** with sodium enolates of β -oxoesters, 1,3-diketones or arylsulfonylketones **2** in MeCN or THF at room temperature gave the corresponding oxoalkylureas **3** in high yields.



Hal = Cl, F; EWG = COOEt, Ac, Bz, SO₂Ph, Ts; R = H, Ac; R¹ = Me, Ph, CF₃

Treatment of **3** (R = H) with TsOH in refluxing MeCN or EtOH led to heterocyclization of **3** into hydroxypyrimidines **4** followed by dehydration of the latter. As a result, target 4-trichloromethyl- and 4-trifluoromethyl-substituted pyrimidinones **5** were formed in good yields. These compounds can also be obtained by refluxing of **3** (R = Ac) in EtOH in the presence of TsOH.

We have shown that trichloromethyl-substituted pyrimidines **5** in the presence of bases (NaH, DBU) transform into previously hardly available 5-functionalized 1,2-dihydropyrimidin-2-ones **6** via elimination of chloroform.

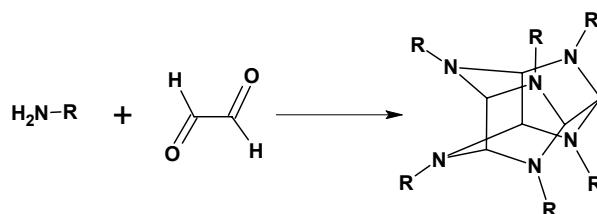
SYNTHESIS AND TRANSFORMATIONS OF HEXAAZAISOWURTZITANE DERIVATIVES

S.V. Sysolyatin

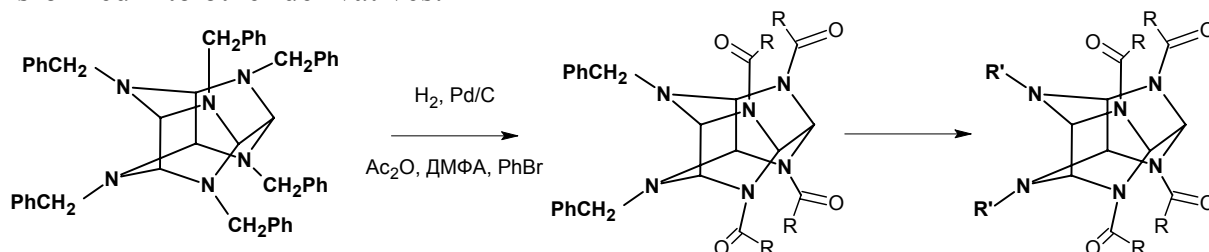
Institute for Problems of Chemical and Energetic Technologies, Siberian
Branch of the Russian Academy of Sciences (IPCET SB RAS)
admin@ipcet.ru

The interest in 2,4,6,8,10,12-hexaazatetracyclo[5,5,0,0^{3,11},0^{5,9}]dodecane (hexaazaisowurtzitane) derivatives, which were previously synthesized exclusively to obtain high-energy compounds [1], has been attracted by their unusual structure. These species are caged nitrogen heterocycles, which implies them to have biologically active properties. *In vivo* studies with mice have corroborated their biological activity and revealed their low toxicity (LD₅₀ >1000 mg/kg), which allows hexaazaisowurtzitane derivatives to be classified as Toxicity Class III materials (slightly toxic) [2].

Hexaazaisowurtzitane derivatives are prepared by condensation of glyoxal with primary amines.



The use of amines with substituents at α -position as well as amides does not result in the formation of the isowurtzitane structure. When benzylamine is condensed with glyoxal, there is formed hexabenzylhexaazaisowurtzitane in 80% yield, which can readily be transformed into other derivatives:



Synthesis methods and transformations of different hexaazaisowurtzitane derivatives are considered.

References:

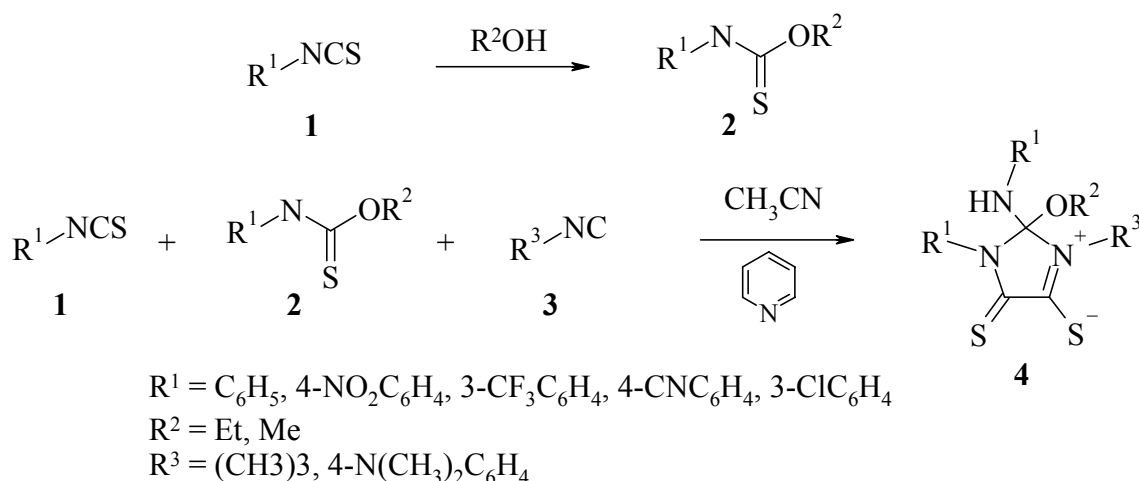
1. S.V. Sysolyatin, A.A. Lobanova, Yu.T. Chernikova, G.V. Sakovich, Synthesis methods and properties of hexanitrohexaazaisowurtzitane, *Uspekhi khimii*, 2005, Vol. 74, No. 8, pp. 830-838.
2. T.G. Tolstikova, E.A. Morozova, S.V. Sysolyatin, Yu.I. Zhukova, A.I. Kalashnikov, V.N. Surmachev, Synthesis and biological activity of 2,4,6,8,10,12-hexaazatetracyclo [5,5,0,0^{3,11},0^{5,9}] dodecane derivatives, *Chemistry for Sustainable Development*, 2010, Vol. 18, No. 4, pp. 511-516.

NEW THREE-COMPONENT REACTION OF ISOCYANIDES WITH THIOCARBAMATES AND ISOTHIOCYANATES

M.I. Tokareva
M.A. Mironov

Urals Federal University, Chemical Technology Department,
Ekaterinburg, Russia
tokarevami@mail.ru

We found new three-component reaction of isocyanides with thiocarbamates and isothiocyanates giving a new heterocyclic system - 5-thioxo-2,5-dihydro-1*H*-imidazolium-4-thiolate. These compounds may be the starting reagents to a new method for the asymmetric ethandithioamides. As the imidazolium-4-thiolates as the ethandithioamides are potential complexing agents for analytical chemistry, reagents for photolithography and thermography technologies, laser technologies, as well potential biologically active compounds¹⁻⁵.



Structural assignments for products **4** were made on the basis on ¹H NMR, mass spectrometry data and X-rays analyse. Introduction of electron-withdrawing substituents in isothiocyanate and electron-donating substituents in thiocarbamates results in shortening of the reaction time and increase yield of the product.

References:

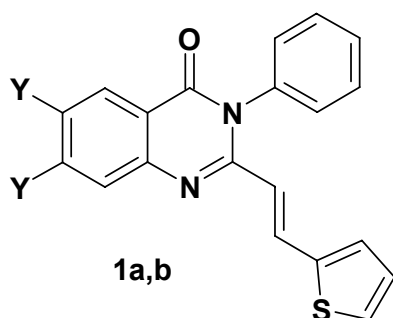
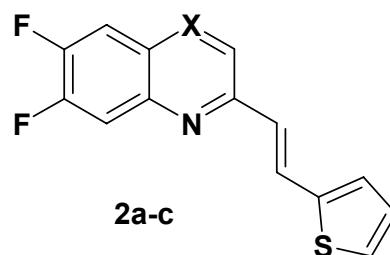
1. Hurt R.N. Review of scientific and patent literature on dithiooxamide: Its substituted derivatives and their metal complexes. Mallinckrodt Chemical Works, St. Louis, Mo., **1963**.
2. Xerox Corp., British Patent 1,029, 997 (May 18, **1966**).
3. Dewar M.J.S. and Talati A.M. // *J. Am. Chem. Soc.* **1964**. Vol. 86. P. 1592.
4. Haske B.J., Matthews M.E., Conkling J.A., Perzanowski H.P. // *J. Org. Chem.* **1967**. Vol. 32. P. 1579-1583.
5. Aragoni M.C., Arca M., Demartin F., Devillanova F.A., Garau A. et al. // *Journal of the American Chemical Society*. **1999**. Vol. 121. P. 7098-7107.

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF 2-(E)-(THIENYL-2)VINYLDERIVATIVES OF FLUORINATED BENZAZINES

T.V. Trashakhova¹E.V. Nosova¹N.A. Malih¹M.S. Valova²G.N. Lipunova²V.N. Charushin²1 - Ural Federal University named after the First President of Russia
Boris N. Yestsin, Yekaterinburg, Russia2 - I.Ya. Postovskiy Institute of Organic Synthesis, Ural Division of
the Russian Academy of Sciences, Yekaterinburg, Russia
ten786@mail.ru

Organic molecules that contain styryl moiety are an important fluorescent class and show a number of attractive photophysical and electro-optical properties. It is known that replacing of aryl fragment by π -excessive thiophene leads to large red-shift in absorption and emission spectra.

The synthesis of 3-phenyl-2-(*E*)-(2-thienyl)vinylquinazolin-4-ones **1a,b** was achieved by refluxing of correspondent 2-methylquinazoline with thiophen-2-carbaldehyde and sodium acetate in acetic acid during 12-36 h in 36-70% yield. Novel *trans*-2-(2-thienyl)vinyl-6,7-difluorobenzazines **2a-c** have been synthesized by condensation of 6,7-difluoroquinazoline, 2-methyl-6,7-difluoroquinolin-4-carboxylic acid or 2-methyl-6,7-difluoroquinoxaline with thiophen-2-carbaldehyde under reflux in glacial acetic acid in the presence of AcONa during 6-12 h.

**1a,b****2a-c**

1: Y=H (**a**), F(**b**); **2:** X=CH (**a**), C-COOH (**b**), N (**c**).

Upon photoexcitation, compounds **1**, **2** display photoluminescence in MeCN solution and demonstrate emission wavelength 439-502 nm. Derivative **2c** has the largest value of quantum yield (0.016). At decrease in temperature with 273 to 77 K intensity of emission increases in 77-143 times.

This work was supported by the Russian Foundation for Basic Research (grant 11-03-00718), the Grant of the Progressive Scientific Schools NSh-65261.2010.3 and State Contract GK-02.740.11.0260.

Yu.G. Trishin
M.V. Shafeeva
L.A. Tamm
M.A. Yazvenko
E.A. Artemenko
G.V. Votintseva
A.I. Medvedeva

REACTIONS OF PERFLUOROCARBOXYLIC ACIDS WITH MONOTERPENS

St. - Petersburg State Technological University of Plant Polymers,
Department of Organic Chemistry, St. - Petersburg, Russia
trish@YT4470.spb.edu

Addition of perfluorocarboxylic acids (PFCA) to the olefins is one of the important methods of esters $R^F C(O)OR$ synthesis. The properties such esters vastly differ from characteristic anfluorinated analogues. Such compounds containing as R residue of terpens are very interesting as perspective biologically active material. We found that selectivity of addition PFCA to monoterpens is mainly defined the structure of monoterpens in reaction with electrofilic reagents undergo the different rearrangements.

Perfluoroacylation of camphene by carboxylic perfluoroaliphatic acids is chemo- and stereoselective and result in isobornylperfluoroacylates (yield 85-90%). In reaction of such acids with limonene according to conditions participate only exocyclic or both bonds $C=C$. As a result are formed terpinylperfluoroacylates or terpinylbisperfluoroacylates (yield 70-85%). It was found that rate these reactions decrease with an increase of carbon acid chain.

However addition of perfluorobenzoic and 2,3,4,5-tetrafluorobenzoic acids to camphene and limonene occurs only in the hard conditions (heating, catalyst - a sulfuric acid) and is accompanied by the partial isomerization of monoterpens.

The interaction PFCA with α - and β -pinenes, α - and γ -terpinenes is characterized variety of rearrangements of the intermediates. This processes do not allow to get terpenilperfluoroacylates with predominance one of the isomers.

Addition of PFCA to endocyclic bond of cycloalkenes investigated in detail by the example of cyclohexene.

All new compounds were characterized by ^1H , ^{13}C , ^{19}F NMR, IR spectrometry.

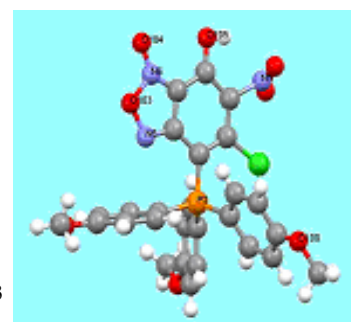
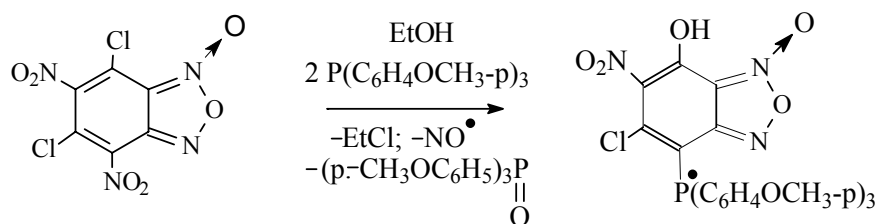
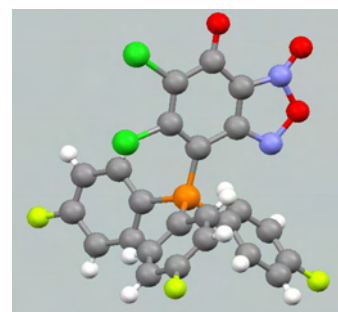
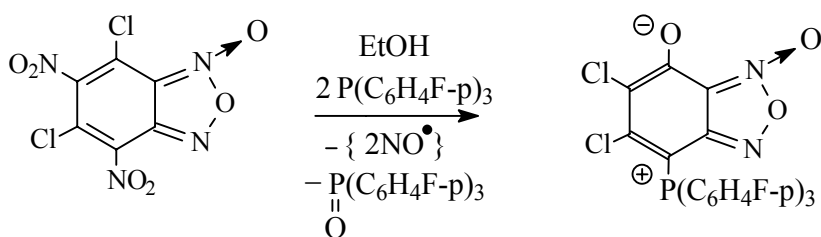
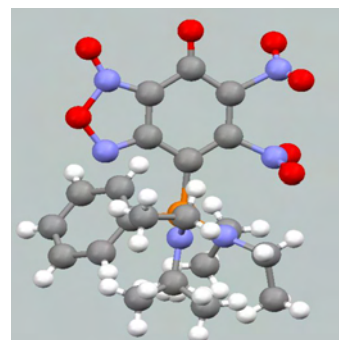
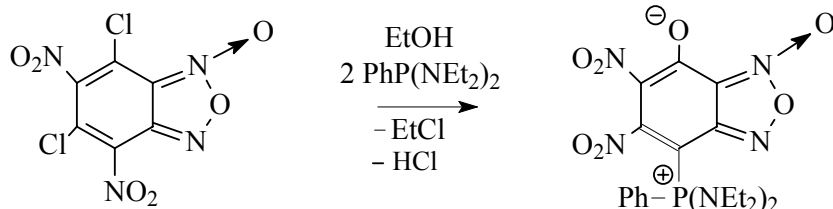
SOME NEW PHOSPHORYLATION REACTIONS OF 5,7-DICHLORO-4,6-DINITROBENZOFUROXAN

E.V. Tudriy¹
 I.V. Galkina¹
 O.N. Kataeva¹
 L.M. Yusupova²
 V.I. Galkin¹

1 - Kazan Federal University, A.M. Butlerov Chemical Institute,
 Kazan, Russia

2 - Kazan State Technological University, Kazan, Russia
 tev_25@mail.ru

In continuation of our systematic investigations of phosphorylation of 5,7-dichloro-4,6-dinitrobenzofuroxan by various tertiary phosphines we report about some new results in this field.



The structure of obtained products has been confirmed by X-ray analysis, mass-spectrometry, elemental analysis, NMR ³¹P, IR, EPR, TG/DSC analysis.

Synthesized products showed high antibacterial biological activity.

The research is supported by grants of Academy of Sciences of Tatarstan Republic.

UNUSUAL INTERACTION OF 2-METHYLRESORCINOL AND PYROGALLOL WITH PHOSPHORYLATED AMINOACETALS

L.I. Vagapova¹
A.R. Burilov¹
D.R. Sharafutdinova²
J.K. Voronina²
M.A. Pudovik¹

1 - A.E. Arbusov Institute of Organic and Physical Chemistry Kazan Scientific Center of the Russian Academy of Science, Department of Organoelemental Chemistry, Kazan, Russia

2 - A.E. Arbusov Institute of Organic and Physical Chemistry Kazan Scientific Center of the Russian Academy of Science, Department of Physical-chemistry Research, Kazan, Russia

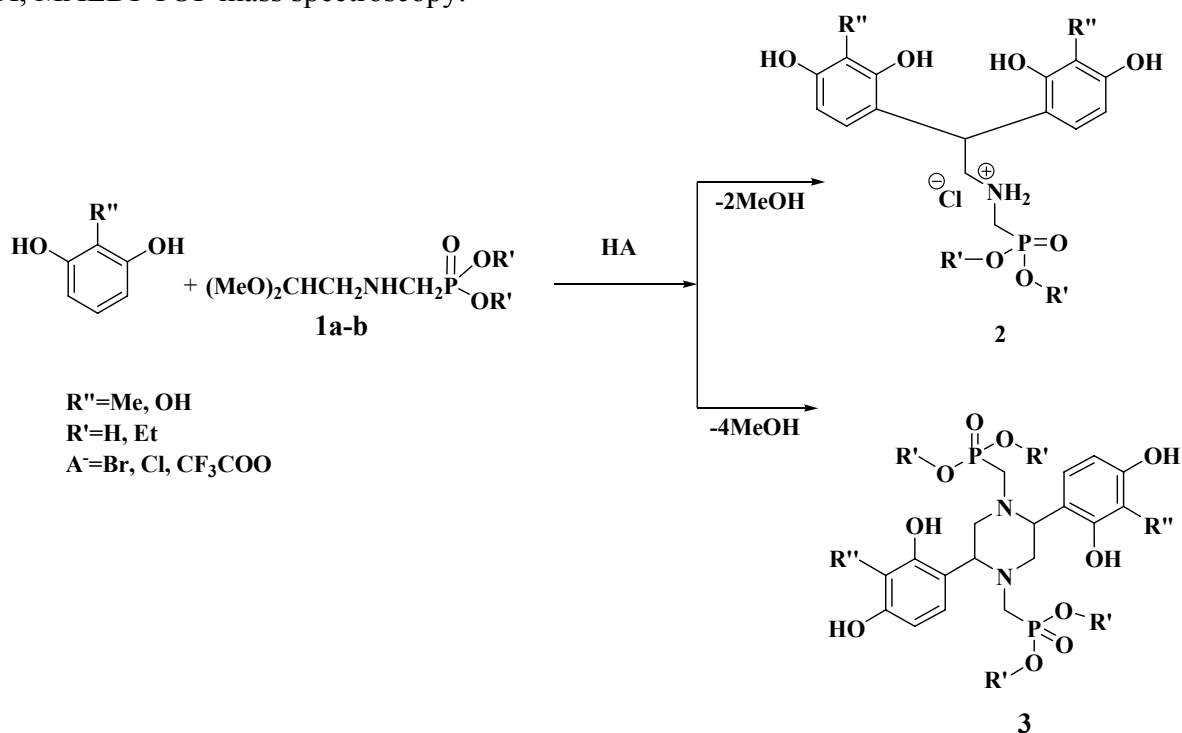
vagapovan@mail.ru

Aminophosphonates and their peptidic analogues are mostly recognized as the biologically active compounds with variety of useful activities ranging from inhibitors of many metalloenzymes to herbicides. Thus the availability of new derivatives of aminophosphonates is still very important.

Early it was shown that condensation of (P/N)-containing acetals with resorcinol and its derivatives can lead, depending on experimental conditions, to the formation of calix[4]resorcinols or diarylmethane compounds containing on the lower rim organoelemental fragments.

In order to obtain new aminophosphonates derivatives we have investigated the condensation of 2-methylresorcinol, pyrogallol with phosphorylated aminoacetals **1**. It has appeared that this reaction leads to the formation of two products: diarylmethane (**2**) and piperazine (**3**) derivatives, containing in its structure phosphonate groups.

The structures of synthesized compounds were proved by means ¹H, ³¹P NMR spectroscopy, RCA, MALDI-TOF mass spectroscopy.



The influence of experimental conditions (the nature of acids, solvents, stoichiometric ratio of the starting reagents) on the result of this reaction will be discussed.

This work was supported by the Russian Foundation for Basic Research (grant 11-03-00416a)

E.V. Verbitskiy
E.M. Cheprakova
P.A. Slepukhin
O.N. Zabelina
M.G. Pervova
M.A. Samorukova
G.L. Rusinov
V.N. Charushin

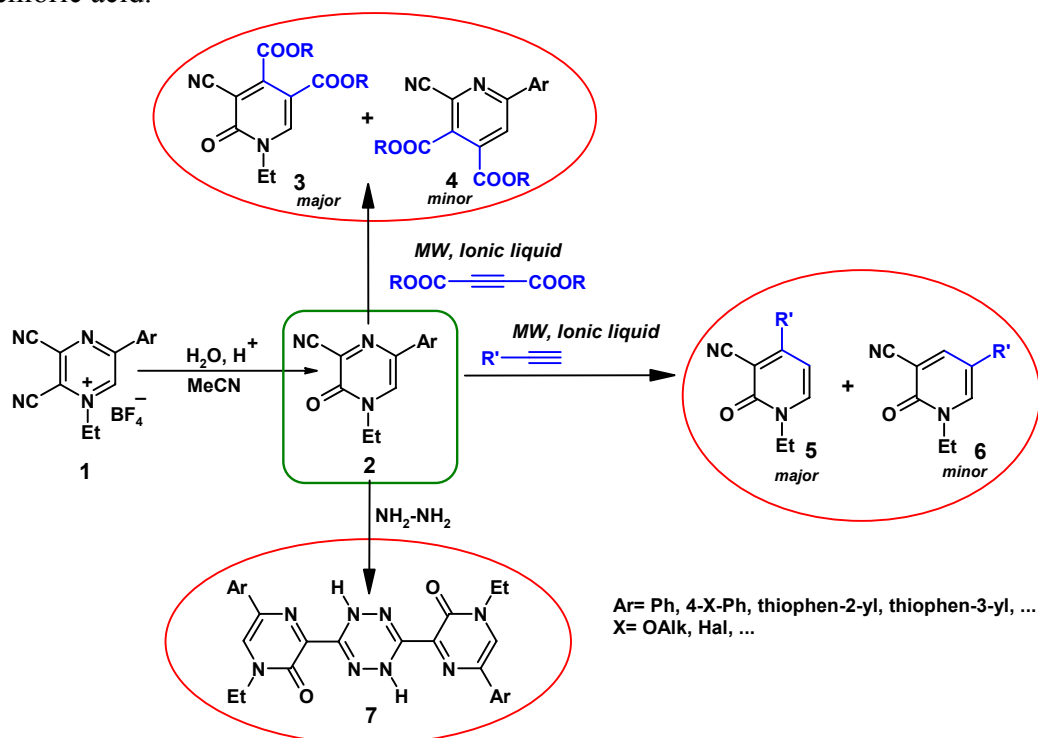
REACTIONS OF 3 CYANO-1-ETHYL-5-(HET)ARYL-2-(1H)-PYRAZINONES

I.Ya. Postovsky Institute of Organic Synthesis (Ural Division of the Russian Academy of Sciences), Ekaterinburg, Russia
Verbitskiy@ios.uran.ru

2(1H)-Pyrazinones **2** are easily accessible from corresponding from 5-(het)aryl-substituted 1-ethyl-2,3-dicyano-1,4-diazinium salts **1** through acidic hydrolysis.

5-(Het)aryl-1-ethyl-3-cyano-2(1H)-pyrazinones **2** have been found to undergo intermolecular hetero-Diels-Alder reaction with acetylenes under controlled microwave irradiation. In case of symmetric acetylenes, for example dimethylacetylenedicarboxylate, these Diels-Alder reaction leads to a mixture of pyridone **3** and pyridine **4** products. It should be noted that the formation of 2(1H)-pyridone **3** is a predominant cycloaddition reaction. On the other hand, reactions with terminal acetylenes have been found to result in the formation of a mixture 4-(het)aryl- **5** and 5-(het)arylsubstituted **6** 2(1H)-pyridones without of the corresponding pyridine derivatives. Regioselectivity of these processes have been studied by NMR spectroscopy and GC/MS data.

Also, 3,6-bis(2-(1H)-pyrazinon-3-yl)-1,4-dihydro-1,2,4,5-tetrazines **7** can be prepared by the reaction of 5-(het)aryl-1-ethyl-3-cyano-2(1H)-pyrazinones **2** with hydrazine hydrate in the presence of hydrochloric acid.



Compounds obtained are of interest as ligands for the synthesis of complexes.

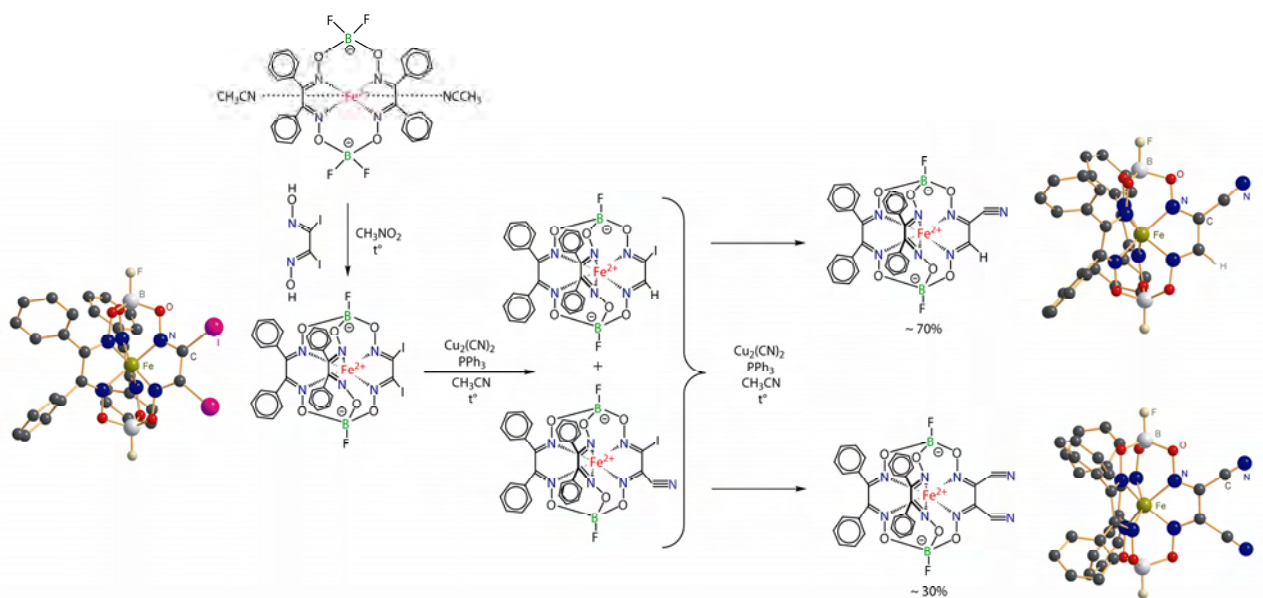
This work was supported by the Programs of Ural Division of RAS 09-II-3-2004, 09-II-3-1015, 09-T-3-1022, State Contract № 02.740.11.0260., the Russian Foundation for Basic Research (grant no. 09-03-12242-ofi_m) and the State Program for Supporting Leading Scientific of the Russian Federation (grant no. NSh-65261.2010.3)

FIRST MACROBICYCLIC COMPLEXES WITH INHERENT NITRILE SUBSTITUENTS AND UNEXPECTED DEHALOGENATION – REDUCTION REACTION AT A CLATHROCHELATE FRAMEWORK

Y.Z. Voloshin¹
A.S. Belov¹
O.A. Varzatskii²
Z.A. Starikova¹
E.G. Lebed¹

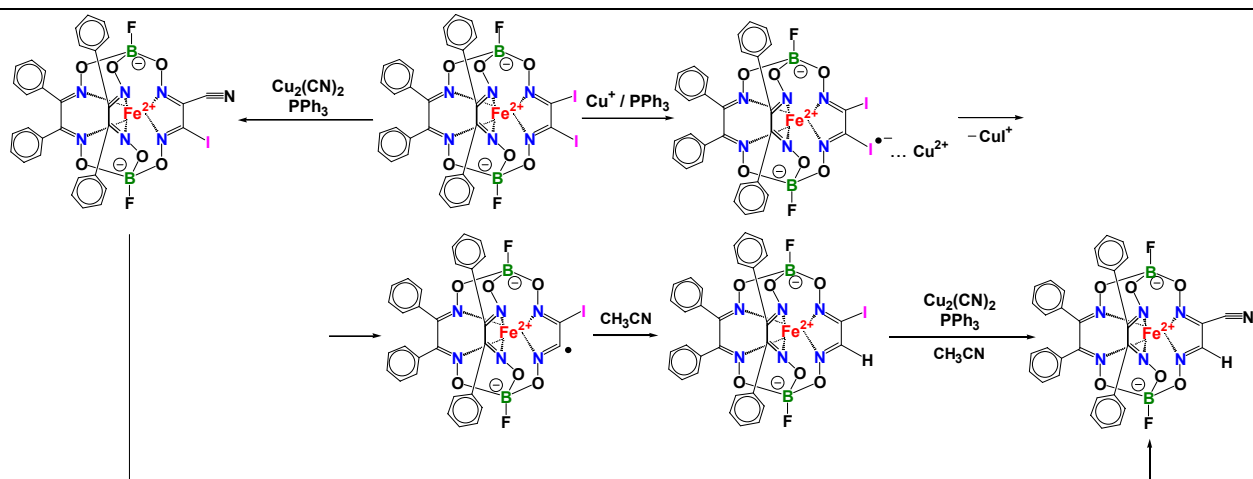
1 - Nesmeyanov Institute of Organoelement Compounds RAS,
Moscow, Russia
2 - Vernadskii Institute of General and Inorganic Chemistry NANU,
Kiev, Ukraine
voloshin@ineos.ac.ru

The monoribbed-substituted mono- and difunctionalized iron(II) macrobicycles with inherent nitrile substituents were obtained for the first time by the reaction of the iron(II) diiodoclathrochelate with copper(I) cyanide – triphenylphosphine complex under the mild conditions (Scheme 1).



Scheme 1

The target dinitrile clathrochelate is a minor product of this reaction, whereas the major product contains one cyano group in its molecule. The single crystals suitable for the X-ray crystallography were obtained only in the case of the crystallization from a mixture of the products and their unit cell contains one dinitrile and one mononitrile molecules (Scheme 1). The mechanism of the dehalogenation – reduction reaction that resulted in substitution of iodine atoms by cyano group and hydrogen atom (Scheme 2) includes the anion-radical hydrodehalogenation of the diiodoclathrochelate with acetonitrile as a source of hydrogen atom, whereas the product underwent a substitution with cyano group only. The copper(I) cyanide – triphenylphosphine – acetonitrile system is proposed as a tool for the synthesis of nitrile derivatives of the electron-withdrawing heterocycles starting from their halogen-containing precursors.



Scheme 2

The authors gratefully acknowledge support of the RFBR (grants 09-03-00540, 09-03-00688, 10-03-00613, 10-03-01069 and 10-03-00837) and RAS (programs 6, 7 and P18)

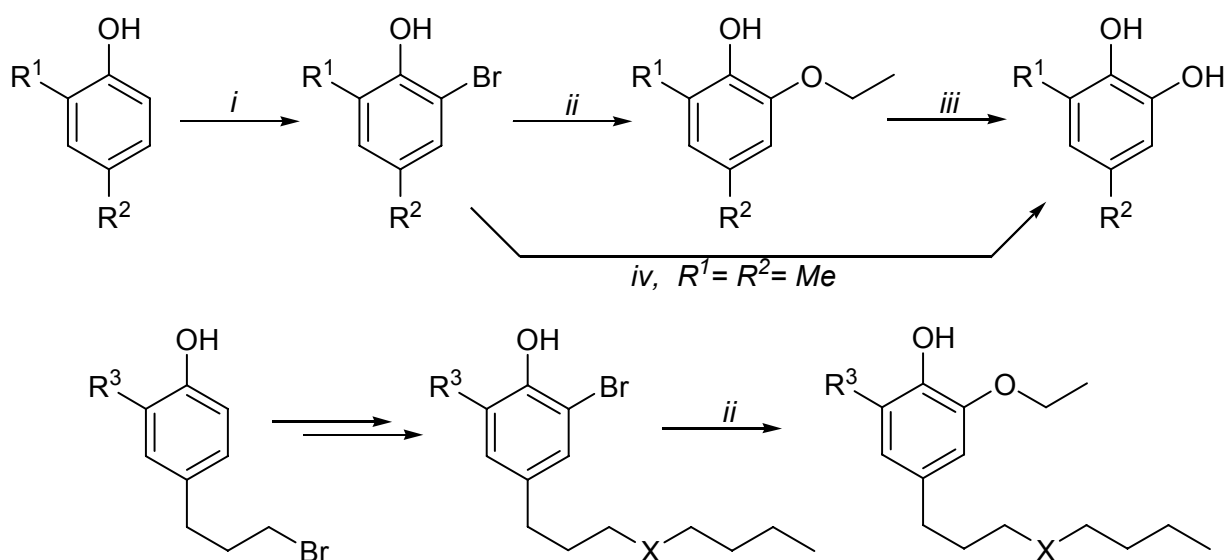
COPPER-CATALYSED COUPLING REACTION IN SYNTHESIS OF NEW ANTIOXIDANTS

S.E. Yagunov
N.V. Kandalintseva
A.E. Prosenko

Novosibirsk State Pedagogical University, Research Institute of
Antioxidant Chemistry, Novosibirsk, Russia
syagunov@yandex.ru

Extensive studies of the dependence of antioxidant activity on the structure of the phenolic fragment suggest that the activity of the most effective of the monohydric phenols is close to the theoretical limit. It causes the search for new and more effective inhibitors among the derivatives of polyhydric phenols.

The formation of carbon-heteroatom bonds by transition metal catalysed cross-coupling reaction has been the subject of significant interest during the past years. Copper-catalysed coupling of alcohols (or alkoxides) and arylhalogenides (Ullmann condensation) is a very useful method of phenol derivatives synthesis. In this work we present a very efficient procedure for the synthesis of sulfur and selen substituted alkyl derivatives of polyhydric phenols.



$R^1, R^2, R^3 = \text{H, Me, Cy, t-Bu}; \text{X} = \text{S, Se}$

i: $\text{Br}_2, \text{CCl}_4, \text{r.t.}$; *ii*: $\text{EtONa, CuI, TMEDA, DMF, EtOH, } 80^\circ \text{C}$; *iii*: $\text{HBr, AcOH, } \Delta$; *iv*: $\text{NaOH, CuSO}_4, \text{H}_2\text{O, } \Delta$

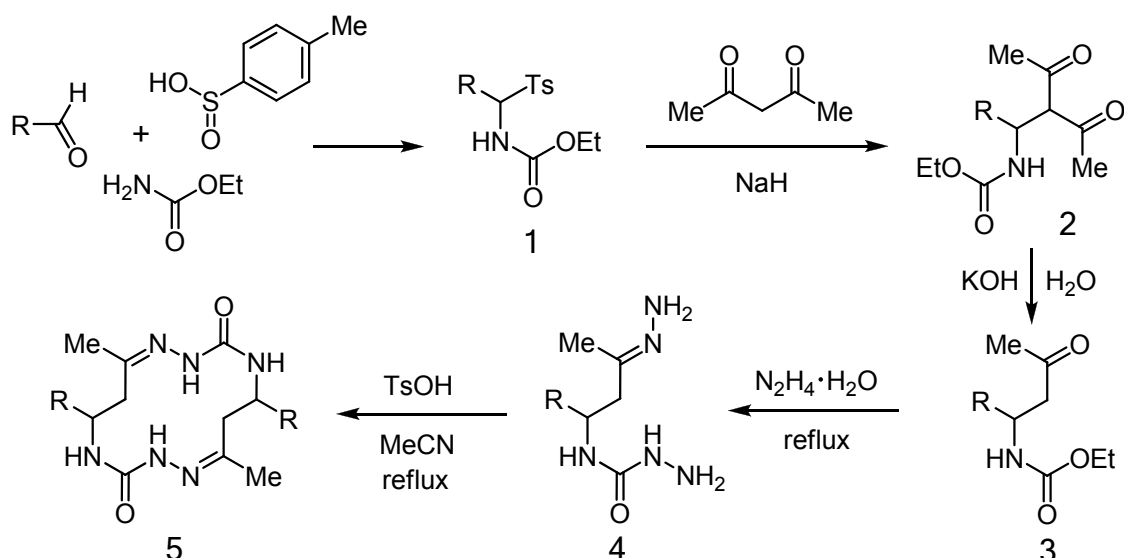
The target 2-ethoxyphenols were prepared from mono- and dialkylphenols via bromides. The sulfur and selen substituted derivatives were obtained in high yield under those conditions. It is known that water solution of alkali can be used in the same transformation. The 3,5-dimethylpyrocatechol was obtained in high yield using one stage process. The alkylpyrocatechols, sulfur and selen substituted derivatives which were prepared in this work are potentially effective antioxidants.

SYNTHESIS OF NOVEL 14-MEMBERED
HEXAAZAMACROCYCLES

I.A. Zamilatskov¹
O.M. Kuzmina¹
D.V. Albov²
A.D. Shutalev¹

1 - Moscow State Academy of Fine Chemical Technology, Department of Organic Chemistry, Moscow, Russia
2 - Moscow State University, Department of Chemistry, Moscow, Russia
joz@mail.ru

Azamacrocycles are currently of great interest owing to their useful properties. Design of new types of these compounds is an important goal of organic chemists. In continuation of our studies on hydrogenated nitrogen containing heterocycles we interested in synthesis of original polyazamacrocyclic compounds. Here we wish to report convenient approach to novel 14-membered hexaazamacrocycles.



The synthesis started with preparation of α -tosyl substituted ethyl carbamates **1** by three component condensation of ethyl carbamate, aldehydes and *p*-toluenesulfonic acid in water. Reaction of **1** with sodium enolate of acetylacetone in acetonitrile at room temperature gave the corresponding products of tosyl group substitution, carbamates **2**, in good yields. Treatment of **2** with aqueous KOH at room temperature led to formation of ethyl *N*-(3-oxobutyl)carbamates **3** in result of retro-Claisen reaction. Reflux of **3** in excess of hydrazine hydrate proceeded with incorporation of two hydrazine fragments to produce semicarbazides **4** as single (*E*)-stereoisomers. Heterocyclisation of the latters involving two molecules occurred by reflux in acetonitrile in the presence of TsOH to give previously unknown macrocyclic 1,2,4,8,9,11-hexaazacyclotetradeca-7,14-diene-3,10-diones **5**. The structures of **5** were unambiguously confirmed by NMR data and powder X-ray diffraction.

THE BLAISE REACTION AS EFFECTIVE METHOD OF FUNCTIONALIZATION OF 2-METHYLTHIO-3-CYANOPYRIDINES

V.K. Zavyalova
A.A. Zubarev
A.M. Shestopalov

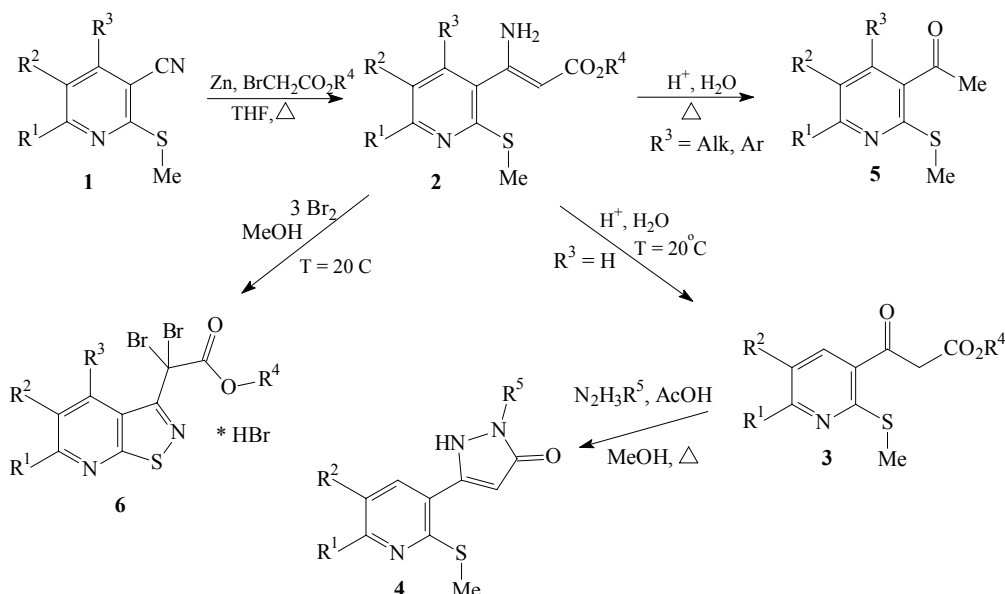
N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of
Sciences, Moscow, Russia
zvkv@ioc.ac.ru

The development of effective modification methods of the cyano group in 3-cyanopyridine-2(1*H*)-thiones and their alkylthio derivatives is an important trend, because pyridine compounds are key building blocks in preparation of biologically active compounds and for the synthesis of new fused heterocyclic systems¹.

We have studied, for the first time, the action of organometallic compounds, in particular, of methyl- and butyllithium, on substituted 3-cyanopyridine-2(1*H*)-thiones and their alkylthio derivatives **2**. Products of this reaction were used in the synthesis of fused compounds of thienopyridine, pyridothienopyran, 2,7-naphthyridine and some other classes², and 3-hetarylpyridines³.

It was found that the action of zinc dust / alkylbromoacetate system (the Blaise reaction) on substituted 2-methylthio-3-cyanopyridines **1** leads to 3-amino-3-(2-methylthiopyridine-3-yl)prop-2-enoates **2** with good yields. This compounds are interesting as building blocks.

The hydrolysis of esters **2** ($R^3 = H$) under mild conditions leads to appropriate β -ketoesters **3**, which were used in the synthesis of 2-methylthio-3-(3-oxo-2,3-dihydropyrazol-5-yl)pyridines **4**. Esters **2** ($R^3 = \text{Alk, Ar}$) were hydrolysed only under drastic conditions to appropriate 3-acetylpyridines **5**.



It was found that the action of an excess of bromine on enamines **2** leads to isothiazolopyridines **6**.

References:

1. V. P. Litvinov, L. A. Rodinovskaya, Yu. A. Sharanin, A. M. Shestopalov, A. Senning, *Sulfur Reports*, 1992, vol. 13(1), p. 1-155.
2. V. K. Zav`yalova, A. A. Zubarev, V. P. Litvinov, *Russian Chemical Bulletin*, 2008, vol. 57, p. 1534 – 1538.
3. V. K. Zav`yalova, A. A. Zubarev, A. M. Shestopalov, *Russian Chemical Bulletin*, 2009, vol. 58, p. 1939 – 1944.

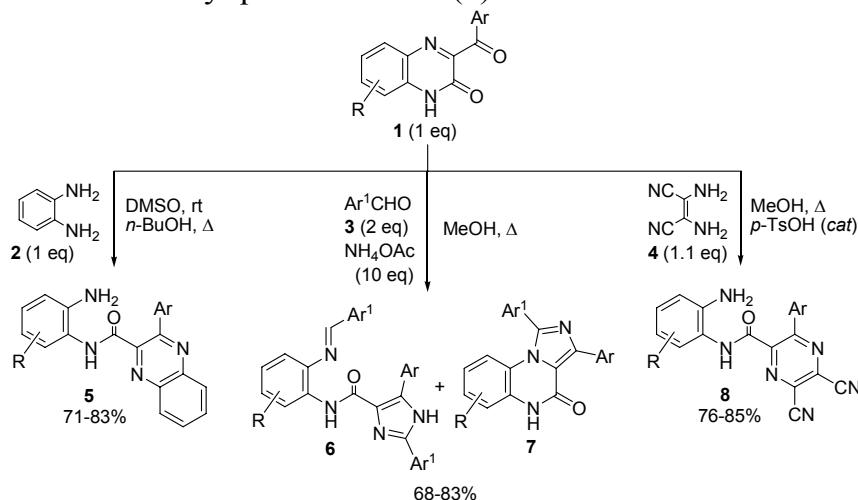
N.A. Zhukova
T.N. Beschastnova
S.F. Kadyrova
E.I. Zakirova
A.I. Samigullina
E.V. Mironova
A.T. Gubaidullin
V.A. Mamedov

A VERSATILE ONE-STEP METHOD FOR SYNTHESIZING 2-AMINOANILIDES OF HETEROCYCLIC CARBOXYLIC ACID FROM QUINOXALIN-2(1H)-ONES

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia
zhukova@iopc.ru

One of the major concerns of synthetic organic research is the development of new simple methods for synthesizing the key scaffold of various drugs used in medical practices. Among the medicines currently used compounds with the carbamoyl C(O)-NH- bond prevail. As a rule, a carbamoyl bonds are introduced into all these compounds by the reaction of the corresponding amines with carboxylic acid derivatives, not always easily obtainable from available reagents. This problem is further complicated if the derivatives of amines and acids containing other functional groups, compete with the processes of amidation.

In this report, we propose a simple method for the synthesis of anilides of quinoxaline- (5), imidazole- (6) and pyrazine (8) carboxylic acids starting from easily available derivatives of 3-arylquinoxalinones (1).



The key advantages of this method are its simplicity when introducing any given substituent into any position of the amine and carboxylic acid fragments, high yields, easy work-up and purification of compounds by crystallization.

References:

1. V.A. Mamedov, N.A. Zhukova, T.N. Beschastnova, A.T. Gubaidullin, A.A. Balandina, Sh.K. Latypov *Tetrahedron*, **2010**, 66, 9745.
2. V.A. Mamedov, N.A. Zhukova, T.N. Beschastnova, A.T. Gubaidullin, D.V. Rakov, I.Kh. Rizvanov *Tetrahedron Lett.*, **2011**, doi: 10.1016/j.tetlet.2011.06.014.

Acknowledgement. We thank the Russian Foundation for Basic Research (Grant No. 10-03-00413) for financial support.

Section 4.

Catalysis in Organic Synthesis



● **D2 PHASER** Desktop X-Ray Diffractometer

The D2 PHASER is a novel desktop analyzer that utilizes X-ray powder diffraction for qualitative and quantitative analysis of crystalline phases. The D2 PHASER is equipped with an integrated PC and a flat screen monitor. The new and very easy-to-use workflow software DIFFRAC.SUITE allows measurement and analysis right out of the box. Implemented with LYNXEYE™ compound silicon strip detector technology, the D2 PHASER is able to collect high quality data with unprecedented speed.

We implemented innovative technologies to make the D2 PHASER the most compact and fastest, all-in-one phase analyzer available on the market. The unit is mobile and easy to install with only the need for standard electrical power. It is therefore ideal for laboratory or on-location operation, in other words, it is a true Plug'n Analyze system.

Ease-of-use, high performance and low cost of ownership are the key features of the D2 PHASER. The D2 PHASER was developed to open new applications and markets beyond traditional XRD analysis. D2 PHASER – the price/performance leader for XRPD in laboratories and QC/PC applications for e.g. cement, industrial minerals, geology, chemistry, pharmaceuticals, as well as for educational purposes.

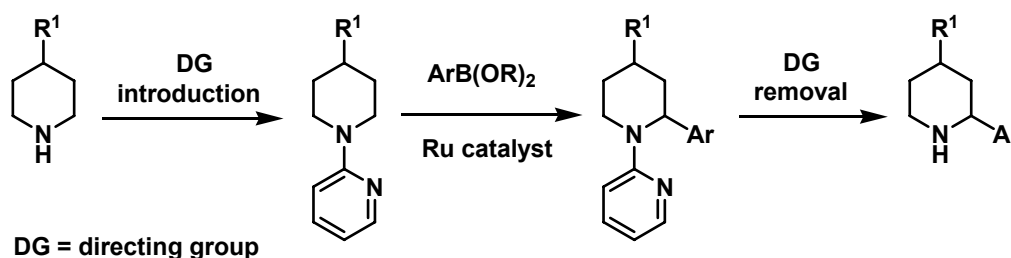
Innovation with Integrity

XRD

**FUNCTIONALIZATION OF HETEROCYCLES VIA
TRANSITION METAL-CATALYZED REACTIONS:
HALIDE EFFECTS AND DIRECT C-H
FUNCTIONALIZATIONS****Bert U.W. Maes**Organic Synthesis, Department of Chemistry, University of Antwerp,
Belgium
bert.maes@ua.ac.be

Transition metal-catalyzed cross-coupling reactions involving organometallic reagents are widely used to perform lead optimization in medicinal chemistry and agrochemistry programs. When halogenated heterocyclic substrates and/or heterocyclic organometallic reagents are used lower reaction rates are often observed in comparison to analogous reactions involving carbocycles. While slow cross-coupling reactions are hitherto typically optimized by modifying the ligands of the catalyst, we have investigated the effect of halide salts. In the first part of the lecture an unprecedented dual rate effect of halides in the Stille reaction will be discussed, which can be seen as a model for other cross-coupling reactions.¹

The second part of the lecture will deal with the development of transition metal-catalyzed methods for the direct functionalization of C-H bonds. Such synthetic methods are used both for the decoration and synthesis of heterocycles. These approaches are more sustainable than classical cross-coupling reactions involving organometallic reagents as either the halogenated (C-X bond) or metalated (C-M bond) coupling partner can be replaced by an unfunctionalized (C-H bond) molecule (at the desired coupling position). In addition, the diversity of commercially available or easily accessible building blocks (substrates and reagents) is larger, which makes library design based on transition metal-catalyzed direct functionalization of C-H bonds more attractive than classical cross-coupling reactions. As an example the direct Ru-catalyzed C-2 arylation of piperidines will be presented.²

**References:**

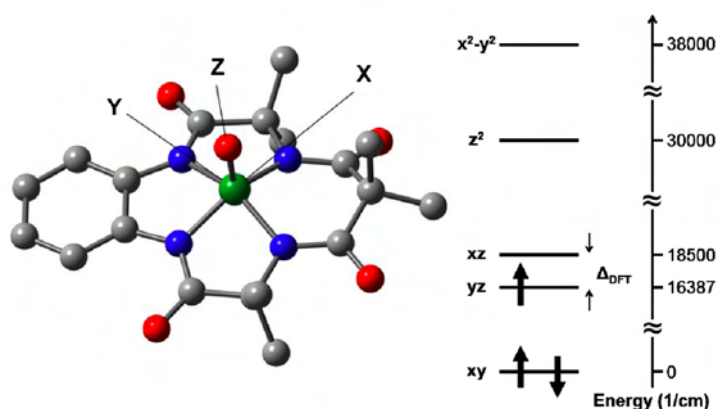
1. Verbeeck, S.; Meyers, C.; Franck, P.; Jutand, A.; Maes, Bert U.W. *Chem. Eur. J.* **2010**, *16*, 12831.
2. Prokopcová, H.; Bergman, S.D.; Aelvoet, K.; Smout, V.; Herrebout, W.; Van der Veken, B.; Meerpoel, L.; Maes, Bert U.W. *Chem. Eur. J.* **2010**, *16*, 13063.

TAML ACTIVATORS: EFFECTIVE SMALL MOLECULE PEROXIDASE MIMICS FOR CONSTRUCTING AND DECONSTRUCTING ORGANIC COMPOUNDS

T.J. Collins

Carnegie Mellon University, Department of Chemistry, Pittsburgh, USA
tc1u@andrew.cmu.edu

TAML activators are miniaturized replicas of the peroxidase enzymes, which activate hydrogen peroxide throughout nature. The design, development, mechanism of action, and myriad uses of TAML activators will be discussed. The Collins iterative design protocol led to the discovery and development of TAML activators. This protocol is focused primarily on obtaining strongly electron-donating ligand systems where derivative complexes are able to resist both hydrolytic and oxidative degradation under the aggressive conditions of peroxidase-like processes. After being pursued for 15 years, the protocol yielded the prototype TAML activator. Further advancement to higher generation catalysts has led to over 20 TAML activators that exhibit varying reactivities (with H_2O_2 and other peroxides), selectivities and lifetimes.



An iron(V)-oxo Complex produced from a TAML Activator [1]

Toxicity testing to date reinforces the idea that TAML activators and their processes are green. With peroxides TAML activators with iron produce extremely reactive intermediates, probably several, separately or jointly depending on the conditions. One is an iron(V)-oxo complex that has been trapped at low temperature (Figure). TAML activator catalysis is distinguished by low catalyst requirements (nM to low mM), efficacy under ambient conditions over a broad pH range (especially neutral to highly basic), rapidity, high efficiencies and turnover numbers, and flexibility for both selective synthetic and non-selective destructive processes. The latter processes represent “fire-in-water” and can be used to purify water of numerous recalcitrant pollutants, including many endocrine disrupting chemicals (EDCs) which are green chemistry’s principal concern.

References:

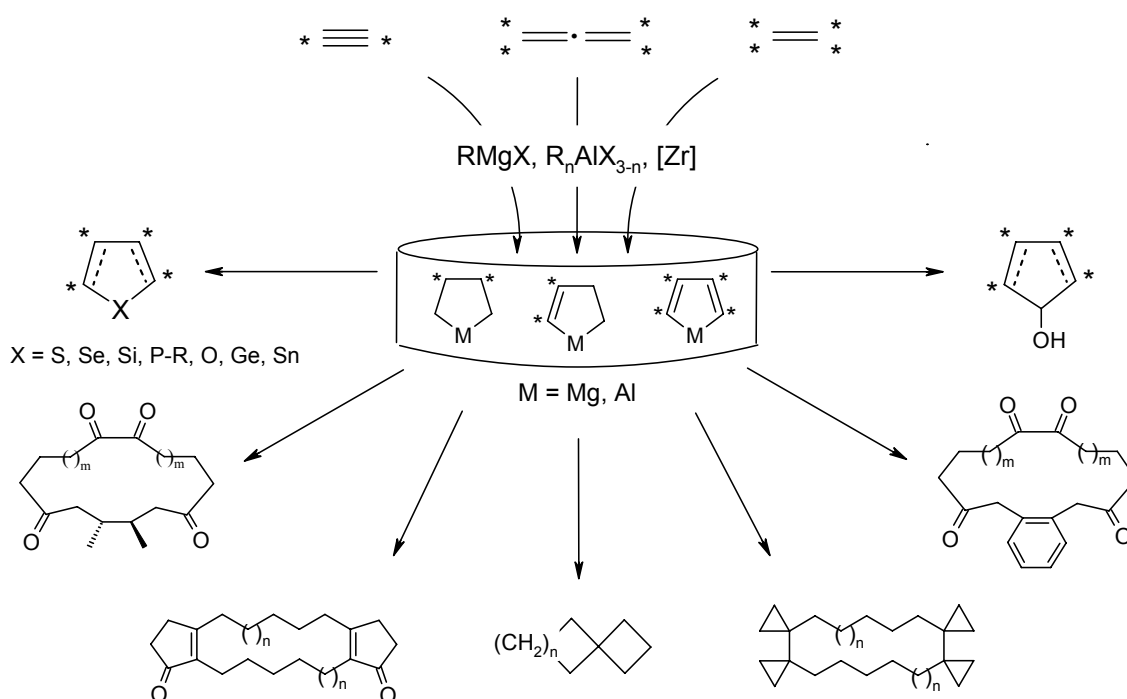
1. Tiago de Oliveira, F. T.; Chanda, A, et al., Chemical and spectroscopic evidence for an Fe(V)-oxo complex, *Science*, **2007**, 315, 835–838.

NEW STRATEGY IN DESIGN AND CONSTRUCTION OF SMALL, MEDIUM AND MACROCYCLES

V.A. Dyakonov
U.M. Dzhemilev

Institute of Petrochemistry and Catalysis of RAS, Ufa, Russia
DyakonovVA@rambler.ru

In this report, the investigation results for the recent 3-5 years on developing one-pot procedures to synthesize small (C3-C5), medium (C6-C11) and macrocarbocycles (more than C12) as well as their functional derivatives are presented. New methods are based on the discovered in the laboratory phenomenon of the catalytic replacement of transition metal atom in metallocarbocycle on the atom of non-transition metal and include the catalytic cyclometallation reactions of olefins, acetylenes and allenes [1-3].



Carbo- and heterocycles synthesized are promising as selective ionophores, effective extractants and sorbents for isolation, separation and purification of noble, rare and radioactive metals, pharmaceutical preparation prolongators, monomers for the synthesis of unique polymers, potential biologically active preparations consumed by people and animals, as well as high-energy fuels for aviation, rocket and space technology.

References:

1. U.M. Dzhemilev, A.G. Ibragimov, *J. Organomet. Chem.*, 2010, **695**, 1085.
2. V.A. D'yakonov, *Dzhemilev Reactions in Organic and Organometallic Synthesis*; NOVA Sci. Publ.: New-York, 2010, 96 p.
3. U.M. Dzhemilev, *Mendeleev Commun.*, 2008, **18**, 1.

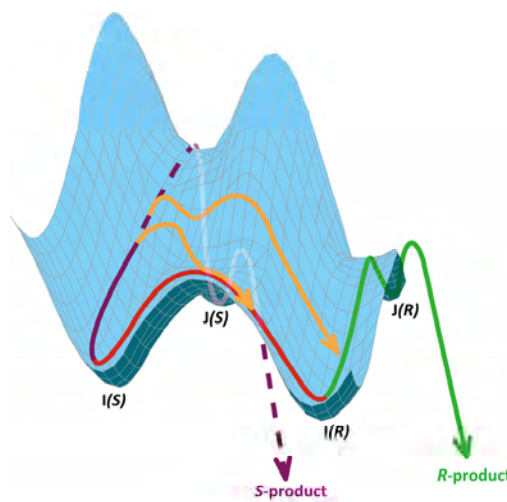
This work was supported by Russian Foundation for Basic Research (grants 10-03-00046, 11-03-00103, 11-03-97001).

TRIAL AND ERROR MECHANISM OF ENANTIOSELECTION IN ASYMMETRIC HYDROGENATION

I.D. Gridnev

Tokyo Institute of Technology, Graduate School of Science and Engineering, Tokyo, Japan
gridnev.i.aa@m.titech.ac.jp

The mechanism of enantioselectivity in the Rh-catalyzed asymmetric hydrogenation based on the difference in reactivities of the square planar catalyst-substrate complexes¹ has remained in the mainstream thinking for over three decades. However, recent findings give ample reasons to reconsider the stereodiscriminating step in the Rh-catalyzed asymmetric hydrogenation.^{2,3} We were first to characterize solvate dihydrides of the Rh-diphosphine complexes⁴ that gave opportunity to study their low temperature reactions with prochiral substrates of asymmetric hydrogenation. Since all these reactions gave quantitatively the corresponding hydrogenation products with the ee's of the same sign and order as the catalytic reactions. The sense and order of the enantioselection is determined on the stage of the formation of the chelate cycle in the octahedral Rh(III) dihydride intermediate. This stage is immediately followed by the very fast migratory insertion step that fixes the results of the reversible enantioselection. Importantly, the stereodifferentiating step within this mechanism of enantioselection is neither the rate-limiting one, nor irreversible. Considering this conclusion carefully, one can realize that such a situation is actually beneficial for the successful stereoselection. The rapid pre-equilibrium between **I(R)** and **I(S)** that takes place immediately prior to the fast and irreversible migratory insertion step, makes possible a "trial and error" method of enantioselection, since there are possibly numerous sideways leading back to **I(R)** (and ultimately to **J(R)**), which can be surpassed while trying to climb the high barrier for the association of the double bond forming **J(S)**. This mechanism resembles the three-step mechanism of protein/substrate interactions in the photosynthetic redox chain,⁵ which involves the initial formation of a multitude of pre-oriented complexes, their isomerization to the fully bound complex and the immediate reaction of the latter after the proper conformation is achieved. The conclusions of these studies would affect the approach to the catalyst design as well as general views on the principles of enantioselection.



References:

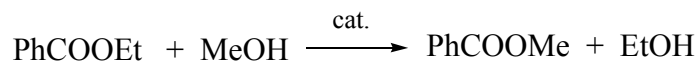
1. J. Halpern, *Science*, 1982, **217**, 401.
2. I. D. Gridnev, T. Imamoto, *Acc. Chem. Res.*, 2004, 633.
3. I. D. Gridnev, T. Imamoto, *Chem. Commun.*, 2009, 7447.
4. I. D. Gridnev, N. Higashi, K. Asakura, T. Imamoto, *J. Am. Chem. Soc.*, 2000, **122**, 7183.
5. P. B. Crowley, M. Ubbink, *Acc. Chem. Res.*, 2003, **36**, 723.

STABLE CARBENES IN CATALYSIS OF TRANSESTERIFICATION

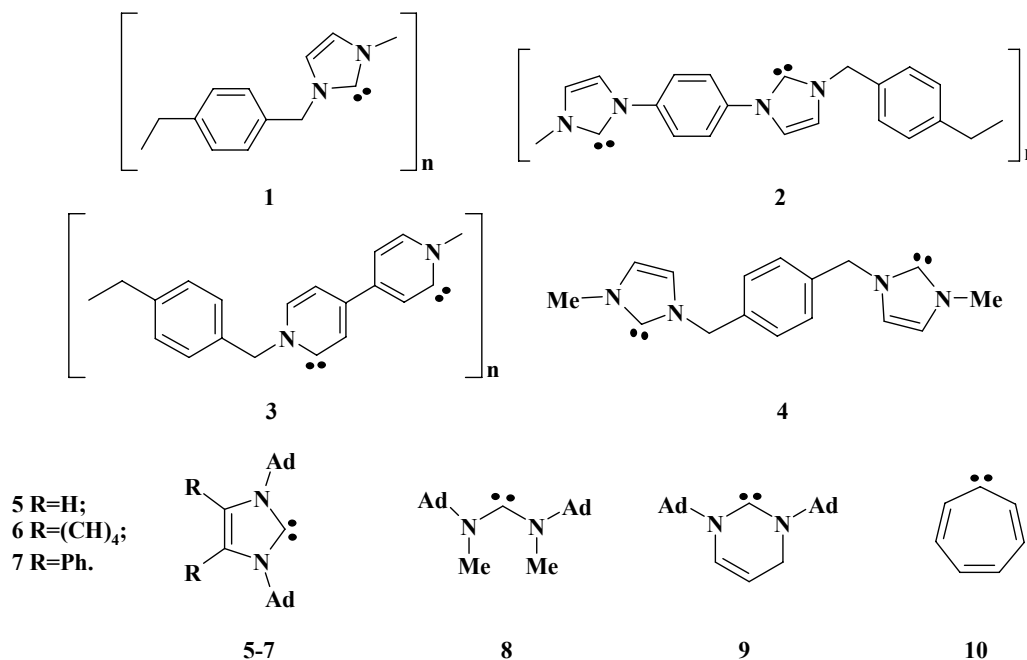
K.A. Marichev
N.I. Korotkikh
A.V. Kiselyov
A.V. Knishevitsky
O.P. Shvaika

L.M. Litvinenko Institute of Physical Organic & Coal Chemistry of the
Ukrainian Academy of Sciences; Chemistry of Nitrogen Containing
Heterocyclic Compounds Department; Donetsk; Ukraine
marichev1985@mail.ru

Transesterification is one of the mild and effective synthetic methods for producing esters. As catalysts for this reaction stable carbenes have been proposed recently. But the described catalysts were not enough efficient [1-3]. In the present work new types of conjugated and unconjugated polycarbene precursors of imidazole and pyridine series were synthesized and corresponding stable polycarbenes **1-4** were generated on their basis. The catalytic properties of the indicated carbenes were studied using the model reaction of ethyl benzoate into methyl benzoate in the methanol excess.



The catalytic efficiency was estimated at the values of TON and TOF. Polycarbenes **1** (TON until 4000, TOF until 5750 h⁻¹), **2** (TON 2350, TOF 590 h⁻¹), **3** (TON 2100, TOF 520 h⁻¹) and biscarbene **4** (TON 2170, TOF 540 h⁻¹) are highly efficient. The catalytic properties of the earlier obtained in our research group carbenes were also studied. The high efficiency was observed for carbenes containing sterically hindered adamantyl substituents **5-9** and cycloheptatrienylidene **10** (TON until 2350, TOF until 588 h⁻¹). The scope and generality of this catalytic method was also expanded to the readily available vegetable oils. So, the effective catalysis of sunflower oil transformation into biodiesel fuel (fatty-acid methyl esters) was carried out using polycarbene **1** (TON 2667, TOF 667 h⁻¹).



References:

- 1) Connor E. F., Nyce G. W., Myers M., Mock A., Hedrick J. L. *J. Am. Chem. Soc.* **2002**, 124 (6), 914.
- 2) Grasa G. A., Gveli T., Singh R., Nolan S. P. *J. Org. Chem.*, **2003**, 68 (7), 2812.
- 3) Singh R., Kissling R. M., Letellier M.-A., Nolan S.P. *J. Org. Chem.*, **2004**, 69 (1), 209.

RHODIUM CARBENOID-AZIRINE COUPLING AS A NOVEL ROUTE TO 4-6-MEMBERED HETEROCYCLES

M.S. Novikov
A.F. Khlebnikov
N.V. Rostovskii
I.A. Smetanin

Saint-Petersburg State University Department of Chemistry,
 St. Petersburg, Russia
ms.novikov@mail.ru

Due to its high activity towards single and multiple bonds as well as heteroatomic centers rhodium carbenoids have been shown in recent years to be highly versatile synthetic intermediates.

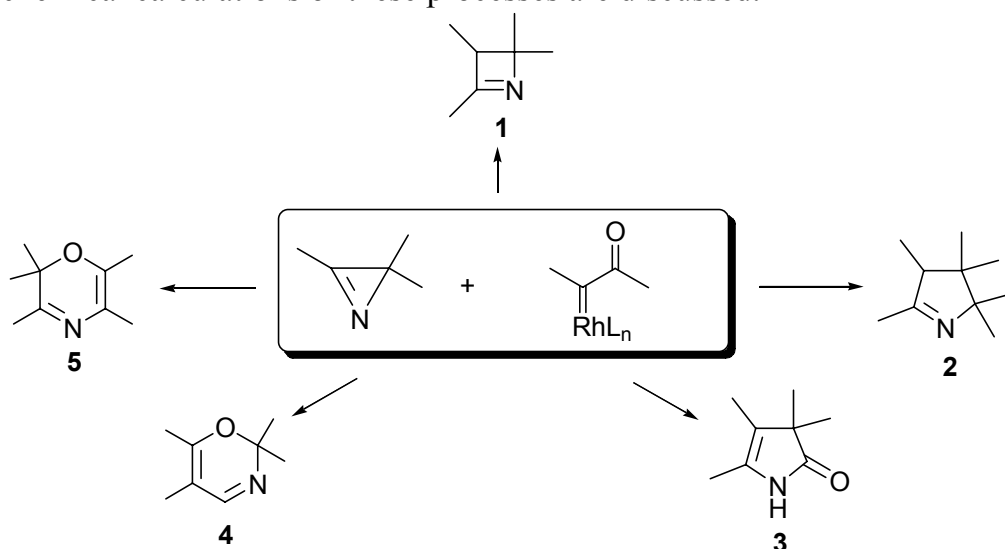
In this report the synthetic possibilities and mechanistic details of rhodium carbenoid-induced *2H*-azirine ring expansion to 4-6-heterocycles of azetine, pyrroline and oxazine families are discussed.

$\text{Rh}_2(\text{OAc})_4$ -Catalyzed decomposition of diazo esters and diazo keto esters in the presence of substituted *2H*-azirines is the domino reaction proceeding via three intermediates: Rh(II)-carbenoid, azirinium ylide, and 2-azadiene, the substitution pattern and stereochemistry of which define the outcome of all the process. Depending on structure of starting diazo ester and azirine the reaction can lead to one-carbon azirine-ring expansion to give azetine derivatives **1** or two-carbon aziring-ring expansion in pyrroline derivatives **2**.

A novel rearrangement of 2-azadiene intermediates derived from diazo keto esters and electron-deficient azirines to pyrroline derivatives **3** was disclosed. The use in this protocol of azirine-2-carbaldehydes leads to substituted *2H*-1,3-oxazines **4**.

Most notable is Rh(II)-catalyzed reaction of *2H*-azirines with diazo keto esters which is the sole method for the preparation of non-fused photochromic *2H*-1,4-oxazines **5**.

The scope and limitations of azirine ring expansion reactions as well as the results of quantum-chemical calculations of these processes are discussed.



This work was supported by the Russian Foundation for Basic Research (project 11-03-00186) and Federal Grant-in-Aid Program «Human Capital for Science and Education in Innovative Russia» (Governmental Contract no. 16.740.11.0442).

REACTIONS OF AZIRINES WITH CYCLIC AND ACYCLIC DIAZO KETO ESTERS: TWO TYPES OF CATALYSIS

N.V. Rostovskii¹
M.S. Novikov¹
A.F. Khlebnikov¹
S.M. Korneev²

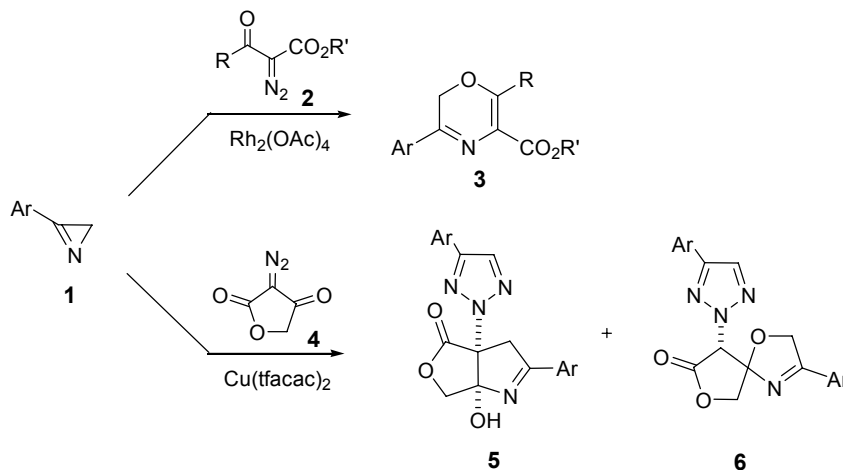
1 - Saint Petersburg State University, Department of Chemistry,
 Saint Petersburg, Russia

2 - University of Osnabrueck, Department of Biology and Chemistry,
 Osnabrueck, Germany
 rostovskiinikola@yandex.ru

The chemistry of 2*H*-azirines is extensively explored due to the high reactivity of this strained ring system [1]. In the context of our investigations towards the discovery of novel ylides useful as building blocks for heterocyclic design, we study reactions of 3-aryl-2*H*-azirines with various diazo compounds in the presence of metal-containing catalysts.

Herein we report the Rh₂(OAc)₄-catalyzed reaction of 3-aryl-2*H*-azirines **1** with acyclic 2-acyl-2-diazoacetates **2** that leads to the formation of non-fused 2*H*-1,4-oxazines **3** [2]. This transformation proceeds via unstable azirinium ylide, formed from azirine and metal carbenoid. The catalytic action of Rh₂(OAc)₄ in this reaction consists in decomposition of diazo compound with formation of Rh(II)-carbenoid.

There are *only a few examples of the use* of cyclic diazo keto ester, diazo tetronic acid **4**, in metal catalyzed reactions, due to increased stability towards these catalysts [3]. The reaction of diazo tetronic acid **4** with 3-aryl-2*H*-azirines **1** in the presence of Cu(tfacac)₂ unexpectedly proceeds with retention of nitrogen from diazo group giving rise to triazole derivatives **5** and **6**. The role of the catalyst as well as mechanism of formation of triazole derivatives **5** and **6** will be discussed.



References:

1. F. Palacios, A. M. O. de Retana, E. M. de Marigorta, J. M. de los Santos *Eur. J. Org. Chem.* 2401-2414 (2001).
2. V.A. Khlebnikov, M.S. Novikov, A.F. Khlebnikov, N.V. Rostovskii *Tetrahedron Lett.* **50**, 6509-6511 (2009).
3. H. Stachel, H. Poschenrieder, J. Redlin, J. Schachtner, K. Zeitler *Liebigs Annalen der Chemie* **2**, 129-132 (1994).

We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (project 11-03-00186), and Federal Grant-in-Aid Program «Human Capital for Science and Education in Innovative Russia» (Governmental Contract no. 16.740.11.0442).

**THE STUDY OF INTERMEDIATES OF
Pd-CATALYZED REACTIONS BY ESI-MS AND NMR
METHODS**

**J.V. Ivanova
V.P. Ananikov**

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of
Sciences, Moscow, Russia
ivanova@ioc.ac.ru

Despite well-established practice in the structure determination of stable compounds, mechanistic studies and the nature of transient species are still the field of debates. Most of the dedicated mechanistic studies performed so far were done by one of these methods. Getting chemically reliable and mutually agreed mechanistic data by both methods for chemical reactions studied under the same conditions until recently was quite rare and remained a difficult problem.^[1,2] The importance of the development of a proper methodology for such joint studies is unquestionable in order to facilitate the solution of complicated mechanistic problems and achieve future progress in the development of organic synthesis.

High sensitivity of mass spectrometry makes it possible to analyze even trace amounts of samples. The progress of atmospheric pressure ionization, in particular, electrospray ionization (ESI), provided a great tool for studying liquid solutions by mass spectrometry. In fact, the method was successfully applied to solve different mechanistic and structural problems including the reactions involving transition metal complexes.

We have studied Pd- and Ni-catalyzed reactions of carbon-heteroatom bond formation using combined ESI-MS and NMR approach in solution.^[3,4] The study has revealed the active species of the reaction and the resting states. It was found, that interconversion between the active species and resting states may be achieved simply by changing the number of ligands coordinated to the metal center.

References:

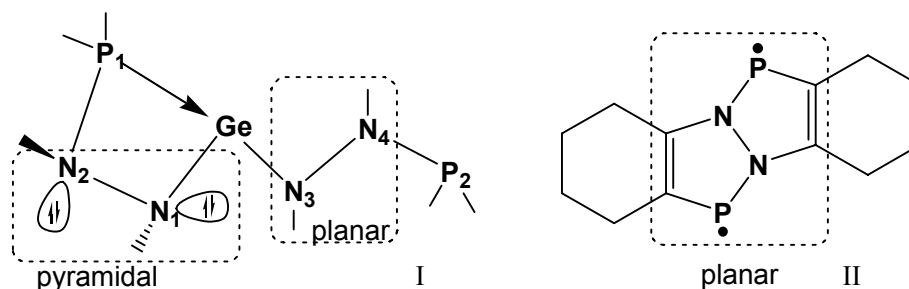
1. Belyakov P. A., Kadentsev V. I., Chizhov A. O., Kolotyrkina N. G., Shashkov A. S., Ananikov V. P., *Mendeleev Commun.*, 2010, 20, 125.
2. Santos L. S., *Eur.J.Org.Chem.* 2008, 223.
3. Ananikov V. P., Khemchyan L. L., Beletskaya I. P., *Synlett*, 2009, 2375.
4. Ananikov V. P., Khemchyan L. L., Beletskaya I. P., Starikova Z.A., *Adv. Synth. Catal.*, 2010, 352, 2979.

HETEROCYCLIC SYSTEMS CONTAINING N-N-P CHAIN: FROM UNIQUE REARRANGEMENTS IN METAL COORDINATION SPHERE TO THE AROMATIC MOLECULES OF FUNDAMENTALLY NEW TYPE

A.N. Kornev
O.V. Lukyanova
V.V. Sushev
O.Ya. Gorak
Yu.S. Panova
G.A. Abakumov

G.A. Razuvaev Institute of Organometallic Chemistry, Russian
Academy of Sciences, Nizhny Novgorod, Russia
akornev@iomc.ras.ru

Properties of organophosphorus ligand systems, containing P^{III} -N-N chain are dramatically dependent on the behavior of lone pairs at nitrogen atoms, which is determined by the charge localization and possibility of endocyclic conjugation. Appearance of negative charge at hydrazido nitrogens in phosphinohydrazides ($R_2P-NR-NR-M$, M-metal atom) enforces repulsion of the lone pairs and results in cleavage of the N-N bond, followed by the rearrangement to form iminophosphoranates ($RN=PR_2-NR-$). This transformation is close aza-analog of the Michaelis-Arbuzov rearrangement. On the contrary, including both lone



pairs into the conjugation results in formation of high stable diazaphospholes. Annulated *bis*-diazaphosphole II contains planar 10e-aromatic system. Both unpaired electrons (depicted here for clarity) on phosphorus atoms are involved in the strong endocyclic conjugation to form the molecule with singlet ground state, which is by 40.1 kcal/mol more stable than triplet state. The electronic absorption spectrum of II contains strong narrow band at 438 nm, which is in accordance with calculated HOMO – LUMO gap of 2.8 eV. Synthetic and mechanistic aspects, DFT calculations and unusual properties of above mentioned compounds are discussed.

This work was supported by The Russian President's program "Leading Scientific Schools" (No. 7065.2010.3) and RFBR regional grant No 11-03-97029.

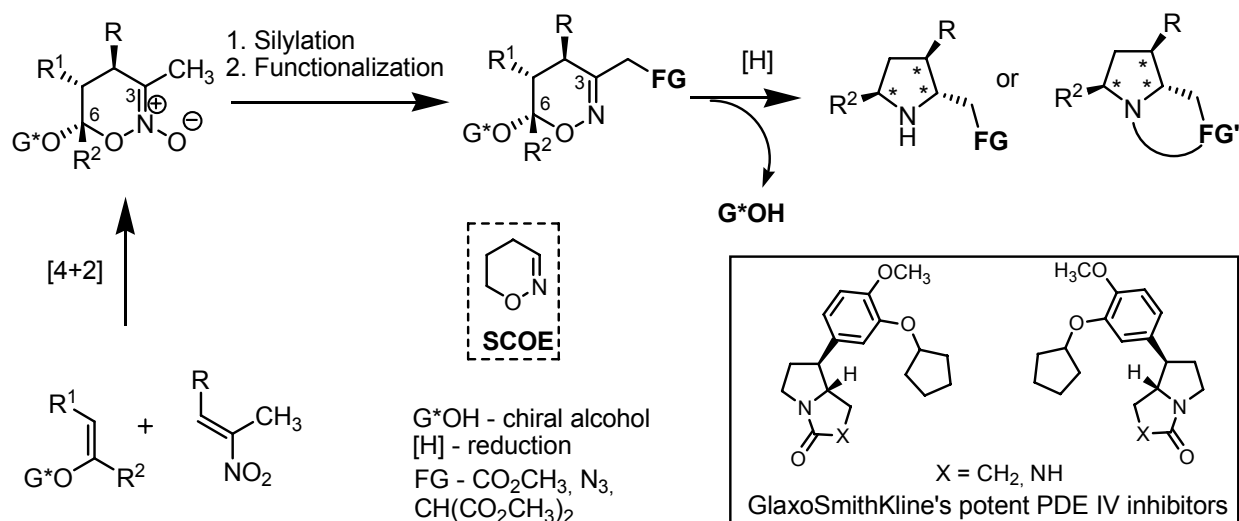
SIX-MEMBERED CYCLIC OXIME ETHERS IN STEREOSELECTIVE AND ASYMMETRIC SYNTHESIS

A.Yu. Sukhorukov
P.A. Zhmurov
Y.D. Boyko
S.L. Ioffe
V.A. Tartakovsky

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia
sukhorukov@server.ioc.ac.ru

Cyclic oxime ethers represent considerable interest as intermediates in the synthesis of stereochemically complex natural and bioactive molecules. Five-membered cyclic oxime ethers, e.g. isoxazoles and isoxazolines, have found numerous applications in total synthesis since the early 1960s. On the contrary, the synthetic potential of six-membered cyclic oxime ethers (SCOE) is much less explored. At the same time, the chemistry of SCOE is more versatile as compared to their five-membered analogs, since, in addition to ring-opening reactions typical for isoxazoles and isoxazolines, ring contraction reactions to pyrrolidines and furans are common for SCOE.

The report summarizes recent advances in the application of SCOE in total synthesis of pharmacologically relevant products. Examples of stereoselective and asymmetric syntheses of unnatural amino-acids and known phosphodiesterase inhibitors containing bicyclic pyrrolizidinone and pyrroloimidazolidinone scaffolds *via* C-3 functionalized SCOE will be discussed in the presentation.



References:

1. A. Yu. Sukhorukov, S. L. Ioffe, *Chem. Rev.*, **2011**, doi: 10.1021/cr100292w and references cited therein.

The financial support from the RFBR (grant 11-03-00737a) and Federal Agency for Science and Innovations (MK-1361.2011.3) is greatly acknowledged.

HIGH PRESSURE EFFECT ON THE RATE AND EQUILIBRIUM OF COMMON AND CATALYZED CYCLOADDITION REACTIONS IN SOLUTION

V.D. Kiselev
A.I. Kononov

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia
vkiselev.ksu@gmail.com

Two main factors determining the reactivity of $(4\pi+2\pi)$ -cycloaddition, - energy of intermolecular orbital interaction and the balance on energy of disruption and formation bonds, were considered for about hundred Diels-Alder reactions. A simple dependence, $\lg k_2 = -28.81 + 316.3/(IP_D - E_A) - 69.9 R_{1-4}/(IP_D - E_A) - 0.054\Delta H_{r-n}$ ($r = 0.972$; $n = 93$), for the reaction rate as a function of the ionization potential of π -donor dienes, electron affinity of π -acceptor dienophiles, heat of reaction and diene structure (R_{1-4}) was obtained. It was observed strong enhancement of orbital interaction energy at dienophile activation by Lewis acids and reactivity (k_{cat}/k_{noncat} up to 10^7). It is well known that the derivative of the Gibbs energy ΔG on the pressure P corresponds to volume change of the process:

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{1}{RT} \left(\frac{\partial \Delta G}{\partial P}\right)_T = -\frac{\Delta V}{RT} = -\frac{V_{prod} - V_{reag}}{RT} \quad (1)$$

The pressure dependence of the reaction rate k is determined by the activation volume $\Delta V^\ddagger$:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{1}{RT} \left(\frac{\partial \Delta G^\ddagger}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT} = -\frac{V_{TS} - V_{reag}}{RT} \quad (2)$$

When the molar volumes of transition state (TS) and products is less than the molar volumes of reagents the pressure elevation can significantly increase the reaction rate constant and equilibrium constant of the process.

High pressure effect on the common and catalyzed cycloaddition reactions was studied. From these results the invariability of the bond distance in complexes under pressure up to 1000 bar has been concluded.

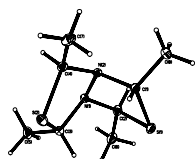
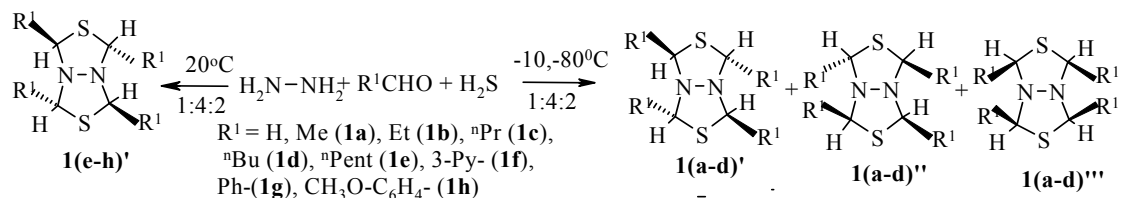
For a wide range of the Diels-Alder reactions the “normal” ($\Delta V_{forw}^\ddagger/\Delta V_{r-n} < 1$) and “abnormal” volume ratio ($\Delta V_{forw}^\ddagger/\Delta V_{r-n} > 1$) has been explained by different ability of the solvent molecules to penetrate for interaction with the surface of shielded structure of reagents, transition state and products. Positive and negative values of the activation volume of retro Diels-Alder reaction in some solvents were discussed [1,2].

References:

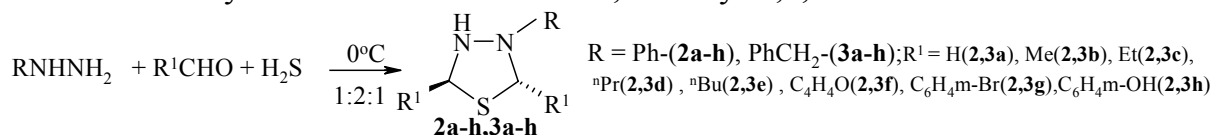
- [1]. V.D. Kiselev and A.I. Kononov. Internal and external assistance to the proceeding of the Diels-Alder reaction. *J. Phys. Org. Chem.* 2009. 22, 466-483.
- [2]. V.D. Kiselev. Why can the activation volume of the cycloadduct decomposition in isopolar retro-Diels-Alder reactions be negative? *Int. J. Chem. Kinetics.* 2010, 42, 117-125.

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, Ufa, Russia
vnirara@mail.ru

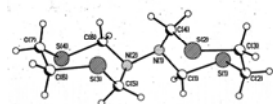
The developed methodology of regioselective synthesis of series of novel 2,4,6,8-tetraalkyl-1,3,4-thiadiazolo[3.4-c][1,3,4]thiadiazolidines **1a-h** based upon multi-component reactions of hydrazine, aldehydes and H₂S will be presented in the report. It will be shown that configuration stereoisomer *ttt*, *ccc*, *ttc*, *ctc* are formed depending on the nature of the substituents.



Heterocyclization of monosubstituted hydrazines with aldehydes and H_2S stereoselectively leads to a series of *trans* 2,5-dialkyl-1,3,4-thiadiazolidines **2a-h** and **3a-h**.


$$\begin{array}{c}
 \text{S} \quad \text{S} \quad \text{N} \quad \text{N} \quad \text{S} \quad \text{S} \\
 \diagup \quad \diagdown \quad \diagdown \quad \diagup \\
 \text{4}
 \end{array}
 \xleftarrow[\text{CH}_2\text{O}]{0^\circ\text{C}}
 \text{NH}_2\text{NH}_2 + 2 \text{HS}(\text{CH}_2)_2\text{SH}
 \xrightarrow[\text{RCHO}]{0^\circ\text{C}}
 \begin{array}{c}
 \text{S} \quad \text{S} \quad \text{N} \quad \text{N} \quad \text{S} \quad \text{S} \\
 \diagup \quad \diagdown \quad \diagdown \quad \diagup \\
 \text{5a-d}
 \end{array}$$

R=Me(**5a**), Et(**5b**), ⁿPr(**5c**), ⁿBu(**5d**)



The present work supported by Department of chemistry and material sciences of RAS (OHNM - 7), Russian Foundation for Basic Research (grants 11-03-00101a, 11-03-97011-p-povolzh'e a).

EFFICIENT SYNTHESIS OF N-(1,5,3-DITHIAZEPINAN-3-YL) AMIDES BASED ON CARBOXYLIC ACID HYDRAZIDES

R.R. Khairullina¹B.F. Akmanov²R.V. Kunakova²A.G. Ibragimov¹U.M. Dzhemilev¹

1 - Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, Ufa, Russia

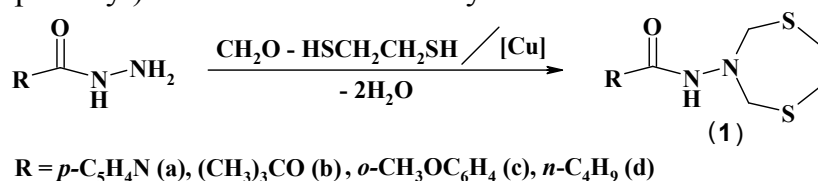
2 - Ufa State Academy of Economics and Service, Ufa, Russia

reginessa@mail.ru

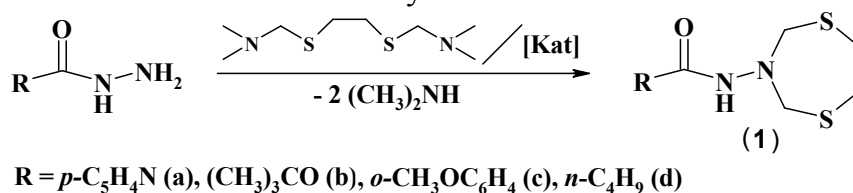
Sulfur- and nitrogen-containing heterocycles are used as phase transfer catalysts, extractants, sorbents, flotation reagents, analytical reagents, biologically active compounds for medicine and agriculture [1,2]. Synthetic approaches to these types of compounds are usually multistage.

In this report, two new approaches to the synthesis of N-(1,5,3-dithiazepan-3-yl)-amide employing the cyclothioalkylation reaction of carboxylic acid hydrazides with CH₂O and 1,2-ethanedithiol or N¹,N¹,N⁶,N⁶-tetramethyl-2,5-dithiahexane-1,6-diamine under the action of catalytic amounts of Cu, Sm or Zn compounds are discussed.

Thus, cyclothioalkylation of carboxylic acid hydrazides involving formaldehyde and 1,2-ethanedithiol occurred in the presence of CuCl₂·2H₂O as a catalyst (RC(O)NHNH₂ : 1,2-ethanedithiol : CH₂O : CuCl₂·2H₂O = 10:10:20:0.5) at 80 °C within 45–48 hours giving N-(1,5,3-dithiazepan-3-yl)-amides **1** in 75–84% yield.



The cyclothioalkylation reaction between carboxylic acid hydrazides and N¹,N¹,N⁶,N⁶-tetramethyl-2,5-dithiahexane-1,6-diamine provides the alternative approach to the preparation of such class of compounds. This reaction effectively proceeds in the presence of Sm(NO₃)₃·6H₂O or ZnCl₂·2H₂O as catalysts taken in a molar ratio of RC(O)NHNH₂ : N¹,N¹,N⁶,N⁶-tetramethyl-2,5-dithiahexane-1,6-diamine: catalyst = 10:10:0.5 at 80 °C for 20–28 h to afford **1** in 62–83% yield.



References:

- 4) [1] M. D. Mashkovskii, *Lekarstvennye sredstva [Drugs]*, Meditsina, Moscow, 1993, **1**, 322 pp. (in Russian).
- 5) [2] Yu. I. Murinov, V.N. Maistrenko, and N.G. Afzaletdinova. *Ekstraksiya metallov S,N-organicheskimi soedineniyami*, Nauka, Moscow, **1993**. 192 pp. (in Russian).

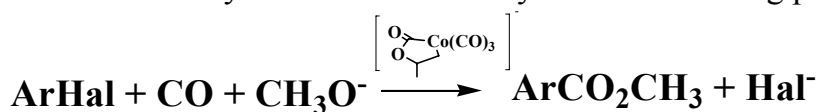
This work was financially supported by Russian Foundation for Basic Research (Grant 11-03-00101a).

**"ORTHO-EFFECT" IN RADICAL ANION
NUCLEOPHILIC SUBSTITUTION.
CARBONYLATION OF SUBSTITUTED
HALOBENZENES**

V.P. Boyarskiy
T.S. Khaybulova
N.A. Vinnik
I.A. Boyarskaya

St. Petersburg State University, Department of Chemistry,
St. Petersburg, Russia
vadimpb@yahoo.com

Cobalt-catalyzed carbonylation with use of a complex of potassium tetracarbonylcobaltate and methyloxirane as the catalyst is the following process [1,2]:



A key step of the process is radical anion non-chain activation of the arylhalide with the anion cobalt complex. This reaction provides an unique possibility of radical anion processes studying.

The purpose of the present work was *ortho*-substituted chloro- and bromobenzenes investigation in the cobalt-catalyzed carbonylation, and use of this process as a model reaction for studying of "*ortho*-effect" in radical anion nucleophilic substitution. A method of competitive reactions showed that the overwhelming majority of substituents (both electron donating, and electron withdrawing), being in *ortho*-position to atom of halogen, increase the reaction rate. The exception is only *i*-propyl group, which reduce reactivity of the *ortho*-bromine atom in the corresponding substituted bromobenzene. Studying of substituted dichlorobenzenes carbonylation regioselectivity also demonstrated that the chlorine atom in the *ortho*-position to the substituent reacts mainly.

The observed *ortho*-effect can be explained in view of the radical anion mechanism of aryl halide activation in the cobalt-catalyzed carbonylation. This explanation was confirmed by theoretical calculation of the potential curves using the DFT method (UB3LYP/6-31+G(d)).

References:

1. Boyarskii, V. P.; Larionov, E. V.; Polyakova, S. M.; Boyarskaya, I. A.; Zhesko, T. E. Mechanism of the catalytic carbonylation of aryl halides with a modified cobalt carbonyl. *Russian Journal of General Chemistry* **2007**, 77(5), 915–922.
2. V. P. Boyarskii, G. G. Duka, I. A. Boyarskaya. *Russian Journal of General Chemistry*, **2009**, 79(11), 2449–2451.

The authors thank Saint-Petersburg State University for a research grant, the Federal Targeted Program "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009–2013" (contract P676 from 20/05/2010), and Russian Fund for Basic Research (grant 11-03-00048-a).

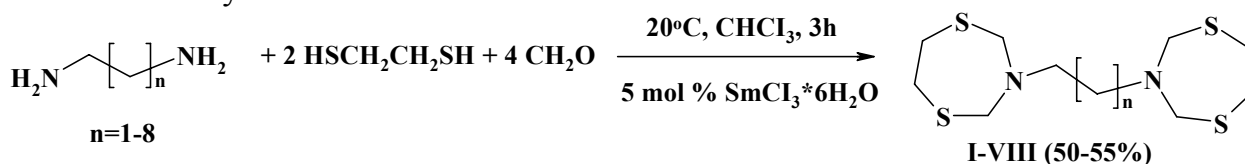
E.B. Rakhimova
E.A. Efremova
Sh.U. Sayfutdinov
A.G. Ibragimov
L.M. Khalilov
U.M. Dzhemilev

NEW APPROACHES TO THE SYNTHESIS OF 1,5,3-DITHIAZEPINANES BASED ON ALIPHATIC DIAMINES

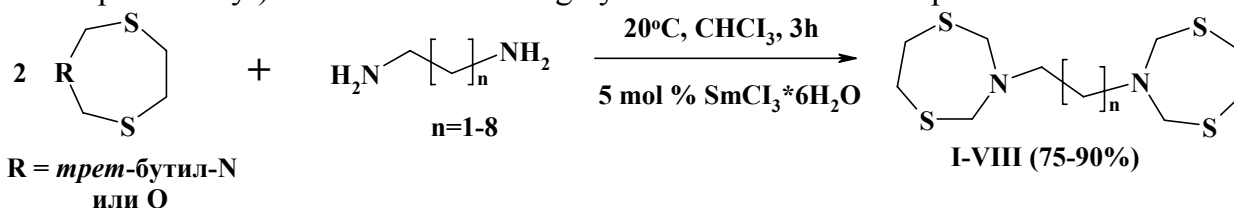
Institute of Petrochemistry and Catalysis, Russian Academy of
Sciences, Ufa, Russia
Rakhimovaelena@mail.ru

Among the large variety of heterocyclic compounds, the saturated *S,N*-containing heterocycles represent particular interest as effective sorbents of noble metals and biologically active compounds.

In order to develop a selective method for the synthesis of practically important saturated *S,N*-containing heterocycles, the heterocyclization of aliphatic α,ω -diamines with 1,2-ethanedithiol and CH_2O was studied. Thus, α,ω -diamines under optimized reaction conditions (5 mol % $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, 20 °C, 3 h, CHCl_3 , 1:4:2 molar ratio) react with formaldehyde and 1,2-ethanedithiol affording α,ω -bis-(1,5,3-dithiazepinane-3-yl)-alkanes **I–VIII** in 50-55% yields.



In continuation of the previous study on the transamination reaction of *N*-methyl-1,3,5-dithiazinane with aryl amines [1], the catalytic transamination reaction of *tert*-butyl-1,5,3-dithiazepinane and recycling of 1,3,6-oxadithiapinane with aliphatic α,ω -diamines were studied. As a result, the new approaches to the selective synthesis of α,ω -bis-(1,5,3-dithiazepinane-3-yl)-alkanes **I–VIII** in high yields have been developed.



The structures of novel α,ω -bis-(1,5,3-dithiazepinane-3-yl)-alkanes **I–VIII** were proved by means of multinuclear NMR spectroscopy and MALDI TOF-MS.

References:

1. Niatshina Z.T., Murzakova N.N., Vasilieva I.V., Rakhimova E.B., Akhmetova V.R., Ibragimov A.G. *ARKIVOC*, **2011**, VIII, 141.

The authors thank the Russian Foundation of Basic Research for financial support (Grant 11-03-00101-a).

R.M. Galimullina
M.I. Valitov
Yu.S. Spiridonova
E.I. Musina
S.A. Krasnov
M.K. Kadirov
A.A. Karasik
Yu.H. Budnikova
O.G. Sinyashin

**ELECTROCHEMICAL EVALUATION OF NICKEL
COMPLEXES WITH P, N-HETEROCYCLIC LIGANDS
AS HYDROGEN OXIDATION / PRODUCTION
CATALYSTS**

A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan
Scientific Center of Russian Academy of Sciences, Kazan, Russia
galimullina_rm@mail.ru

Development of new efficient catalytic systems mimicking the action of metalloenzymes and biological nanoreactors, based on linear and macrocyclic frame structures is important problem. Such systems could implement energy by oxidizing hydrogen fuel in the fuel cell. In this view nickel complexes with macrocyclic ligands where the soft diphosphine ligands stabilize the lower nickel oxidation state and provide favorable environment for the catalytic processes are very interesting. The introduction of basic residues to the central nickel atom helps to control the movement of protons during the catalytic cycle.

The purposes of this study are to test the efficiency of new nickel complexes with P, N-cyclic ligands (such as $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bz}}_2)_2]^{2+}$, $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2]^{2+}$) in the reactions of electrocatalytic reduction of H^+ to hydrogen and the oxidation of H_2 in the coordination sphere-like cavity of the catalyst, establishing of processes laws and relationship between the catalytic properties and the structure of the complex and the redox properties; selection of the most effective structures of catalysts. As a result the most favorable conditions and structures have been revealed. The relationship between the activity of the catalysts and the values of the electrochemical gap has been found.

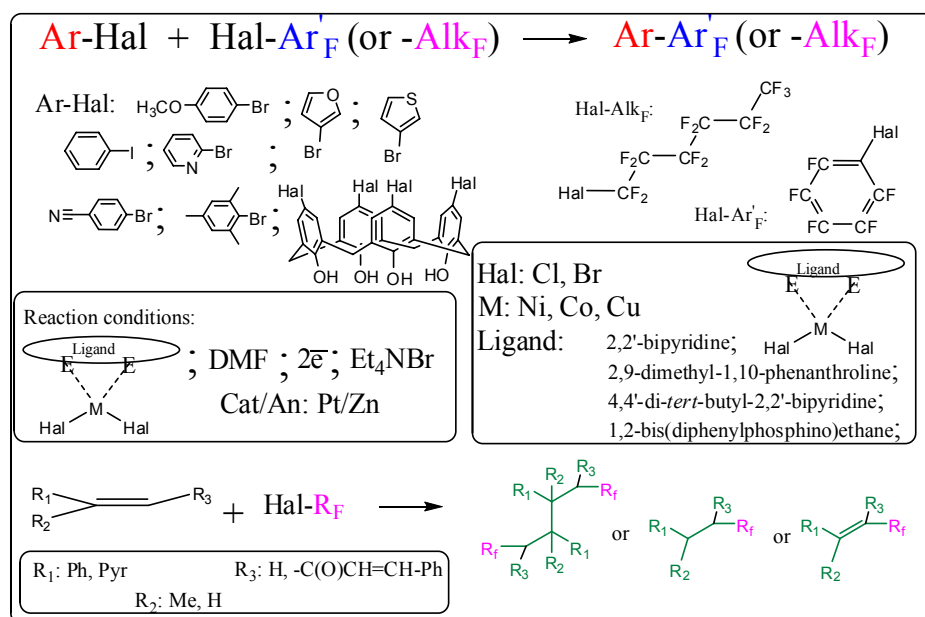
CROSS-COUPLING REACTION BY MEANS OF Co, Ni, Cu COMPLEXES ELECTROCATALYZED AS UNIVERSAL METHOD OF NEW COMPOUNDS PREPARATION

M.N. Khrizanforov¹
Y.G. Budnikova¹
T.V. Gryaznova¹
D.Y. Mikhaylov¹
O.G. Sinyashin²

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry,
 Laboratory of Electrochemical Synthesis, Kazan, Russia
 2 - A.E. Arbuzov Institute of Organic and Physical Chemistry,
 Laboratory of Organometallic and Coordination Compounds, Kazan,
 Russia
 khrizanforov@gmail.com

Elaboration of high selective reactions leading to formation of carbon-carbon bonds belongs to the most important problems in rapidly progressing metallocomplex catalysis.

Here we present first evidence of electrochemical cross-coupling of aryl and perfluoroalkyl in mild conditions, even with homeopathic catalyst content. A convenient method for electrosynthesis of perfluoroalkyl arenes or perfluoroaryl arenes by cross-coupling of perfluoroalkyl (or Aryl) halides and aryl halides catalysed by some metal complexes was elaborated.



We proposed a new universal and simple one-step method for the synthesis in mild conditions and with moderate yields. Some of these compounds are not easily accessible and/or expensive when are obtained by usual classical methods. The method consists in electroreduction of organic halide mixture using M-L catalytic system in an undivided cell. The metals are nickel or cobalt and the ligands are 2,2'-bipyridine, 2,9-dimethyl-1,10-phenanthroline or 4,4'-di-*tert*-butyl-2,2'-bipyridine. Cobalt of di-*tert*-butyl bipy is more efficient for cross-coupling of perfluoroaryl and aryl or heteroaryl halides with Zn soluble anode (yield up to 60% with 0.01% content of catalyst). The method is versatile and gives the adducts to olefins.

The advantages of method are a single-stage and high yields of cross-coupling product at the mild conditions (room temperature).

This work was supported by Russian Foundation for Fundamental Research (grant № 10-03-00335-a)

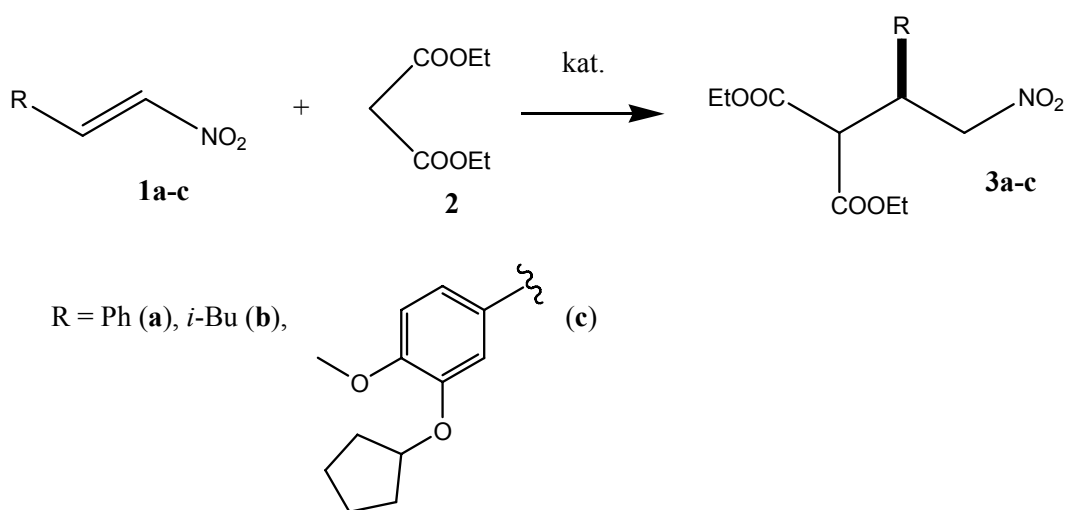
CHIRAL DIAMINES COMPLEXES AS CATALYSTS FOR ENANTIOSELECTIVE MICHAEL ADDITION TO NITROALKENE

Yu.N. Klimochkin¹A.N. Reznikov²A.P. Turin¹

1 - CYCLAN Co. Ltd., Samara, Russia

2 - Samara State Technical University, Samara, Russia
orgphosphorus@yandex.ru

The Michael reaction ranks as one of the most useful C-C bond constructions, and the development of catalytic enantioselective variants has become an important endeavor. We report the transition metal catalyzed enantioselective addition of malonates to nitroalkenes:



Catalyst design was based on the hypothetical catalytic cycle included 1,3-dicarbonyl enolization following nucleophilic attack of acetylacetonate type ligand on nitroalkene.

The reaction of diethyl malonate with nitroalkenes **1a-c** were investigated in the presence of Ni, Co, Mn, Cu, Cr, Ag and Pd complexes with 1,2-diaminocyclohexane, *l*-proline and camphor derived chiral diamine ligands. The yield of products and enantioselectivity of reaction (40 – 92 % *ee*) depend significantly on the structure of nitroalkenes and complexes employed.

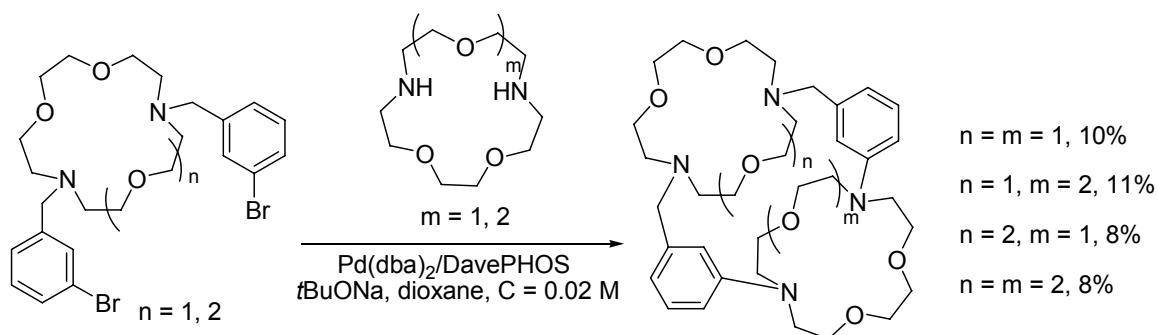
The work is supported by Russian Ministry of Education and Science (16.512.11.2011).

CYLINDRICAL MACROPOLYCYCLES COMPRISING CYCLEN, CYCLAM, AZA- AND DIAZACROWN ETHER MOIETIES

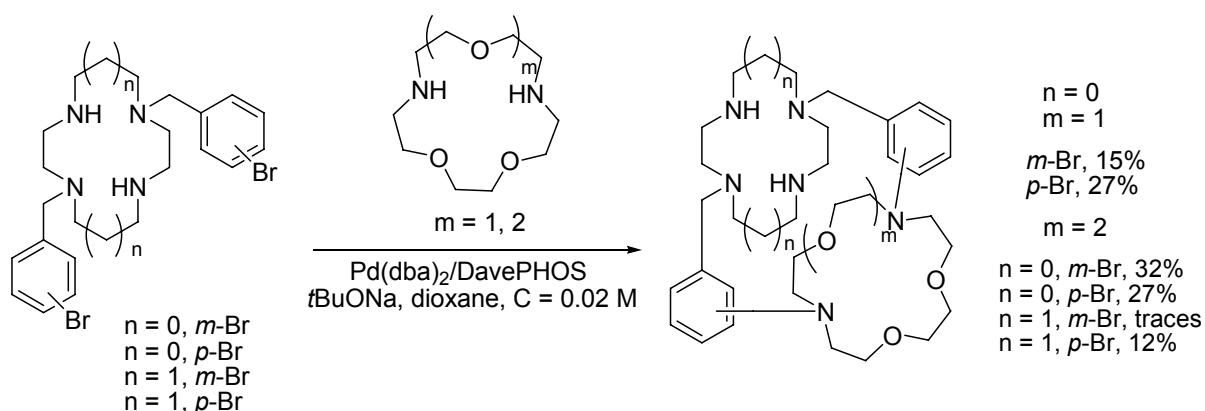
S.M. Kobelev¹
 A.A. Yakushev¹
 M.V. Anokhin¹
 A.D. Averin¹
 F. Denat²
 R. Guillard²
 I.P. Beletskaya¹

1-M.V. Lomonosov Moscow State University, Chemistry Department, Moscow, Russia
 2-ICMUB-LIMRES, UMR CNRS 5260, Universite de Bourgogne, Dijon, France
 sgkobelev@gmail.com

Cylindrical macrotricycles containing two diazacrown ether moieties were synthesized by the reaction of *N,N'*-di(bromobenzyl) substituted diazacrown ethers with diazacrown ethers *via* Pd-catalyzed amination. The reactions afforded only tiny yields of corresponding macrotricyclic compounds due to oligomerization processes.



Similar macropolycyclic compounds based on cyclen and cyclam were obtained under the palladium catalysis conditions generally in much better yields. We have established the dependence of the yields of the target products on the nature of tetraazamacrocycles and diazacrown ethers.



The work was supported by the RFBR grant N 09-03-00735.

**NEW APPROACH TO NICKEL-MEDIATED
HOMOCOUPLING OF ARYL HALIDES**

V.N. Valaeva¹
A.Z. Vokcoboynikov¹
V.R. Flid²

1 - Moscow State University, Chemistry Faculty, Moscow, Russia
2 - Moscow State Academy of Fine Chemical Technology, Moscow,
Russia
valaeva@gmail.com

The synthesis of symmetrical biaryls is an important problem of modern preparative chemistry, since many pharmaceuticals, agrochemicals, dyes, chiral ligands include fragments containing functionalized biphenyl.

One of the most common ways to achieve functionalized biphenyls is homocoupling of aryl halides in the presence of nickel complex with triphenylphosphine ligand, zinc dust and Et₄Ni. Though this method works very well for different aryl halides it requires large amount (10-30 mol %) of expensive and toxic phosphine ligand. So the following time-consuming purification procedure is required to isolate analytically pure product and remove phosphine materials.

Our aim was to overcome these drawbacks and to design more effective catalytic system of aryl halides.

It was found out that a set of nickel with diazabutadiene ligand can form the high-performance catalytic system for homocoupling of aryl halides. Only 1 mol % of this complex is required for homocoupling of aryl bromides and aryl chlorides with high yields. The availability of non-toxic diazabutadiene ligands, the tolerance to functional groups, no necessity to use large amounts of expensive, toxic or corrosive reagents can be designated as the advantages of this method.

A number of diazabutadiene ligands were synthesized, and the ligand structure effect on the activity of catalysts in the synthesis of biaryls was studied. Various functionalized biphenyls were synthesized to show the versatility of the method.

Section 5.

Supramolecular Organic Chemistry: VI International Symposium “Design and Synthesis of Supramolecular Architectures”



Bruker BioSpin

They said it couldn't be done...



- **World's First 1 Gigahertz NMR Spectrometer**

Record Breaking 23.5 Tesla Standard-Bore,
Persistent Superconducting Magnet

Only from Bruker

Contact us for more details: +7(495)502 9006

avance1000@bruker.ru or www.bruker-biospin.com/avance1000

think forward

nmr@bruker.ru

NMR

Our offices and service overall in Russia

Leninskiy prospekt 47
119991 Moscow

Moscow: +7(495)502 9006
Kazan: +7(843)290 8189

SUPRAMOLECULAR CHIRALITY OF COLLOIDAL SURFACTANTS

A.I. Rusanov
A.G. Nekrasov

St. Petersburg State University, Mendeleev Center, St. Petersburg,
Russia
rusanov@AR1047.spb.edu

The concept of supramolecular chirality is well known in supramolecular chemistry with the possibility of chirality for supramolecules composed of both chiral and achiral compounds. For example, two molecules of different achiral substances can form a complex possessing chirality. We discovered a similar phenomenon in the process of micellization of colloidal surfactants, although this process is not accompanied with weak (non-covalent) interactions. In this presentation, we illustrate the phenomenon with the examples of sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium bromide, and polyoxyethylene(4)mono-n-dodecyl ether (Brij-30) as typical representatives of anionic, cationic, and nonionic surfactants. The three surfactants are achiral chemical compounds and do not possess optical activity in the monomeric form. However, molecular aggregates exhibiting dextro-rotatory optical activity, arise in the process of micellization.

The dependence of the optical rotation on the concentration of the aqueous surfactant solution is characterized by the presence of a pronounced maximum. The phenomenon occurs near the critical micelle concentration (CMC) and develops still before the CMC, which gives evidence of chirality of pre-micellar surfactant aggregates. In the process of micellization, the surfactants form spherical micelles, which cannot possess optical activity because of the presence of the symmetry center in them. Therefore, the formation of spherical micelles is accompanied with lowering the solution optical activity down to a certain almost constant level corresponding to the contribution of the chiral part of the equilibrium distribution of aggregates in their aggregation numbers (the further increase of concentration only leads to the growth of the number of optically inactive spherical micelles). Remarkably, the formation of spherical micelles of SDS is completed at a concentration about 15 mole/m³, although the known value of the CMC for SDS is 8.3 mole/m³. This shows the study of optical activity to be a new useful tool for the investigation of the process of micellization in surfactant solutions.

According to the first Biot's law, the optical rotation should be proportional to the thickness and concentration of the solution. The proportionality to the solution thickness was verified and confirmed, but the proportionality to concentration is evident not to be fulfilled because of the existence of the above maxima. This makes a principal difference between the chirality observed in this work and the chirality described in supramolecular chemistry, and we may conclude that Biot's law is inapplicable to colloid surfactant solutions. This is related to the fact that Biot's law refers to the real concentration of optically active particles, whereas we deal with the total surfactant concentration including both active and inactive particles. In addition, Biot's law was formulated for an optically one-component system but not for a complex aggregative mixture, which is a micellar system.

The above experiments were carried out using white light, but we also verified and confirmed the second Biot's law that reads that optical activity is proportional to the square

of the light wavelength. The experiment was performed for the SDS solution with monochromatic beams of the wavelengths of 0.45, 0.48, 0.57, and 0.61 μm . For each wavelength, the concentration maximum of optical rotation was again obtained, and the maximal effect was attained for the minimal wavelength, the maximum being shifted to the left from the CMC. All the measurements were made at 20°, i.e. above the Krafft point which is 8° for SDS. To verify that the effect observed was caused by micellar aggregation, we repeated the experiment at 7° and discovered no optical activity.

Thus, we have presented a new kind of supramolecular chirality, which can be termed as the aggregative or concentration chirality since it results from the molecular aggregation process and within a certain concentration range. Naturally, this kind of chirality, typical for colloidal surfactants, is not universal and depends, as chirality at all, on the nature of a surfactant. For example, we found no optical activity for dodecanoyl-N-methylglucamide, which is also a colloidal nonionic surfactant.

This work was supported by the RF President Program “Leading Scientific Schools of Russian Federation (Grant 6291.2010.3).

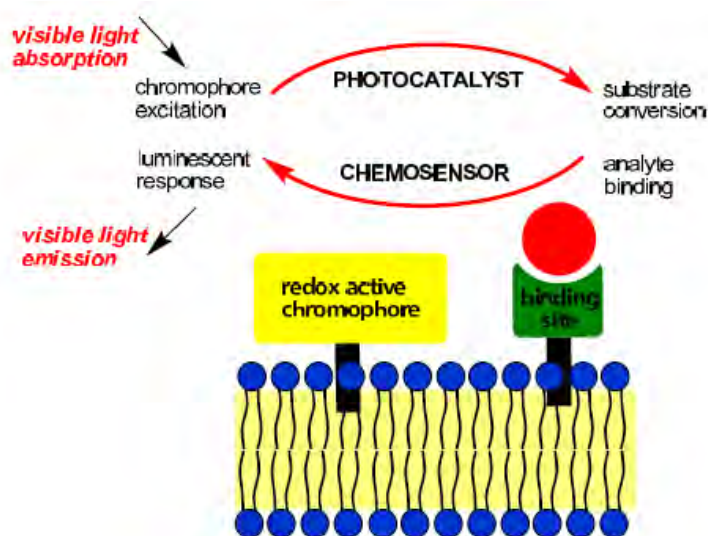
LUMINESCENT CHEMOSENSORS AND CHEMICAL PHOTOCATALYSTS FROM SELF-ASSEMBLY OF AMPHIPHILIC RECEPTORS AND DYES

B. König

University of Regensburg, Institute of Organic Chemistry,
Regensburg, Germany
burkhard.koenig@chemie.uni-regensburg.de

Co-embedding of amphiphilic synthetic receptors and dye molecules in membranes is a fast and easy strategy to assemble binding sites and chromophores in close distance. Binding of analyte molecules induce changes of the self-assembled membrane composition close to the binding sites leading to altered emission properties of the reporter dyes. The modular supra-molecular system allows therefore the facile preparation of luminescent chemosensors for a wide variety of analytes. The same assembly can be used as visible light chemical photo-catalyst: Now the chromophore acts as an antenna collecting light energy that induces redox reaction on substrates at the nearby binding site. The use of chiral binding sites allows enantioselective transformations.

We discuss the principles of the technique and its applications in chemical bioanalysis and photocatalytic synthesis.



References:

- D. A. Jose, B. König, *Org. Biomol. Chem.* **2010**, 655.
- D. Amilan Jose, S. Stadlbauer, B. König, *Chem. Eur. J.*, **2009**, 15, 7404.
- D. Vomasta, C. Högner, N. R. Branda, B. König, *Angew. Chem. Int. Ed.* **2008**, 47, 7644.
- B. Gruber, S. Stadlbauer, A. Späth, S. Weiss, M. Kalinina, B. König, *Angew. Chem. Int. Ed.* **2010**, 49, 7125.
- A. Riechers, F. Schmidt, S. Stadlbauer, B. König, *Bioconjugate Chem.* **2009**, 20, 804.
- M. Neumann, S. Földner, B. König, K. Zeitler, *Angew. Chem.* **2011**, 123, 981.
- D. S. Turygin, M. Subat, V. V. Arslanov, B. König, M. A. Kalinina, *Chem. Eur. J.* **2010**, 16, 10560.
- T. Meierhofer, I. C. Rosnizeck, T. Graf, K. Reiss, H. R. Kalbitzer, M. Spoerner, B. König, *J. Am. Chem. Soc.* **2011**, 133, 2048.
- I. C. Rosnizeck, T. Graf, M. Spoerner, J. Tränkle, D. Filchtinski, C. Herrmann, L. Gremer, I. Vetter, A. Wittinghofer, B. König, H. R. Kalbitzer, *Angew. Chem.* **2010**, 122, 3918.

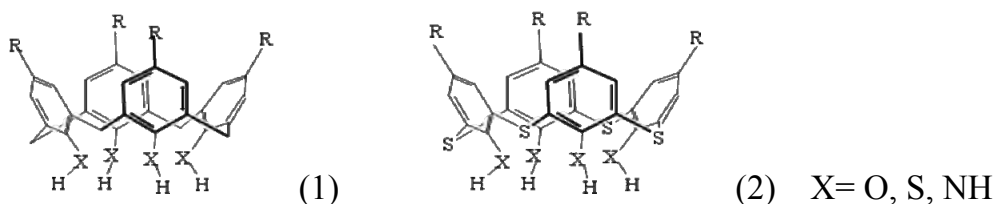
**CALIX[4]ARENES BASED SUPRAMOLECULAR
SYSTEMS: FROM MOLECULAR DESIGN TO
NANOTECHNOLOGICAL APPLICATIONS**

I.S. Antipin¹
S.E. Solovieva²
I.I. Stoikov¹
A.I. Konovalov²

1 - Kazan (Volga region) Federal University, Department of Organic Chemistry, Kazan, Russia
2 - A.E. Arbuzov Institute of Organic & Physical Chemistry, Kazan, Russia
iantipin@ksu.ru

Now one of the most perspective ways of the nanomaterials design is the "bottom-up" technology in which the higher organized nanosystems are spontaneously formed due to supramolecular self-organization and self-assembly from individual atoms and molecules. A key element of supramolecular chemistry, and now nanotechnology, is the principle of the molecular recognition. From this point of view, one of the actual problems of supramolecular chemistry is the molecular design and synthesis of preorganized receptor and amphiphilic molecules which are capable on the principles of molecular recognition and multipoint interactions to form host-guest complexes as well as self-organized supramolecular ensembles and devices.

Nanotechnological approach "bottom-up" can be effectively implemented on the basis of meta-cyclophanes: calix[4]arene 1, thiacalix[4]arene 2



The report will be presented the main approaches to the stereo and chemoselective functionalization of calix[4]arene platforms that allows to change significantly hydrophilic-lipophilic properties of macrocycles and to raise efficiency and selectivity of the interaction with substrates. The strategies and methods for the synthesis of a new class of nanosized macrocyclic compounds - calixarene conjugates will be demonstrated as well. There will also be examined regularities of aggregation and complexation of calixarenes with substrates of different nature: non-electrolytes, cations, anions. Particular attention will be paid to the application of calixarene derivatives for the construction of various supramolecular and nanosystems, devices and "smart" materials: nanoparticles, metal-coordinated networks, Langmuir-Blodgett nanolayers etc.

Financial support of RFBR (grant No 10-03-00728) and Russian Education and Science Ministry (contract No 14.740.11.0384) are gratefully acknowledged.

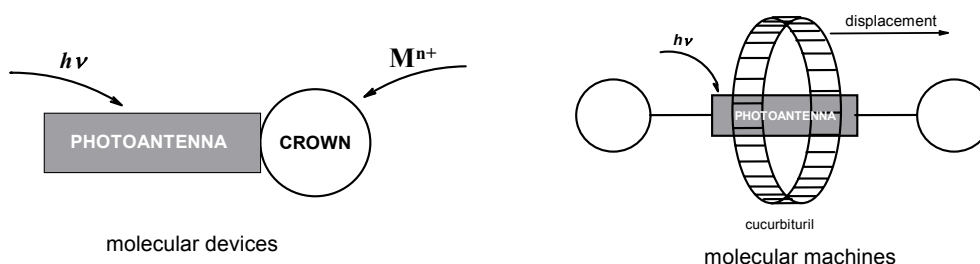
**DESIGN OF LIGHT-SENSITIVE MOLECULAR
DEVICES AND MACHINES BASED ON
UNSATURATED AND MACROCYCLIC
COMPOUNDS**

S.P. Gromov¹
E.N. Ushakov²
A.I. Vedernikov¹
L.G. Kuzmina³
M.V. Alfimov¹

1 - Photochemistry Centre of the RAS, Moscow, Russia
2 - Institute of Problems of Chemical Physics of the RAS,
Chernogolovka, Russia
3 - N.S. Kurnakov Institute of General and Inorganic Chemistry of the
RAS, Moscow, Russia
spgromov@mail.ru

Currently a new trend is formed in nanotechnology “bottom-up”: molecular engineering of molecular devices and machines for various purposes. We propose a new unique class of polyfunctional light-sensitive compounds: unsaturated dyes functioning as photochromes, fluorophores and ionophores. A large body of research has been performed for their synthesis, determination of their spatial structures, study of self-assembly features to give nanosized systems, and also study of fluorescent, photochemical and complexing properties.

Resulting from the research, we elaborated for the first time universal molecular meccano, allowing one to accomplish building-up, with using a limited number of complementary compounds, light-sensitive and light-emissive nanosized systems of varied architecture with adjusted properties. Within the same class of compounds one can construct in solution, solid and at the air-water interface new types of photoswitchable molecular devices, photocontrolled molecular machines, photosensitive monolayers and monocrystals susceptible to all of the key photoprocesses.



The high practical value of these studies deserves attention. They provide a new strategy for the design of materials for nanophotonics, which was demonstrated, first of all, by the creation of practically important sensor and photochromic materials.

This work was supported by the RAS, the RFBR, the Ministry of Science and Education, the Moscow Government, the INTAS, the CRDF, the DFG, and the Royal Society.

**SYNTHESIS, STRUCTURE AND FUNCTIONAL
PROPERTIES OF MICROPOROUS ZINC
CARBOXYLATES**

V.P. Fedin
S.A. Sapchenko
D.G. Samsonenko

Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk,
Russia
cluster@niic.nsc.ru

Among the metal-organic frameworks, coordination polymers based on zinc carboxylates play a special role because of large number of possible building units, varying from Zn(II) monomers to small di-, tri-, tetranuclear clusters or even infinite chains, assembled into robust porous frameworks with catalytic, luminescent and gas sorption properties.

Herein we report the synthesis, structure, thermal, luminescent and sorption properties of new microporous metal-organic coordination polymers $[\text{NH}_2(\text{CH}_3)_2]_2[\text{Zn}_2(\text{bdc})_4]\text{DMF}\cdot\text{H}_2\text{O}$ (**1**), $[\text{NH}_2(\text{CH}_3)_2]_2[\text{Zn}_2(\text{bpdc})_4]\cdot 5\text{DMF}$ (**2**) and $[\text{Zn}_4(\text{ndc})_4(\text{ur})_2(\text{dmf})]\text{DMF}$ (**3**) (H_2bdc = 1,4-benzene-dicarboxylic acid, H_2bpdc = 4,4'-biphenyldicarboxylic acid, H_2ndc = 2,6-naphthalenedicarboxylic acid, ur = urotropin, dmf = N,N'-dimethylformamide) [1, 2].

The single-crystal X-ray structure analyses reveal compounds **1** and **2** have 3D anionic framework structure build from zinc(II) carboxylate layers linked by carboxylate anions. Compound **3** has a neutral framework with permanent porosity and high surface area. Guest DMF molecules within the channels of **3** ($9.5 \times 10 \text{ \AA}$) can be evacuated without loss of crystallinity. Guest-free material demonstrates adsorption not only of light gaseous molecules but also aromatic molecules. Single-crystal to single-crystal formation of different host-guest systems (e.g. with benzene and ferrocene) was investigated. Interesting guest-depended luminescence properties of the porous host framework were observed.

References:

- [1] S.A. Sapchenko, D.N. Dybtsev, D.G. Samsonenko, V.P. Fedin, *New J. Chem.*, **2010**, 34, 2445–2450.
[2] S.A. Sapchenko, D.G. Samsonenko, D.N. Dybtsev, M.S. Melgunov, V.P. Fedin, *Dalton Trans.*, **2011**, 40, 2196–2203.

The study was supported by the Russian Foundation for Basic Research (grant No. 11-03-00112). A grant of the Russian Academy of Sciences (program No. 5.6.1) is gratefully acknowledged.

SUPRAMOLECULAR DEVICES BASED ON PHOTORESPOSIVE ASSEMBLIES OF CUCURBIT[7]URIL AND CROWN-ETHER DERIVED STYRYL AND (BIS)STYRYL DYES

O.A. Fedorova¹
E.Yu. Chernikova¹
Yu.V. Fedorov¹
E.N. Gulakova¹
G. Jonusauskas²
L. Isaacs³

1 - A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Moscow, Russia

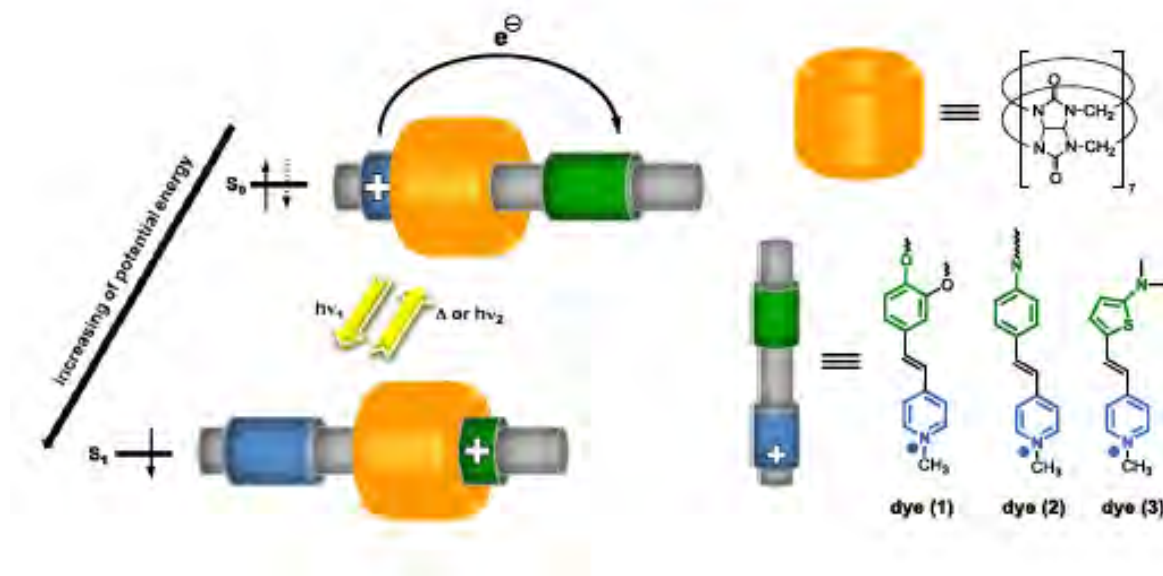
2 - Laboratoire Ondes et Matière d'Aquitaine – Bordeaux University I, UMR CNRS 5798, Talence, France

3 - University of Maryland, Department of Chemistry and Biochemistry, College Park, USA

fedorova@ineos.ac.ru

The rigid structure, good water solubility, and ability to form tight complexes with molecules and ions make CB[7] particularly attractive as a building block for the construction of supramolecular architectures and devices. This report describes the interaction of CB[7] molecular container with crown ether styryl and (bis)styryl dyes by (1) cation-dipole interactions between the positively charged dyes and the ureidyl C=O dipoles which line the CB[n] portals, and (2) hydrophobic interactions between the guest and the CB[n] host cavity. We found that the composition of the formed complexes depends on the relative stoichiometry of dye and CB[7].

For the monostyrylic dyes the photoinduced moving of exited dye in CB[7] cavity was proved by analysis of the steady state and time-resolved fluorescence as well as pump-probe experimental results. The behavior of the complexes of dyes with CB[7] similar to moving of piston in cylinder which uses the light photon energy to move.



Acknowledgments to RFBR program (09-03-00241) and IRG "SUPRACHEM" for financial support.

**MULTIFUNCTIONAL MACROCYCLIC RECEPTORS
IN ELECTROANALYSIS. BROADENING
ELECTROCHEMICAL HORIZONS**

G.A. Evtugyn
E.E. Stoikova
S.V. Beljakova
R.V. Shamagsumova

Kazan University, Analytical Chemistry Department, Kazan, Russia
Gennady.Evtugyn@ksu.ru

There is a growing need in the development of novel analytical techniques for specific and effective recognition of organic species, among them those exerting biological activity. Such receptors are urgently demanded in the extraction and membrane technologies, drug delivery systems and sensor development. The use of macrocyclic compounds offers new potentialities in the receptor design due to variety of their functionalization and pre-organization of the binding sites in accordance with the substrate species.

In this report, the application of functionalized macrocyclic receptors based on thiacalix[4]arene platform bearing functional groups different in their redox-, acid-base properties and lipophilicity in the assembly of electrochemical sensors is summarized to show their prospects in the analysis of inorganic and organic species. All the receptors were synthesized on the Organic Chemistry Department of the Kazan Federal University. The following applications of macrocyclic receptors in electroanalytical chemistry are considered: the development of solid-contact potentiometric sensors with extended sensitivity toward transient metal ions, organic acids and antioxidants; the application of multi-sensor system (Electronic Tongue) for the quality assessment of foodstuffs and discrimination of hot drinks and beverages; the use of electrochemically active macrocyclic receptors as matrices for the synthesis of metal nanoparticles and their use as mediator systems in amperometric sensors for the determination of dopamine, hydrogen peroxide and halogenide ions; multifunctional macrocyclic receptors as nanosized supports for the development of biorecognition layers in the electrochemical biosensors for the detection of specific analytes interacting with DNA and proteins. The effect of the various structural parameters of the receptors (nature of functional groups of the substituents, the size and configuration of the macrocyclic cavity), recognition layer content and measurement conditions on the analytical performance of the (bio)sensors developed is considered and most important directions of the further progress in this area discussed.

Financial support of RFBR (grant No 11-03-00381-a) and Russian Education and Science Ministry (contract No 16.740.11.0496) are gratefully acknowledged.

**LANGMUIR FILMS OF FULLERENE AND
CALIXARENE DERIVATIVES AS A BIOMIMETIC
MODELS. PHYSICOCHEMICAL CHARACTERISTICS
AND BIOLOGICAL POTENTIALITIES**

N.B. Melnikova

Department Pharmaceutical Chemistry, Nizhny Novgorod State
Medical Academy, Nizhny Novgorod, Russia
melnikow@rol.ru

The study of macrocycles thin films such as self-assembled monolayers, self-organized bilayers and Langmuir-Blodgett films is of interest from both fundamental and practical viewpoints.

This report deals with molecular modeling of the interaction in biosystems by using Langmuir films of fullerene and calixarene derivatives as a tool for investigation the pharmacological effects of biologically active compounds and for development new medicines.

The monolayers of nitroxide mono- and bis- methanomalonate and methanophosphorilate [(NO)₄-bis-phosphonato] fullerenes, amphiphilic tetramethyl-sulphonatocalixresorcinarene (R = C₁₁H₂₃) in cone conformation, *tert*-butylthiacalix[4]arenes (Y=O(CH₂)₃CN; OCH₂CN; NH₂; OCH₂PhCN-*p*) and thiacalix[4]arene (Y=O(CH₂)₃CN) in *1,3-alternate* conformation able to be a biomimetic model of antioxidant activity.

Monolayers of the calixarenes have good receptor capacity for macromolecules such as enzymes – cytochrom c and ceruloplasmin. It has been shown, that molecular area A₀ of calixarenes in monolayers and surface pressure coefficient $-d\pi/dA$ reflect changes of enzymes redox station in the presense of dihydroquercetin and ascorbic acid in aqueous subphase. UV-Vis- and IR- spectra of subphase solution and of transfered monolayers were suggested the oxidation of antioxidants up to quinones and the formation reduced form of enzymes.

The phosphorylated methanofullerenes and their mixtures with lecithin can form stable monolayers at the air-water interface and thin films are able to produce self-organising vesicles. P-methanofullerene – lecithin mixtures in the presence of Ca²⁺ - ions give a good result by medical treatment of osteoporosis in the experiments with rats.

A.R. Mustafina
O.D. Bochkova
V.A. Burilov
V.V. Skripacheva
J.G. Elistratova
R.R. Zairov
A.I. Konovalov

STIMULI RESPONSIVE COLLOIDS FROM LUMINESCENT NANOPARTICLES

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
asiyamust@mail.ru

Multifunctional stimuli responsive nanoparticles gain much attention as the basis of nano-materials for drug delivery and bio-sensing. The present report represents some of potential ways to obtain lanthanide doped core-shell nanoparticles. The first of them is the the doping of luminescent lanthanide complexes into silica nanoparticles through the microemulsion and Stober procedure. The main advantages and shortcomings of microemulsion and Stober procedures will be discussed. The second way to get core-shell luminescent nanoparticles is to encapsulate the reprecipitated luminescent Eu(III) complex as a core into polyelectrolyte capsule fabricated through the layer-by-layer (LbL) procedure. Long life times of the excited state, narrow intensive emission bands, low rates of leakage and photobleaching are the main advantages of lanthanide doped nanoparticles. The approaches to get dual luminescent and paramagnetic colloids of nanoparticles containing two various metal complexes will be also represented. The size variation from 30 to 300 nm has been got through the use of various procedures. The wavelength of the emission bands has been modified from visible to near IR, as well as dual visible-near IR by the variation of lanthanide ions (Eu(III), Tb(III), Yb(III), Nd(III)) and/or ligand environment.

The non-covalent adsorption of surfactants at the silica/water interface of lanthanide doped silica nanoparticles and LbL polyelectrolyte assembly are represented as possible ways to modify the shell of core-shell nanoparticles. The substrate induced quenching or sensitizing of the lanthanide centered luminescence will be also represented as a basis to gain sensing function.

References:

1. A.R. Mustafina, S.V. Fedorenko, O.D. Konovalova, A.Yu. Menshikova, N.N. Shevchenko, S.E. Soloveva, A.I. Konovalov, I.S. Antipin. *Langmuir*. 2009, V.25, P.3146-3151.
2. S.V. Fedorenko, O.D. Bochkova, A.R. Mustafina, V.A. Burilov, V.V. Skripacheva, A.Yu. Menshikova, S.E. Soloveva, A.I. Konovalov, I.S. Antipin. *J.Phys.Chem.C* 2010, 114 (14), 6350–6355.
3. A. R. Mustafina, J. G. Elistratova, O. D. Bochkova, V. A. Burilov, S. V. Fedorenko, A. I. Konovalov, S. Ye. Soloveva. Temperature induced phase separation of luminescent silica nanoparticles in Triton X100 solutions. *J.Coll.Interf.Sci.* 2011, 354, 644-649.

We thank RFBR (grant N 10-03-00352) for financial support.

DESIGN AND SYNTHESIS OF SUPRAMOLECULAR ARCHITECTURES BASED ON NOVEL PHOSPHORUS-CONTAINING PORPHYRINS

Yu.G. Gorbunova¹
 Yu.Yu. Enakieva²
 A.A. Sinelshchikova²
 S.E. Nefedov¹
 A. Bessmertnykh-Lemeune³
 R. Guillard³
 A.Yu. Tsivadze²

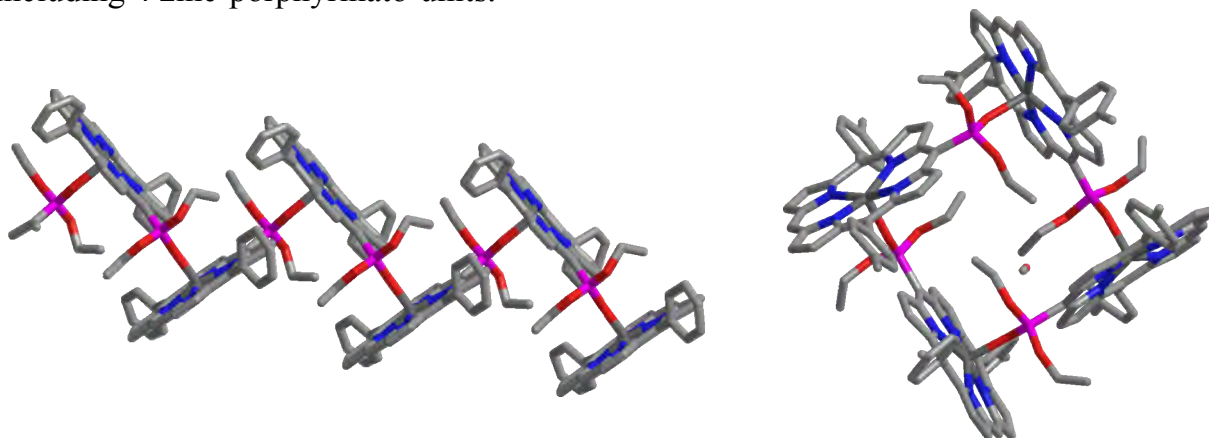
1 - Kurnakov Institute of General and Inorganic Chemistry of RAS, Moscow, Russia

2 - Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, Moscow, Russia

3 - University of Burgundy, ICMUB, Dijon, France
 yulia@igic.ras.ru

Recently we have developed a general method toward new porphyrin synthons possessing various phosphoryl groups^{1,2} at the periphery of the macrocycle (meso and β -positions). It was shown that in the solid state porphyrin derivatives containing one or two diethylphosphoryl units at the 5 and 15 *meso* positions and two 4-aryl moieties bearing various groups (H, CH₃, CN, OCH₃ and COOCH₃) at the 10 and 20 *meso* positions lead, in the presence of a zinc dication, to the formation of different 1-D and 2D networks or coordination cells depending both from the number of phosphoryl groups and the nature and hindrances of functional group in aryl moieties.

Figure shows the examples of the self-assembling of mono-phosphorylated porphyrins. Thus, the complex containing phenyl groups in the *meso* 10,20 positions of porphyrin forms 1D linear polymer, while the self-assembling of complexes containing two 4-aryl moieties bearing CH₃, OCH₃ or COOCH₃ leads toward “calyxarene-like” structure including 4 zinc-porphyrinato-units.



References:

1. Enakieva Y.Y., Bessmertnykh A.G., Gorbunova Y.G., Stern C., Rousselin Y., Tsivadze A.Y., Guillard R. *Org. Lett.*, **2009**, *11*, 3842-3845.
2. Kadish K.M., Chen P., Enakieva Y.Y., Nefedov S.E., Gorbunova Y.G., Tsivadze A.Y., Bessmertnykh-Lemeune A., Stern C., Guillard R. *J. of Electroanalytical Chemistry*, **2011**, *656*, 61-71.

This work was performed in the framework of French-Russian Associated Laboratory “LAMREM” and “SUPRACHEM”, supported by Russian Foundation for Basic Research, the CNRS and Russian Academy of Sciences (Program 6).

**DESIGN OF NANOREACTORS BY
CONTROLLABLE SELF-ORGANIZATION OF
DIMERIC AMPHIPHILIC COMPOUNDS**

E.A. Karpichev¹
L.Ya. Zakharova²
A.F. Popov¹
A.I. Konovalov²

1 - L.M. Litvinenko Institute of Physical Organic Chemistry and Coal Chemistry, National Academy of Sciences of Ukraine; Donetsk, Ukraine

2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences; Kazan, Russia
lucia@iopc.ru

The desirable control of the reactivity is one of the key problems of modern chemistry. Perfect catalytic systems are known to be biocatalysts, which demonstrate polyfunctional concerted mechanism and high selectivity. Immediate analogues of biosystems modeling principles of their self-organization are surfactant assemblies. Facilities of the catalysis in microheterogeneous systems may be essentially enlarged by means of the variation of the structure of aggregates. Within the frameworks of the report, perspectives of the design of supramolecular catalytic systems based on homological series of amphiphilic compounds are considered at the gradual structural changes of head groups and the variation of molecular scaffold. The effect of the nature of head groups and counterions, as well as hydrophobicity on the micellar properties and catalytic activity are exemplified by dicationic surfactants. The molecule of dimeric surfactant is composed of two polar groups and two hydrophobic tails bridged by a more or less flexible fragment (spacer). Dimeric surfactants are characterized by unique properties including anomalous low (by one to three orders of magnitude lower compared to that of conventional surfactants) critical micelle concentration, low Krafft temperature, polymorphism, high surface activity and solubilization capacity, ecological safety, etc. For this surfactant series, the capability of modification of spacer by hydrophilic and hindered groups are discussed; in addition, the ways of functionalization of dimeric surfactants by nucleophilic fragments are proposed. Surfactants with head groups functionalized by alfa-nucleophilic fragments and reactive counterion surfactants are considered. The micellar effect of these amphiphiles upon the cleavage of carbon, phosphorus and sulfur acid esters is discussed. The correlation revealed between the structure of functional surfactants and their reactivity makes it possible to optimize the chemical structure providing the maximum catalytic activity in the nucleophilic cleavage of acyl-containing substrates. As additional building blocks, amphiphilic cyclophanes (calixarenes, pyrimidinophanes, etc.) can be used. Combination of tectones of different chemical nature and geometry in the framework of the uniform composition can essentially extend the spectrum of instruments for desirable control of morphology and functional activity of nanoaggregates due to the variation of the component ratio.

This work was supported by the Russian Foundation for Basic Research, grant 12-03-10 (Ukraine)/10-03-90416 (Russia).

**MOLECULAR RECOGNITION IN FORMATION AND
DECOMPOSITION OF CLATHRATES WITH SOLID
SUPRAMOLECULAR HOSTS**

**V.V. Gorbachuk
M.A. Ziganshin**

Kazan Federal University, Chemical Institute, Kazan, Russia
Valery.Gorbachuk@ksu.ru

Specific features of clathrate formation with calixarenes and beta-cyclodextrin and guest binding with several other macromolecular receptors were used for molecular recognition of organic vapors by sensors and in model experiments with host powders. These features include a cooperativity of guest binding with solid host and clathrate decomposition, partial binding reversibility, multi-step formation and decomposition of clathrates, guest exchange in solid host phase, host polymorphism with a memory of eliminated guest structure, and cooperative hydration effect for hydrophilic hosts with guest encapsulation upon host drying.

The clathrate properties were studied using gas chromatographic headspace analysis, simultaneous thermogravimetry and differential scanning calorimetry combined with mass-spectrometry, and quartz microbalance sensors. For systems with guest vapors and solid host, the vapor sorption isotherms, Gibbs energy of clathrate formation, stoichiometry of saturated clathrates, temperatures and enthalpies of guest elimination from clathrates and of host collapse were determined.

The clathrate parameters were observed to depend much on the host molecular structure and on the related type of guest encapsulation or interstitial binding. Hence, several new approaches were offered to boost a molecular recognition capability of a receptor for determination of single vapors and components of complex binary mixtures.

This work was supported by RFBR (№11-03-01215) and BRHE program (REC-007).

**COMPLEXATION OF Pd WITH
THIACALIX[4]ARENES DURING EXTRACTION
FROM NITRIC ACID SOLUTIONS**

V.G. Torgov¹
G.A. Kostin¹
T.V. Us¹
T.M. Korda¹
A.B. Drapailo²

1 - Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia

2 - Institute of Organic Chemistry NAS Ukraine, Kyiv, Ukraine
kostin@niic.nsc.ru

Increase in acidity of OH-groups in lower rim of thiocalix[4]arenes (TCA) compared with calix[4]arenes leads to increase in extraction properties. In contrast to calix[4]arenes thiaderivatives extract most metal cations from neutral and alkaline media mainly because of proton-cation exchange in LH_4 . According to quantum-chemical calculations and XES-spectra partial charges of sulfur atoms in TCA is similar to that in upper rim modified calix[4]arene-thioesters (CTE) or dialkylsulphides (R_2S). Thus TCA can be applied for extraction of halcophilic metals, including noble metals, also from acidic solutions.

Compared with ungrafted calix[4]arenes demonstrating very low palladium extraction from acidic (0,3 – 1 M HNO_3) media, TCA in “cone” conformation have D_{Pd} 4-5 orders higher because of participation of bridging sulfur atoms. Decrease in D_{Pd} from 10^3 to 10^2 at the concentration of $\text{HNO}_3 > 1$ M can be explained by competitive extraction of nitric acid or by low stability of TCA to oxidation. Palladium distribution coefficients for TCA in “1,3-alternate” conformation are lower ($10^{-1} - 1$) and do not depend on the acidity of water phase. Since the charge state of sulfur atoms in TCA of various conformations is similar the change of extraction properties is determined by spatial “metal-ligand” fitness.

Stoichiometry of palladium extraction by TCA from nitric acid solutions differs from earlier determined for calix[4]arene-thioesters where palladium atom is coordinated by two sulfur atoms and inorganic anions. Saturation of organic phase results in $\text{Pd}:\text{LH}_4$ ratio equal to 4 for TCA and 2 for CTE. Coordination of TCA to palladium during extraction from weak acid media is realized with participation of bridging sulfur atom and two proximate deprotonated phenoxy-groups as $[\text{Pd}_2\text{L}]$ that differ from dimer $\text{Pd}_2(\text{LH}_2)_2$ described earlier. For extraction from nitric acid solution complexes $[(\text{Pd}(\text{NO}_3)_2)_n \text{LH}_4]$ ($n=1-4$) are formed in organic phase. All four constants of addition of $\text{Pd}(\text{NO}_3)_2$ fragment to LH_4 were determined, satisfactorily describing palladium interphase distribution from nitric acid in the range of palladium concentrations from 10^{-3} to 10^{-1} mol/l.

Comparison of TCA with acyclic (2,2-thiobis(4-tert-butyl)phenol) and CTE with monodentate R_2S was carried out. In the first case values of D_{Pd} is similar for TCA and acyclic analogue because of the same coordination mode in the frames of one sulfur-containing fragment at the equal concentration of sulfur atoms in solution. In second case distribution coefficients increase for 2-3 orders for macrocycle because of palladium complexation by two proximate sulfur atoms of one molecule of CTE or by two molecules of R_2S .

Since the silver is not recovered by TCA from nitric acid solutions in contrast to other systems based on sulfur-containing extractants thiocalixarenes can be prospective for extraction separation of fission palladium and silver.

**CONTROL OF STRUCTURE FORMATION AS A
WAY OF THE MODULATING THE
PHOTOPHYSICAL AND RECEPTOR
CHARACTERISTICS OF HIGH-ORDERED
ULTRATHIN FILMS BASED ON CONJUGATED
ORGANIC COMPOUNDS**

S.L. Selektor

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry
RAS, Moscow, Russia
sofs@list.ru

The main scientific goal of this study is to develop new approaches to control the aggregation structure and structurally dependent physical and chemical characteristics of organized ultrathin films based on three types of polyfunctional π -conjugated organic compounds (amphiphilic chromo- and fluoro-ionophores, crown-substituted oligothiophenes and multistable rigid macrocyclic compounds). The ability of the molecules in the high-ordered films to switch between monomeric and aggregates (excimers, H- and J-aggregates) states and the data signal modes related to these structural transformations are demonstrated.

The special attention is focused on identifying the nature and mechanisms of redox processes in Langmuir-Blodgett films (LBFs) of crown-substituted double-decker sandwich phthalocyaninates of lanthanides ($\text{Ln}(\text{R}_4\text{Pc})_2$) with different structural organization. The phenomena of the intramolecular electron transfer in Langmuir monolayers initiated by lateral pressure are revealed and discussed on the base of analysis of the monolayer UV-Vis spectra and the results of the electrochemical and spectro-electrochemical investigations of $\text{Ln}(\text{R}_4\text{Pc})_2$ LBFs.

By means of quite a number of different physico-chemical methods it is shown, that the alteration of the subphase cationic composition, the mixed monolayer composition and molecular structure could directionally affect the type and degree of molecule aggregation in the monolayer, and therefore photophysical properties of LBFs and the efficiency of their interaction with the components of aqueous solutions.

The influence of different aggregation types on the monolayer and LBF fluorescence parameters is revealed. The phenomenon of reversible lateral pressure induced excimer formation in chromoionophore monolayers on liquid substrate upon the monolayer cyclic compression-expansion on cation-containing subphases is found out.

**CROWN ETHER-BASED OPTICAL MOLECULAR
SENSORS AND PHOTOCONTROLLED
IONOPHORES**

E.N. Ushakov¹
S.P. Gromov²
M.V. Alfimov²

1 - Institute of Problems of Chemical Physics, Chernogolovka, Russia

2 - Photochemistry Center, Moscow, Russia

en-ushakov@mail.ru

The main design concepts will be reviewed for crown ether-based optical molecular sensors (colorimetric and luminescent indicators) and photocontrolled ionophores.

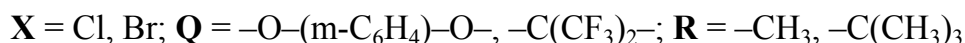
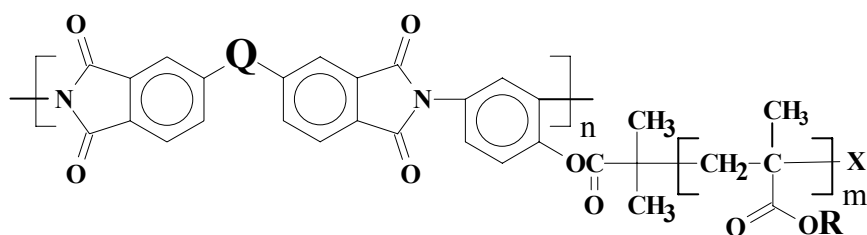
Due to their unique ability to bind selectively alkali metal ions, crown ethers have found a wide application in chemistry, biochemistry and technology. Considerable attention has been focused on the design and physicochemical studies of polyfunctional crown compounds and related supramolecular systems that are capable of operating as optical molecular sensors or photocontrolled ionophores. Currently, targeted synthesis of colorimetric indicators that function in a specified spectral range, from near ultraviolet to near infrared, is practicable. Rational design of molecular systems with cation-triggered luminescence is now possible on the basis of photoinduced charge transfer processes. Considerable progress has been attained in the design of photocontrolled ionophores. Various types of photochromic compounds have been tested for use as photoswitches of the ionophoric function. Multifunctional systems on the basis of styryl dyes and spiro compounds have been developed that can operate both as photocontrolled ionophores and as optical molecular sensors.

A.V. Yakimansky
T.K. Meleshko
N.N. Bogorad
D.M. Ilgach
M.A. Bauman
A.S. Krasova
A.P. Filippov

SUPRAMOLECULAR GRAFT-COPOLYMER ARCHITECTURES ON THE PLATFORM OF POLYIMIDE MACROINITIATORS OF ATRP

Institute of Macromolecular Compounds of the Russian Academy of Sciences, St. Petersburg, Russia
yak@hq.macro.ru

Using ATRP of methylmethacrylate (MMA) and *t*-butyl-methacrylate (TBMA) on polyimide macroinitiators, new supramolecular architectures – polyimide brushes, i.e. regularly grafted copolymers with polyimide backbone and polymethacrylic side chains, are synthesized:



Kinetic studies of MMA propagation on the polyimide macroinitiators and obtained M_n dependences on the monomer conversion degree prove the controlled character of the ATRP process. However, the initiation efficiency is only ~50%, which is, probably, due to a slow initiation compared to the propagation. The incomplete initiation leads to the broadening of the molecular weight distribution (MWD) of the polyimide-*graft*-PMMA copolymers compared to that of the macroinitiator.

Such a broadening of MWD is virtually absent in the case of the polyimide-*graft*-PTBMA copolymers. This is, probably, due to a more advantageous balance between the initiation and propagation rate constants in the case of TBMA polymerization, propagating slower than MMA.

According to the results of light scattering, viscosimetry and diffusion studies, polyimide brush macromolecules are characterized by a dense compact structure in solution. Rather high form-factor values ($R_g/R_h = 2.5\text{--}4.5$) are typical of strongly elongated rod-like or cylinder-like particles. The value of R_g/R_h increases with the lengthening of the backbone and with the shortening of the side chains.

Acidic hydrolysis of side chains in the copolymers polyimide-*graft*-PTBMA made it possible to obtain novel polyimide brushes with the side chains of polymethacrylic acid (PMA). Thus obtained polyimide-*graft*-PMA copolymers may find numerous applications as polyanions for ionic assembling of multilayered shells of nano- and microcapsules and compositions with magnetic, conducting, or luminescent nanoparticles, as polymeric substrates for the preparation of branched chromophore-containing polymer materials with improved second-order nonlinear optical properties, etc.

The work is supported by Russian Fund for Basic Researches (project 11-03-00353-a) and by the grant of the program U.M.N.I.K. for participants of the Youth Contest in Science and Innovations.

A.G. Mirochnik¹
E.V. Fedorenko¹
P.A. Zhikhareva¹
T.V. Sedakova¹
B.V. Bukvetskii¹
I.V. Kalinovskaya¹
I.V. Zhizhchenko²
O.B. Vitrik²
Yu.N. Kulchin²
V.A. Sazhnikov³
V.P. Aristarkhov³
M.V. Alfimov³

**SUPRAMOLECULAR ARCHITECTURE AND
CONTROL OF PHOTO-STIMULATED PROCESSES
IN POLYFUNCTIONAL MATERIALS**

1 - Institute of Chemistry Far Eastern Branch of RAS, Vladivostok, Russia

2 - Institute of Automation and Control Processes Far Eastern Branch of RAS, Vladivostok, Russia

3 - Center of Photochemistry, RAS, Moscow, Russia
mirochnik@ich.dvo.ru

The report presents the data on interrelationship between the structure, luminescent, triboluminescent, size-dependent luminescent, thermochromic and photochemical properties of heterometallic complexes of lanthanides and polymer composites on their basis, compounds of Sb(III) and Te(IV) halogenides with nitrogen-containing outer-sphere cations, and boron difluoride β -diketonates. The geometric and electronic aspects of the mechanism of triboluminescence and thermochromism of lanthanide complexes and s^2 – ions were discussed.

The results were obtained by the luminescent, time-resolved spectroscopy, fluorescent electronic microscopy, diffuse reflection spectroscopy and low-temperature X-ray analysis. The performed studies results can be used in purposeful search and development of light-transforming materials of high luminescence intensity and photostability.

The examples of nano- and microstructured functional optical materials on the basis of complex compounds of lanthanides, boron, tellurium(IV), and antimony(III) were demonstrated. The obtained data can be used in development of sensor materials for detecting vapors of chemical compounds, in particular, those of polar solvents and monocyclic aromatic hydrocarbons. The examples of optical materials prospective for development of the devices to be used in transformation and processing of optical signals were also demonstrated.

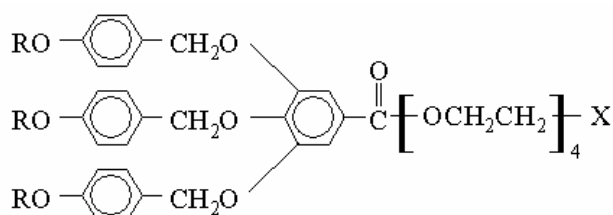
The research was supported of RFBR, grant 11-02-98517

SELF-ASSEMBLING SUPRAMOLECULAR STRUCTURES, FORMED BY TAPERED DENDRONS OF VARIOUS NATURE

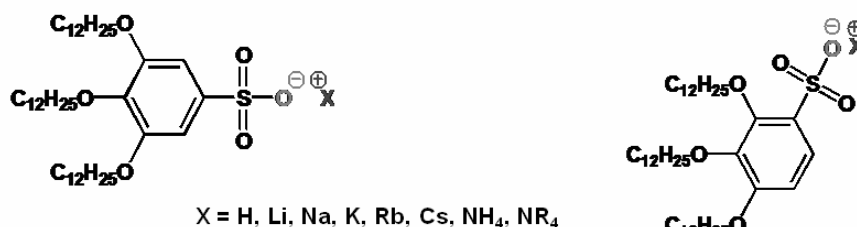
S.N. Chvalun

 Institute of Synthetic Polymer Materials RAS
 shcherbina@ispm.ru

Supramolecular chemistry and molecular technology are among the most claimed fields of modern materials science. Attention of researchers is concentrated on fundamental principles of self-assembling, embracing molecular recognition of exo- and endoreceptors, as well as on the possibilities for manipulating the nanosystem structure by moderate changes of environment conditions and of outer fields of different nature (including geometrical confinement). Self-assembling is a co-operative process, giving substantial benefits for manufacture rates. Moreover, it is a “bottom-up” process, in which molecules of particular compound form supramolecular aggregates to be used as building blocks of the macroscopic system. Thus, the use of self-assembly process allows for much more accurate manipulation by the material structure and for the design of neat, precise structures.



We have carried out comparative analysis of the structure of supramolecular aggregates formed by tapered and conical dendrons, and ordered by different driving forces: van-der-Vaals (compounds on the basis of gallic acid), ionic (symmetric and asymmetric benzene-sulfonates of alkaline metals), fluorophobic effect. Variety of structures of different symmetries have been obtained, forming crystalline, ordered or disordered columnar mesophases, cubic bicontinuous gyroid (Ia3d) and micellar (Pm3n, I23), smectic layers and bilayers and so on. Mechanisms of mesophase transitions, as well as various applications of such materials are discussed.



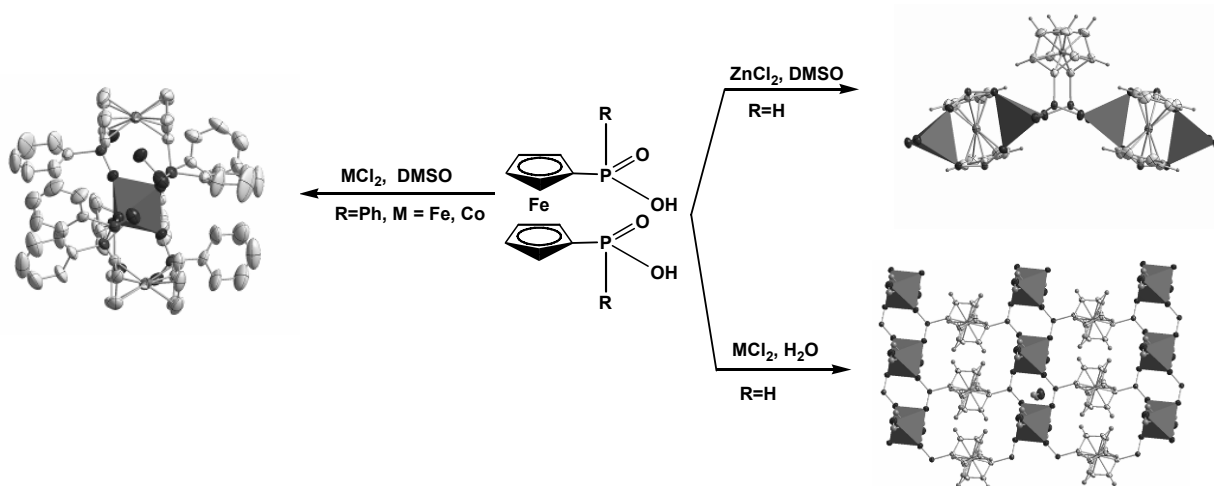
O.N. Kataeva
R.P. Shekurov
D.B. Krivolapov
T.P. Gryaznova
S.A. Katsyuba
V.A. Milyukov
O.G. Sinyashin

METAL ASSISTED SELF-ASSEMBLY OF PHOSPHORUS DERIVATIVES OF FERROCENE

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia
olga-kataeva@yandex.ru

A series of new phosphorus containing ferrocene derivatives was synthesized and used for the design of supramolecular architectures based on their complexes with transition metals.

The number of the donor atoms, reciprocal rotation of the cyclopentadienyl rings in the ligand, coordination geometry of the metal center, reaction and crystallization conditions determine the formation of coordination networks. A variety of supramolecular architectures was obtained, characterized by vibrational spectroscopy and proved by X-ray single crystal diffraction, the factors stabilizing supramolecular organization of coordination polymers being analyzed.

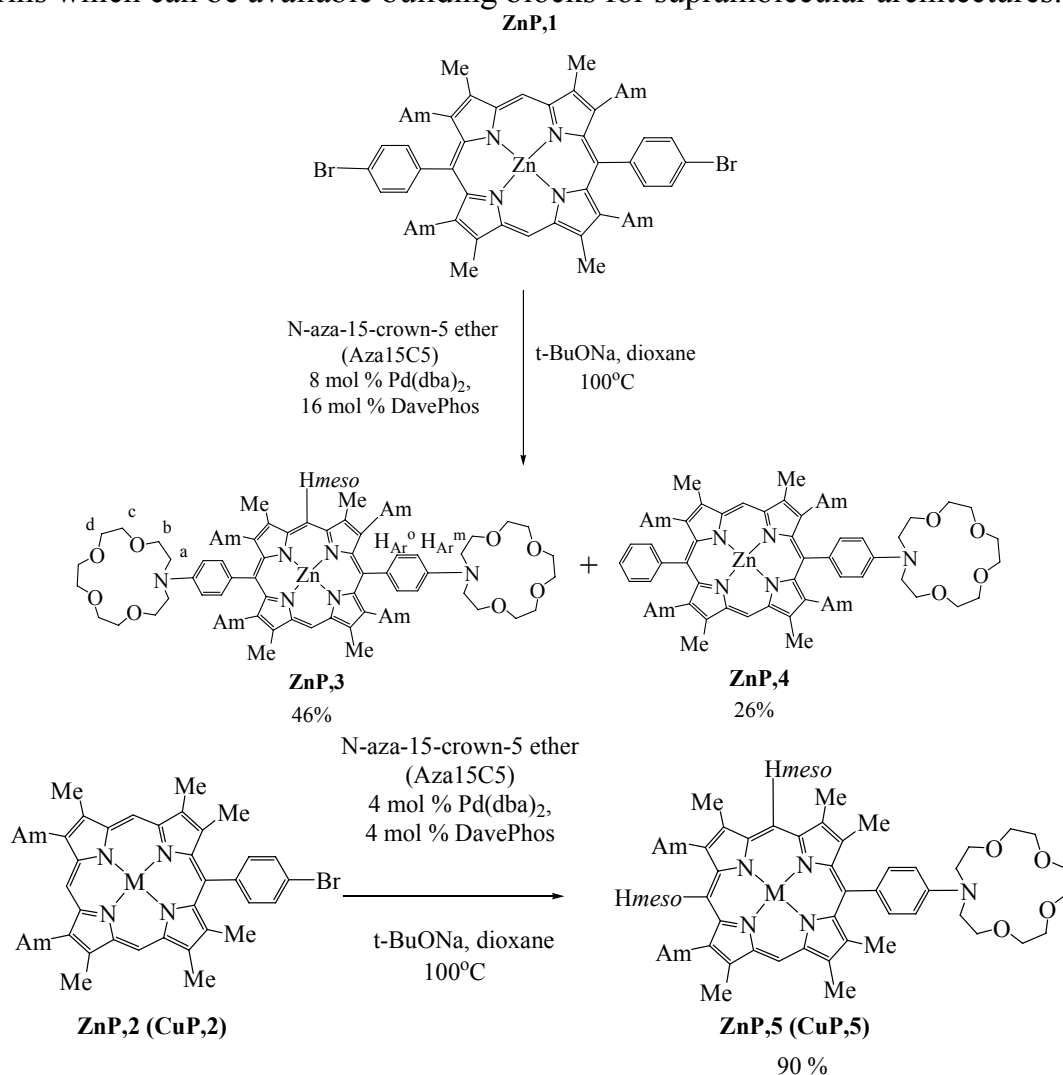


SYNTHESIS AND CHARACTERIZATION OF NEW SUPRAMOLECULAR STRUCTURES BASED ON AZA-CROWNED-PORPHYRINS

E.A. Mikhaliitsyna¹
V.S. Tyurin¹
I.P. Beletskaya²

1 - IPCE RAS, Laboratory of New Physical and Chemical Problems,
Moscow, Russia
2 - M.V. Lomonosov State University, Department of Chemistry,
Moscow, Russia
silwija@mail.ru

The synthesis of crowned-porphyrins has been investigated for the last two decades. Due to porphyrins are chromophores, supramolecular coordination of crown ether moieties attached to *meso*-positions of porphyrin ring to metal cations can be observed by shifts of porphyrin absorption spectra. To synthesize these compounds we used Pd-catalyzed reaction of amination to functionalize *meso*-4-bromophenyl-octaalkylporphyrins by N-aza-15-crown-5 ether (Aza-15-C5) (Scheme 1) and obtain new direct mono- and diaza-crowned-porphyrins which can be available building blocks for supramolecular architectures.



Scheme 1. Synthesis of aza-crowned-porphyrins via Pd-catalyzed reaction of amination.

Ability of aza-crowned-porphyrins to chelate alkali metal cations into aza-crown cavity and axially coordinate nitrogen-containing bidentate ligand (1,4-diazabicyclo[2.2.2]octane) to metalloporphyrins was studied. ^1H NMR and UV/Vis titrations of $\text{ZnP},3$; $\text{ZnP},5$; $(\text{ZnP},3)_2\cdot\text{DABCO}$ and $(\text{ZnP},5)_2\cdot\text{DABCO}$ in CHCl_3 by CH_3OH solution of KI and NaBr show that coordination of K^+ leads to cation-induced dimerization by potassium cations and formation of sandwiched dimers of aza-crowned-porphyrins with alkali cations (Fig.1). Coordination of Na^+ to crowned-porphyrins does not cause dimerization.

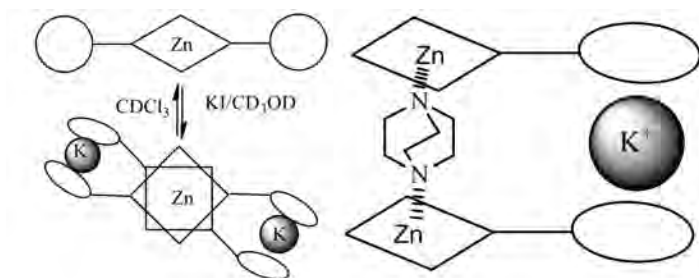


Fig. 1. Sandwiched dimers of $(\text{Zn},3)_2\cdot 2\text{K}^+$ and $[(\text{Zn},5)_2\cdot\text{DABCO}]\cdot\text{K}^+$

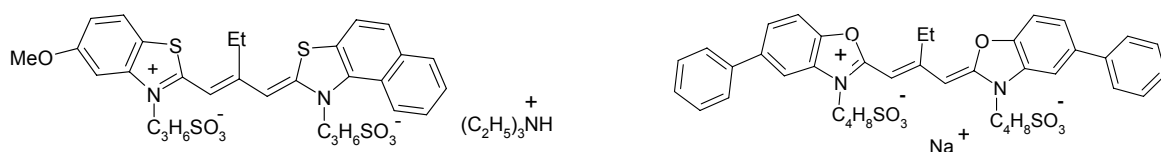
In summary, prepared compounds can be used as polytopic receptors for binding metal cations and bidentate ligands to develop new sensors and photonic materials.

J-AGGREGATES OF CYANINE DYES AS SUPRAMOLECULAR SYSTEM

A.K. Chibisov¹
 T.D. Slavnova¹
 H. Goerner²

1 - Center of Photochemistry RAS, Moscow, Russia
 2 - Max-Planck Institute of Bioinorganic Chemistry, Muelheim-Ruhr, Germany
 chibisov@photonics.ru

Cyanines are synthetic organic dyes which demonstrate the ability to form J-aggregates as nanostructured self-associated assemblies. J-aggregation usually occurs for anionic cyanines in aqueous solution in the presence of inorganic salts and proteins. In the case of metal ions as



additives the formation of ionic pairs are necessarily condition for J-aggregation. The kinetics and mechanism of J-aggregation are rationalized in terms of autocatalysis (Fig. 1). In the case of proteins (gelatin, trypsin, ribonuclease A (RNase), lysozyme) the binding of the dye molecule to a protein is a cooperative process and the kinetics of J-aggregation is described by a stretched exponential function. The presence of organic solvents as additives usually results in the decrease of the rate of J-aggregation due to a decreasing of the dimer concentration. The J-aggregates were found to demonstrate the chirality in the presence of optically active additives (D-, L- tartaric acids, proteins and others), and J-aggregates might serve as a chirality-sensing supramolecular system (Fig. 2).

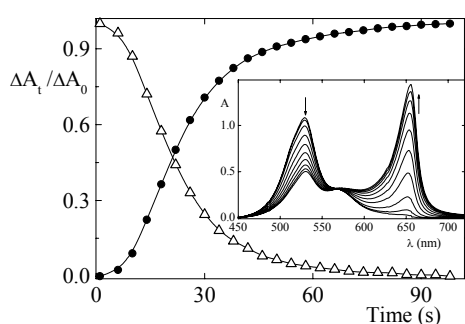


Fig. 1. Normalized time course of absorbencies; inset: absorption spectra at various time intervals ($\Delta t = 4$ s).

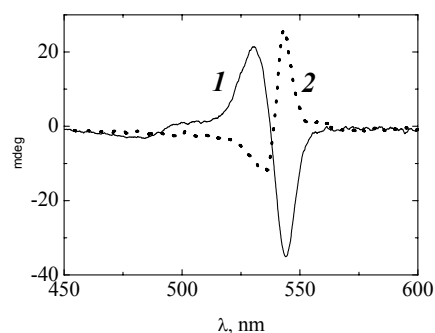


Fig. 2. CD spectra in the presence of lysozyme (1) and gelatin (2).

This work was supported by The Russian Fund of Basic Researchers (grant 09-03-00170).

**SUPRAMOLECULAR COORDINATION POLYMERS:
NEW LIGANDS AND NOVEL METHODS OF
MODIFICATION**

S.Z. Vatsadze
V.N. Nuriev

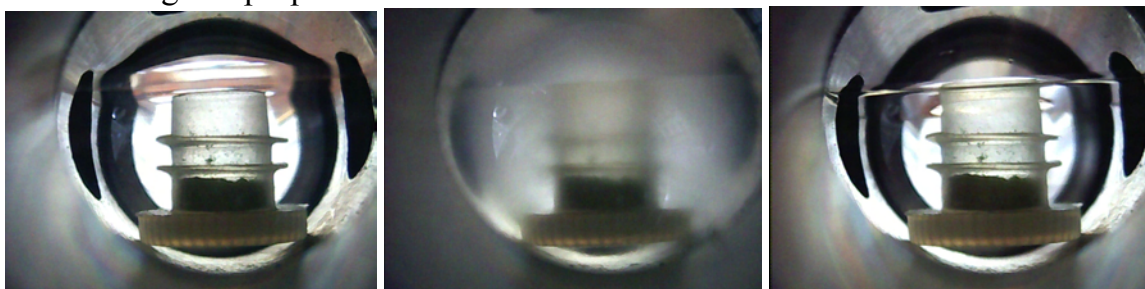
Chemistry Department, Lomonosov Moscow State University,
Moscow, Russia
szv@org.chem.msu.ru

Construction of polymeric coordination networks is an extremely topical area of current research within supramolecular chemistry. During last ten years we have been working on the ligand design and synthesis of new types of metal containing coordination polymers as well as synthesis of discrete coordination nano-aggregates. We have experienced in synthesis of new conjugated di- and tri-pyridine ligands acting as *exo*-dentate bridges in formation of anisotropic coordination polymers. More than hundred of new crystalline supramolecular polymers have been already characterized in our lab. Particular attention is given to the non-crystalline gel-like coordination polymers which are one of the most promising families of “smart materials” since they could change (sometimes reversibly) their physical and/or chemical behavior under the action of an external stimulus (light, sound, chemicals, pH, temperature, share force, redox, magnetic field etc).

Our polymers are now persistently investigated in several important applied areas:

1. Molecular sieves, psedo-zeolite activity, including gas adsorption, ion exchange and selective separation;
2. Cooperation of catalytic centres;
3. Photochemical studies including both light adsorption and luminescence;
4. Chiral recognition and separation by coordination polymers.

Our further investigations are focused on the synthesis of supramolecular systems using non-traditional reaction media, first of all, supercritical carbon dioxide (scCO₂). Moreover, scCO₂ could be used as a media for the transformation of a given coordination polymer to change its properties:



Literature:

Vatsadze S. Z., et al: *Chem. Het. Comp.*, **2000**, (9), 1266; **2005**, (9), 1290; *Russ. Chem. Bull., Int. Ed.* **2002**, 51 (3), 476; **2002**, 51 (10), 1957; **2005**, 54 (12), 2771; **2006**, 55 (10), 1810; *Cryst.Eng.Comm.*, **2004**, 6, 112; *Inorg. Chem. Comm.*, **2004**, 7, 799; *Eur. J. Inorg. Chem.*, **2004**, 2008; *Dalton Trans.*, **2005** (22), 3632; *Inorg. Chim. Acta*, **2005**, 358, 50; *J. Solid State Electrochem.*, **2005**, 9, 764; *ARKIVOC*, **2005**, (NZ-1534J) 208; *Mendelev Commun.*, **2007**, 17, 77; *Polyhedron*, **2007**, 26 (14), 3925; *Organometallics*, **2009**, 28 (4), 1027.

The authors thank RFBR for general support and REC MUSIC for SCF equipment (<http://www.chem.msu.ru/rus/supercritical-fluids/welcome.html>).

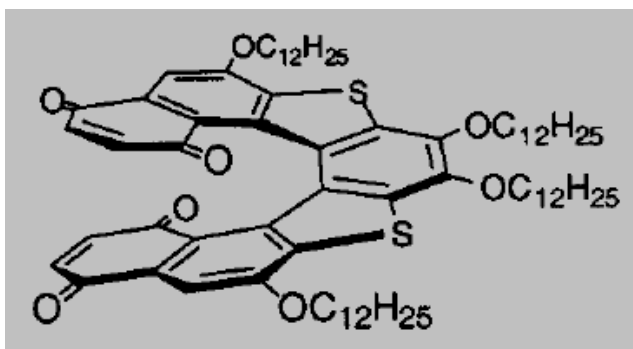
HOLLOW SIX-STRANDED HELICAL COLUMNS OF A HELICENE

M.A. Shcherbina

Institute of Synthetic Polymer Materials, Russia
shcherbina@ispm.ru

Much studied have been helical columnar liquid-crystalline phases of many materials, including such lyotropic systems as DNA, poly(g-benzyl-L-glutamate), xanthan, and such thermotropic materials, some with chiral side chains, as triphenylenes, banana-shaped and mesomorphic twin molecules, foldamers, wedge-shaped dendrons and star-shaped molecules. But the columnar liquid-crystalline phases of helicenes have been studied very little, even though they are particularly interesting because the cores of their constituent molecules are chiral.

Herein we analyze by means of X-ray scattering, in conjunction with electron-density reconstruction, molecular dynamics, and scattering pattern simulation, supramolecular structures, formed by helicenebisquinones with long alkyl substituents, both racemic and enantiopure.



The work herein shows that enantiopure and racemic helicenebisquinones form hexagonal columnar phases in which the internal structures of the columns are 13_2 hollow helices comprised of six-molecule repeat units, hence of 78 molecules and two turns in an 11.2 nm period. The long-range order among the columns is laterally high and longitudinally low. Enantiomer forms a true hexagonal structure of single-handed helices; columns of segregated enantiomers in racemic mixture are displaced longitudinally. Because the helicenes cannot tessellate like wedge-shaped molecules, they leave a void in the column center. Results obtained point to a route to chiral porous materials.

This work is supported by the President Grant for Young Scientists (MK-4006.2010.3) and by Russian Foundation for Basic Research (11-03-00669).

**SUPRAMOLECULAR CYCLODEXTRIN
COMPLEXES IN SOLUTION, SOLID PHASE AND
ON THE SILICA/WATER AND SILICA/GAS
INTERFACES. ESR AND FLUORESCENCE STUDY**

**V.A. Livshits
I.V. Ionova
L.V. Voronina
M.V. Alfimov**

Centre of Photochemistry, Russian Academy of Sciences, Moscow,
Russia
livsh@photonics.ru

A series of guest/host complexes of CD derivatives with biologically important spin labeled guests were prepared in aqueous solutions and studied by ESR and fluorescence methods: spin-labeled indoles, stearic acids in which doxyl group is attached to the 5-th and 16-th positions on the acyl chain, androstane and cholestane analogs of cholesterol. The binding constants and stoichiometries of the complexes were determined from the dependences on CD concentration of the rotational correlation time (τ_R) and hydrophobicity parameter h of the NO group environment. The h values and spin exchange rates with paramagnetic ions enabled to determine the location of the reporter NO group relative to the CD cavity. The calculated structures of the complexes qualitatively agree with experimental results.

It was also of great interest to detect and measure the guest motions inside the CD cavities. For this aim the CD complexes with spin-labeled indoles were prepared in solid phase and studied in a broad temperature interval. It was concluded from ST ESR and simulations of the linear ESR spectra that guest molecules in γ -CD undergo rapid librations whereas in β -CD the motion is described by rotational jumps over the whole body angle.

The ternary solid complexes of β - and γ -CD with two types of guest molecules: spin labeled indoles and "regulating" guests cyclohexane and benzene were also prepared in solid phase. The rotational mobility and environment hydrophobicity were found to increase considerably upon inclusion of a second guest. These effects were explained by the formation of the ternary 2:1:1 complexes. Their structures were obtained based on experimental results and PM3 calculations.

The effects of covalent binding of a CD to silica microspheres modified with aminopropyl groups (AMS) on the molecular dynamics of different spin probes in CD complexes has been studied. Two states with different rotational mobility and environment polarity were found for these spin probes. A strongly immobilized state was attributed to the complex additionally adsorbed on AMS whereas a weakly immobilized state corresponded to the desorbed complex of which the rotational mobility is limited by the linker flexibility. The charged polymers of the carboxymethyl- β -CD (CMCD) and sulfo- β -CD (SCD) adsorbed on AMS were used for the complexation and fluorescence detection of the volatile aromatics from the gas phase. Naphthalene (N) complexes with polymer CD (PCD) have binding constants K_b several times greater than those for the CD monomers. The amount of the bound PCD corresponds to a monolayer on the AMS surface. Fluorescence spectra of aromatics bound to AMS from saturated vapor differ substantially from those in aqueous solutions: the former are much broader bands shifted to long λ . These differences are due to the superposition of the monomer and excimer spectra for the adsorbed hydrocarbons. The spectral shapes and excimer fluorescence contributions were determined by spectral subtractions. For N bound to AMS with adsorbed PCD and AMS with covalently bound CD we observed excimers differing in the position of $\lambda_{\max}$ and the excimer/monomer ratio. These excimers we attribute to the 2:2 complexes with CD and to the N₂ dimers in the hydrophobic environment, respectively. The characteristic times of monomer and excimer formation (150s and 390s, respectively) suggest the diffusion controlled mechanism of monomer and excimer formation in pores. The time-dependent fluorescence energy transfer was discovered on the AMS from the excited N to the dansylglycine fluorophore complexed with the covalently bound β -CD. This phenomenon may be used in chemosensors for the detection of the volatile aromatics.

This work was financially supported by RFBR, grant 10-03-01166a.

**NMR-PARAMAGNETIC PROBING OF
SUPRAMOLECULAR INTERACTIONS**

R.R. Amirov

Chemical Institute of the Kazan Federal University, Inorganic
Chemistry Chair, Kazan, Russia
ramirov@ksu.ru

NMR method is widely used for investigation of wide diversity of supramolecular interactions (e.g. self-aggregation, formation of guest-host complexes etc.). Application of paramagnetic probes in NMR allows receiving important additional information, including the state of metal ions and their complexes in supramolecular systems.

Various aspects of application of NMR-probing for investigation of self-aggregation of individual amphiphilic compounds (surfactants, amphiphilic ligands, metacyclophanes) and their mixtures are considered in the report. The applicability of the suggested approach of using NMR-relaxation method with paramagnetic probes for revealing substrate-receptor interactions is illustrated on the example of complex formation between gadolinium(III) – tetrapentyl tetrasulfonatocalix[4]arene aggregates and a series of methylammonium cations with variable degree of substitution.

Supramolecular interactions may stimulate formation of metal complexes in solutions in unfavorable conditions (solution pH, concentrations). For multicomponent systems (e.g. surfactant – metal ion – ligand – salt) formation of some anionic (cobalt(II) tetrathiocyanate, iron(III) tris-salicylate), cationic (copper(II) bis-ethylenediaminate) or nonionic (gadolinium tris-picrate) complexes is favored by interaction with the charged surface of micelles or “pseudocrown-ether” coordination of the salt cations with polar part of the surfactant molecule.

High values of the proton relaxivity were achieved as a result of interaction of some paramagnetic probes (Gd(III), Mn(II)) with chelating derivatives of tetrabutyl thiocalix[4]arene in surfactant solutions. New opportunities opened by such supramolecular interactions allow to suggest this systems as models of new generation contrast agents for magnetic resonance imaging.

The work was supported by RFBR (grants NN 06-03-32963 and 09-03-00437).

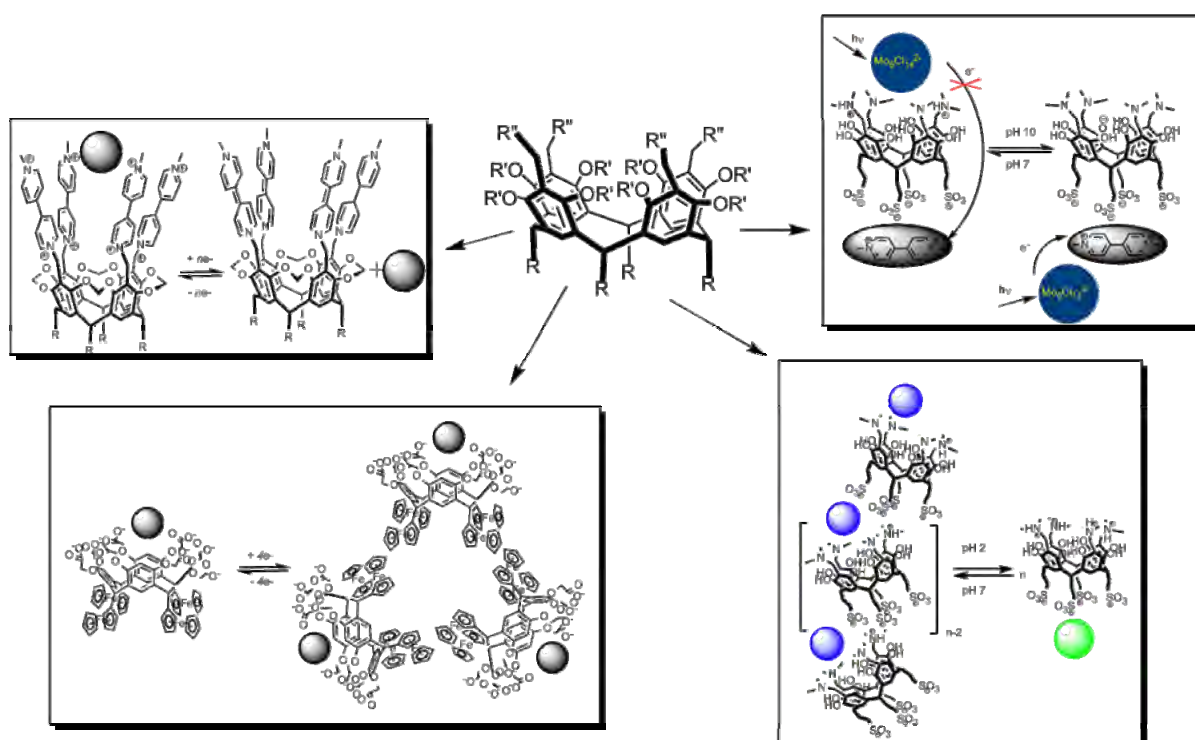
A.Y. Ziganshina
D.E. Korshin
R.R. Kashapov
G.R. Nasybullina
S.V. Kharlamov
Sh.K. Latypov
V.V. Yanilkin
A.I. Kononov

CALIX[4]RESORCINES AS BUILDING BLOCKS FOR MOLECULAR DEVICES

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Science, Kazan, Russia
az@iopc.ru

Calix[4]resorcines are macrocyclic compounds that are widely used in fields of supramolecular chemistry, because of the easy synthesis and the possibilities of modification of their three-dimensional structures. Calix[4]resorcines are one of the most important host molecules in the supramolecular chemistry. The functionalization of their upper and lower rims allows to create host molecules suitable for different guest. Functionalised calix[4]resorcines represent attractive building blocks for the creation of many supramolecular architectures and can be potentially applied to many intriguing areas such as smart materials, molecular devices and nano materials.

The design, synthesis and application in the construction of new molecular devices of a series of the calix[4]resorcine derivatives will be presented and discussed.



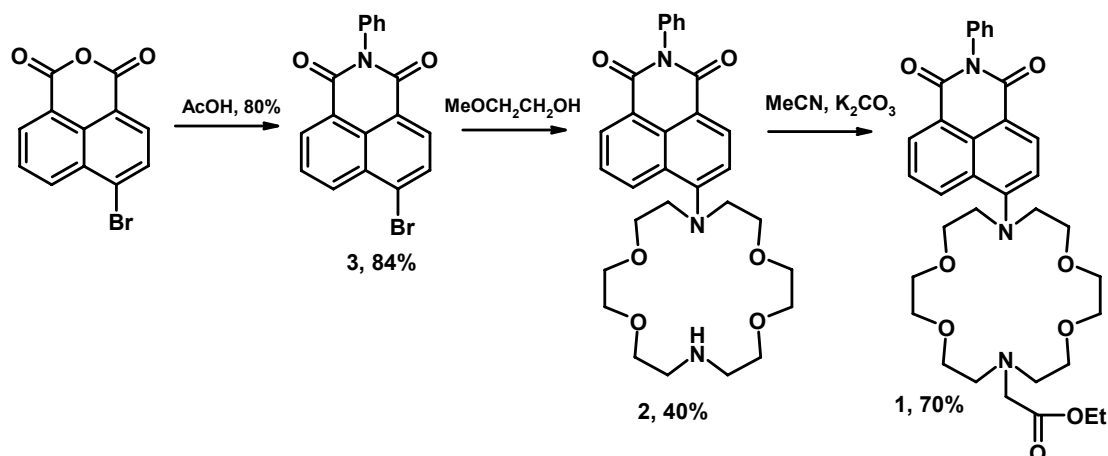
We thank the Russian Foundation for Basic Research (Grant N 09-03-00581) for the financial support of this work.

SYNTHESIS AND SENSOR PROPERTIES OF NAPHTHALIMIDE DERIVATIVES CONTAINING DIAZA-18-CROWN-6 ETHER MOIETY

A.S. Oshchepkov¹
O.A. Fedorova²

1 - Lomonosov Moscow State University, Moscow, Russia
2 - Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, Russia
maxim.os@mail.ru

During the last years, much attention has been paid to the design, synthesis and characterization of photochemical molecular devices, which combine chromophore signaling units and receptor groups capable of binding of molecules and ions. Such devices can find employment in many disciplines such as biochemistry, clinical and medical sciences, analytical chemistry and environmental science. Naphthalimide derivatives with ionophoric fragment at the 4-th position of naphthalene ring are well known organic chromophores and fluorophores showing good photostability and strong emission and absorption bands in the visible region. Thus, this type of compounds has been successfully used as signaling units for the design of ion-active molecular systems.



The present paper reports synthesis and sensor properties of diaza-18-crown-6 ether containing naphthalimide derivatives. Compounds **1** and **2** were prepared from 4-bromonaphthalic anhydride as described in scheme. The addition of Ca²⁺ in the solution of **2** induced the blue shift in absorption and emission spectra. To interpret the observed optical effects the quantum chemical calculations of HOMO-LUMO orbits were done.

The study of molecules included the theoretical and experimental (optical, NMR) methods, analysis of intramolecular charge / electron transfer and fluorescence properties in the presence and absence of metal ions.

This work was supported by financial assistance from the Program for basic research of Ministry of Education and sciences and RFBR

V.V. Semionova¹
 E.M. Glebov¹
 V.V. Korolev¹
 S.A. Sapchenko²
 D.G. Samsonenko²
 V.P. Fedin²

PHOTOCHEMISTRY OF SUPRAMOLECULAR COMPLEX OF STILBENE WITH A METALLOORGANIC FRAME

1 - Institute of Chemical Kinetics and Combustion

2 - Nicolaev Institute of Inorganic Chemistry

semionova@kinetics.nsc.ru

Organic photochromic compounds are used in optics, optoelectronics and holography. Of interest are compounds demonstrating photochromism in the solid phase, because they are resistant to photodegradation. Photochroms incorporation into the polymer matrix leads to side-photoreaction causing degradation. The idea is arisen to incorporate photochromic compound into metalloorganic frame (MOF). We believe this approach will lead to the creation of photochromic materials with high quantum yield and high resistance to photodegradation.

In this work the supramolecular adduct of stilbene with a metaoorganic frame (MOF) was studied. Adduct consist of stilbene (Fig. 1), which is a well-known photochromic molecule, and the recently synthesized [1] MOF $[\text{Zn}_4(\text{dmf})(\text{ur})_2(\text{ndc})_4] \cdot 5\text{DMF} \cdot \text{H}_2\text{O}$ (ndc^{2-} - 2,6-naphtalene-dicarboxylate, ur - urotropin, dmf - N,N'-dimethylformamide) (Fig.2).

Photoisomerisation of *trans*-stilbene in the liquid phase was observed. *Trans*-stilbene was incorporated either into KBr pellets or into the porous glass.

Photochemical activity of the adduct of stilbene with MOF in the solid phase was exhibited. To perform the experiment, the adduct was incorporated into a KBr pellet and the UV spectrum was monitored. The observed changes in the UV spectrum correspond to *trans-cis* isometisation (MOF does not exhibit its own photochemical activity).

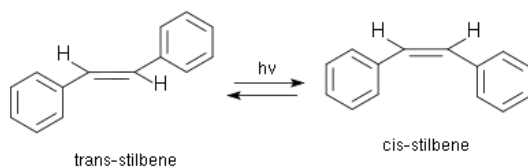


Figure 1. Photochromic reaction of stilbene.

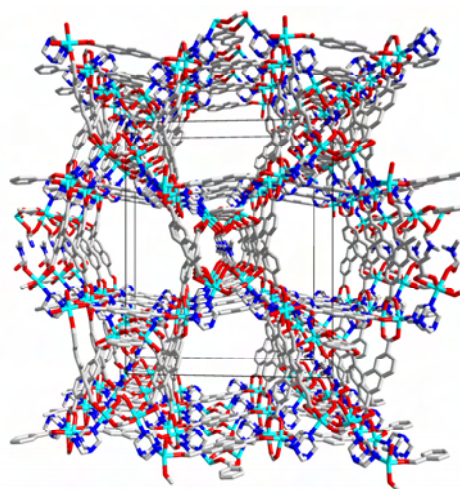


Figure 2. Metalloorganic frame $[\text{Zn}_4(\text{dmf})(\text{ur})_2(\text{ndc})_4] \cdot 5\text{DMF} \cdot \text{H}_2\text{O}$ [1]

These results indicate that the studied MOF can be considered as a promising component for creating supramolecular photochromic compounds.

References:

- [1]. Sapchenko SA, Samsonenko DG, Dybtsev DN, Melgunov MS, Fedin VP, 2011. Microporous sensor: gas sorption, guest exchange and guest-dependant luminescence of metal-organic framework. Dalton Trans. 40: 2196-2203.
- [2]. Schulte-Frohlinde D, Blume H, Gusten H, 1962. Photochemical *cis-trans*-isomerization of substituted stilbenes. J. Phys Chem. 66: 2486-2491.

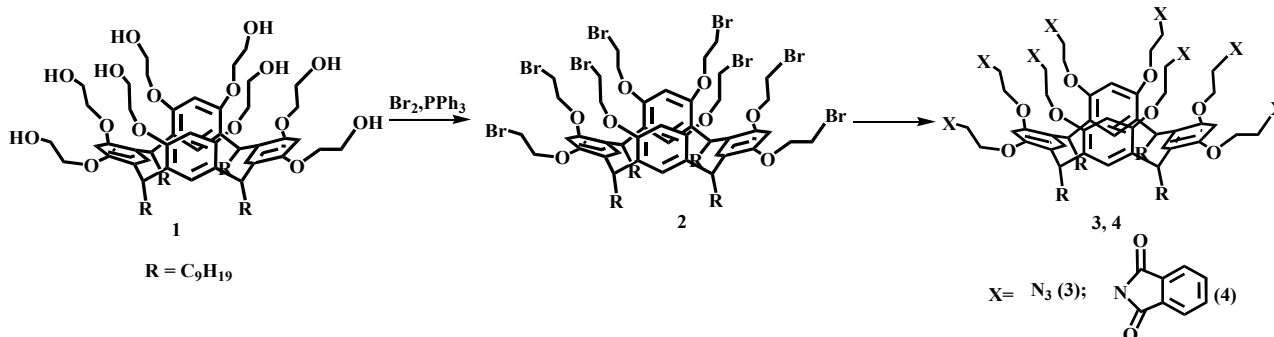
NEW FUNCTION-SUBSTITUTED OCTA-2-HYDROXYETHYLATED CALIX[4]RESORCINOLS

R.R. Azmukhanova¹
E.M. Gibadullina²
A.R. Kayupov²
A.R. Burilov²
M.A. Pudovik²

1 - The Kazan National Research Technological University, Institute of Chemical Engineering and Technology, Faculty Energy Intensive Materials, Department of Chemistry and Technology of Organic Nitrogen Compounds

2 - A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan Scientific Center of Russian Academy of Sciences, the Laboratory of Organoelemental Synthesis
ramilyashka@ya.ru

Perspective starting compounds for the synthesis of O-functionalized calixarenes and also new types of cavitands, container like compounds, nanotubes are calixarenes bearing hydroxyalkyl groups on the upper rim of the molecules. Earlier [1] we have reported the synthesis of such compounds by acid-catalized condensation of 1,3-bis(2-hydroxyethoxy)benzene with various aliphatic aldehydes. Due to the ease of synthesis and ample functionalization possibilities these compounds are perspective building blocks for further design of self-organized systems. We have studied reaction of calixarenes **1** with bromine. Further modification of thus synthesized bromocalixarene **2** allowed to obtain calixarenes **3** and **4** containing azide and phthalimide fragments.



The structure and composition of compounds obtained was proved by NMR ¹H, ¹³C, IR spectroscopy and elemental analysis.

References:

1. Kasymova E.M., Kayupov A.R. et al. *Russ. J Gen.Chem.* 2007, 77, 1395.

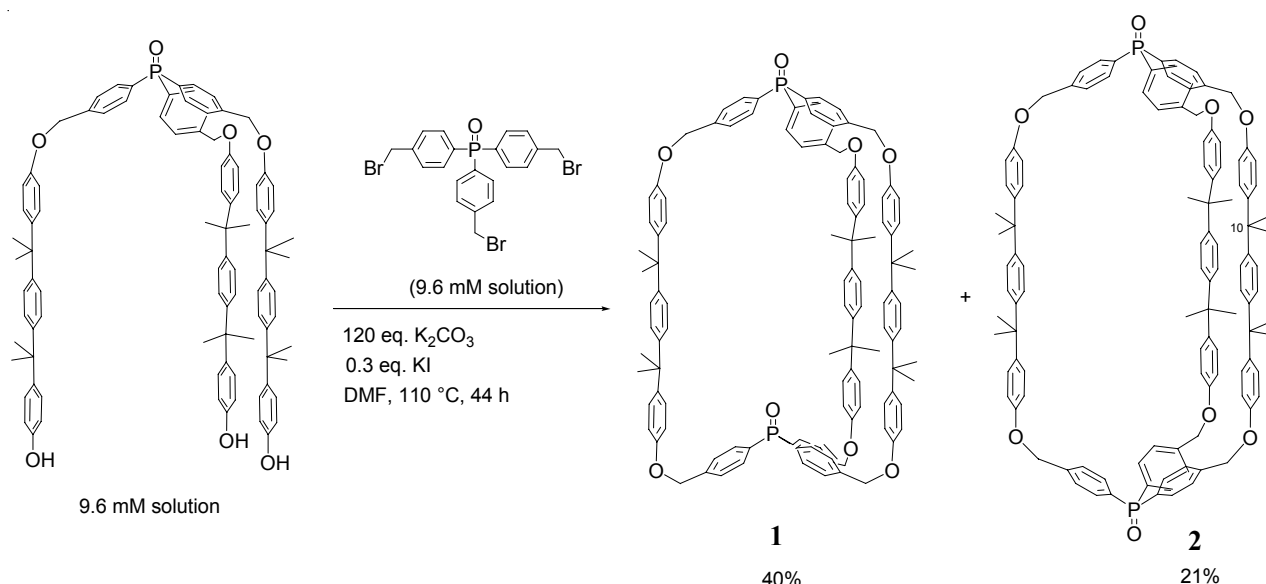
This work was supported by the Russian Foundation for Basic Research (grant no. 11-03-00416-a).

NEW CONFORMATIONAL FLEXIBLE PHOSPHANE AND PHOSPHANE OXIDE MACROBICYCLES

I. Bauer¹
 F. Däbritz²
 G. Theumer¹
 M. Gruner¹

1 - TU Dresden, Chemistry Department, Dresden, Germany
 2 - Leibniz Institut für Polymerforschung, Dresden, Germany
 ingmar.bauer@chemie.tu-dresden.de

The synthesis of two large diastereomeric phosphane oxide macrobicycles **1** and **2** succeeded in comparatively good yield by a tripod-coupling strategy. ¹H, ¹³C and ³¹P NMR spectra of the two cage compounds are in accordance with a *D*_{3h}-symmetry each, which in case of **1** can be attributed to a fast interconversion of two degenerate *in,out*-structures. Kinetic measurements of the reduction of both diastereomeric macrobicycles, and the results of an inversion experiment also support the assumption that the phosphane and phosphane oxide cage molecules described herein are conformational flexible and undergo fast homeomorphic isomerisation. A bisiminophosphorane derivative was prepared and assigned as an *out,out*-isomer.



A.A. Bikmuhametova¹

I.G. Efimova¹

M.A. Ziganshin¹

V.V. Gorbachuk¹

S.A. Ziganshina²

A.P. Chuklanov²

A.A. Bukharaev²

INTERACTION OF THIN FILMS OF L-LEUCYL-L-LEUCYL-L-LEUCINE AND L-VALYL-L-VALINE WITH ORGANIC VAPORS RECEPTOR PROPERTIES AND MORPHOLOGY

1 - Kazan (Volga region) Federal University, Butlerov Institute of Chemistry, Kazan, Russia

2 - Zavoisky Physical-Technical Institute, Kazan, Russia
alsina@lenta.ru

The building blocks based on oligopeptides are attractive materials for bionanotechnology because of their biocompatibility and ability to self-organization into ordered nanostructures.

In present work, receptor properties of the L-valyl-L-valine and L-leucyl-L-leucyl-L-leucine towards organic guest were studied using quartz crystal microbalance (QCM) technique. The surfaces morphology of peptide thin films before and after the interaction with organic guests was determined using atomic force microscopy (AFM).

It was found that tripeptide L-leucyl-L-leucyl-L-leucine has a higher sorption capacity for studied organic compounds in comparison with the dipeptide L-valyl-L-valine. In case of sorption of homologous series of aliphatic alcohols by the thin film of tripeptide the size exclusion effect was found.

It was shown that crystallization of tripeptide from methanol solution leads to formation of a thin film coated with fine nano- and microcrystals. The sorption of relatively large organic compounds (e.g. toluene and pyridine) leads to deformation of crystals even to complete destruction, whereas the film morphology of tripeptide after saturation by water does not change.

Crystallization of dipeptide L-valyl-L-valine from methanol solution leads to formation of triangular nanoislands on the surface of thin film. Binding of methanol vapor gives the significant change of morphology of a thin film in comparison with sorption a pyridine.

This work was supported by programs RFBR № 09-03-97011-volga region and Federal Program "Research and scientific-pedagogical personnel of Innovative Russia" for 2009-2013 (Gov. contract № P2345).

**QTAIM ANALYSIS OF CYCLIC COVALENT-
NONCOVALENT STRUCTURES IN
SUPRAMOLECULAR PHOTOCHROMIC SYSTEMS****M.F. Bobrov**Mendeleev University, Moscow, Russia
mikel@muctr.ru

Computer modeling allows us to successfully solve a number of applications to predict the best ways of obtaining, the optimal structure and properties of substances and materials. Diarilethene (DAE) are promising photosensitive systems, with particular interest is a reversible process under the influence of light of different wavelengths. The Cambridge Structural Database were used to obtain the geometric properties of X-ray analysis DAE. The program Mercury 2.3 a detailed analysis of short contacts, which revealed the existence of noncovalent interatomic interactions that determine the relative orientation of molecules in molecular clusters and crystalline structure. Computer modeling allows us to successfully solve a number of applications to predict the best ways of obtaining, the structure and properties of substances and materials. DAE are promising photosensitive systems, with particular interest is a reversible process under the influence of light of different wavelengths. Was allocated to two different types of clusters consisting of two molecules of DAE. In the first, the most energetically favorable cluster presence of 4 F and H bonds between two molecules to form highly symmetrical DAE dimer allowed to make an assumption about the presence of strong hydrogen bonds. Cluster structure was optimized using the Kohn-Sham theory with B3LYP/6-31G (dp) functional and the electron density is analyzed by quantum-topological analysis, molecular graph of the ensemble is built from two molecules of DAE. In addition to non-covalent interactions of hydrogen fluoride were detected critical points of connection between the carbon atoms of neighboring molecules. In another cluster dimer DAE has 2 short contact with the neighboring molecule at the expense of bonds of the atoms S and H. Cluster structure was optimized using the Kohn-Sham functional with B3LYP/6-31G (dp) and the electron density is analyzed by quantum-topological analysis, molecular graph of the ensemble is built from two molecules of DAE. In addition, were found inside the molecule and communication - communication by hydrogen fluoride formed by intramolecular cycle. Energy of these interactions were assessed by the value of the local density of potential energy in the QD vb connection with the empirical formula: $E_{\text{kont}} (\text{kcal} / \text{mol}) = 313.754 \cdot \text{vb} (\text{AU})$. The total energy of the interatomic non-covalent interactions, calculated in this way amounted to $E_{\text{kont}} = -9.15 \text{ kcal/mol}$. In addition, considered the most energetically favorable options for ensembles of 2 and 4 molecules DAE. The use of complex methods of computational chemistry to computer modeling of molecules and molecular architecture of the ensembles, the intra-and intermolecular interactions in the photochromic systems provides a valuable and adequate result can be used for computer analysis of non-covalent interactions, defining the key properties of supramolecular systems studied nanometric scale.

**INTERACTION OF HYDROPHOBIC AROMATIC
MOLECULES WITH A SURFACTANT LAYER AND
THE DEVELOPMENT OF THE SURFACTANTS WITH
AN INCREASED SOLUBILIZATION ABILITY**

**I. Boldyrev
P. Volynsky
A. Semenova
P. Dubovskii
V. Chupin
A. Chugunov**

Shemyakin & Ovchinnikov Institute of Bioorganic Chemistry,
Moscow, Russia
ivan@lipids.ibch.ru

The "interaction of rigid aromatic molecules with a surfactant layer" covers a broad range of topics including drug-bilayer and dye-surfactant interactions. The common ground between these interactions is an influence of the lateral stress inside the surfactant layer on a dye or a drug. The lateral stress profile across the bilayer or a micell is responsible for location and orientation of an alien molecule. Thus theoretically one can affect the solubility of the hydrophobic molecule (micell capacity) by changing the structure of the acyl chains.

We have designed a phosphatidylcholine with short and rigid chains - di-2,4-hexadienoylphosphatidylcholine (DiSorbPC). The behavior of this lipid in water was studied using dynamic light scattering, tensiometry, ³¹P NMR, fluorescent spectroscopy and molecular dynamics simulations. Due to the reduced flexibility of the acyl chains the lipid demonstrates unusual behavior in water. DiSorbPC was not able to form common micelles. Instead, aggregates of DiSorbPC consisting of alternating hydrophobic and hydrophilic clusters were observed. Ionic interactions between head groups and hydrophobic interactions between sorbic chains of the lipids in extended conformation keep clusters together within an aggregate.

Rigid tails of the DiSorbPC tends to be packed in stacks where they are located parallel to each other. It was shown that solubility of the pyrene in such aggregates is 18 times higher than it is solubility in micells of the dihexanoylphosphatidylcholine (saturated analog of the DiSorbPC).

**THE SENSING OF INTERFACIAL INTERACTIONS
OF Tb-DOPED SILICA NANOPARTICLES WITH
VARIOUS SUBSTRATES THROUGH THE "ON-OFF-
ON" SWITCHING OF Tb-CENTERED
LUMINESCENCE. MECHANISMS AND
APPLICATIONS**

V.A. Burilov¹
A.R. Mustafina²
V.V. Skripacheva²
S.V. Fedorenko²
O.D. Bochkova²
R.R. Zairov²
I.S. Antipin¹
A.I. Konovalov²

1 - Kazan Federal University, A.M. Butlerov Institute of Chemistry,
Kazan, Russia

2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
ultrav@bk.ru

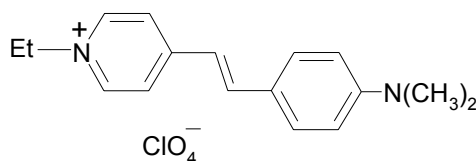
Silica nanoparticles have gained much attention during recent decades due to their wide use in medicine and bioanalysis. Lanthanide complexes have gained a great deal of attention owing to their unique spectroscopic characteristics, including long fluorescence lifetime, large Stokes shift, and sharp line-like emission bands. Therefore lanthanide complexes are applied as dopants into silica nanoparticles. Due to good signal-to-noise ratio such nanoparticles are efficient biomarkers, while their application in biosensing is more sparsely. The present report introduces luminescent core-shell nanoparticles as the nanosized sensors, which recognize inorganic and organic substrates through the "on-off" and "off-on" switching of the emission. Various synthetic procedures have been used to modify the morphology of the core-shell nanoparticles. The comparison of photophysical properties of nanoparticles with various morphology reveals the effect of coating on the luminescence. The "on-off" switching results from the interfacial interactions of the Tb(Eu)-doped nanoparticles with so called quenching molecules and ions, such as dyes and transition metal ions. The "off-on" switching can be achieved through the competitive interfacial binding of the quenching versus nonquenching molecules. Both steady state and time resolved quenching measurements have been analyzed to distinguish the contributions of static and dynamic mechanisms in the quenching of the luminescent core through the interfacial interactions of core-shell nanoparticles with quenching molecules. Though the dynamic quenching through the energy transfer is the key mechanism, the static quenching through the readsorption and light scattering should be also taken into account.

A.K. Chibisov
L.S. Atabekyan
V.G. Avakyan
N.A. Lobova
A.I. Vedernikov
S.P. Gromov

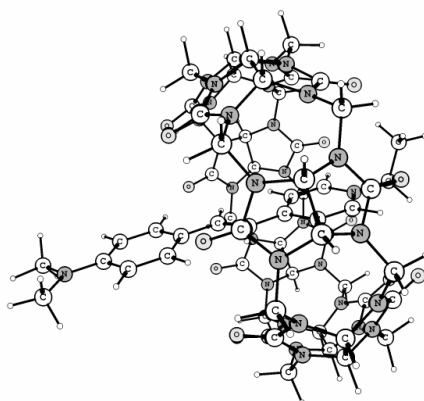
**NS-LASER FLASH PHOTOLYSIS STUDY OF
STYRYLE DYE IN THE PRESENCE OF
CUCURBIT[7]URIL**

Center of Photochemistry RAS, Moscow, Russia
chibisov@photonics.ru

Both 4-styrylpyridine dye and its inclusion complex with cucurbit[7]uril (CB7) in water have been studied by ns-time-resolved absorption spectroscopy.



The triplet state of the dye was populated upon ns-laser excitation, and the triplet-triplet absorption spectrum was measured. In the presence of CB7 changes in absorption and fluorescence spectra as well as fluorescence intensity of the dye were found to occur along with the observation of delayed fluorescence. The TICT state of the dye was found to take place together with an enhancement of the intersystem crossing for inclusion complex of the dye with CB7. Quantum chemical DFT calculations were used to study the microscopic structure of the dye bound to CB7. The inclusion complex of the dye with CB7 appeared to be stable thermodynamically as well as kinetically.



The structure of the dye inclusion complex with CB7. ΔE_0 –39.5 kcal/mol

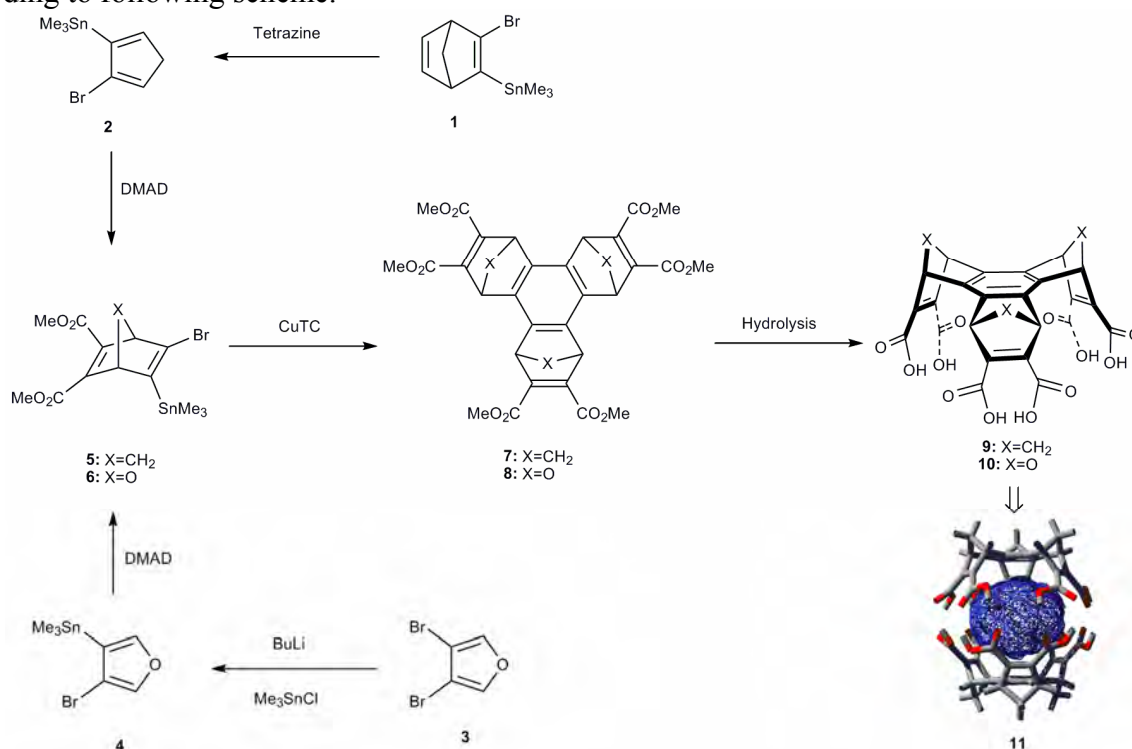
The work was supported from RFBR (projects no. 09-03-00170 and no. 09-03-00638) and by the Fundamental Research Program of the Chemistry and Material Science Division of the Russian Academy of Sciences “Chemistry and physical chemistry of supramolecular systems and atom clusters” (program no. 6).

SYNTHESIS OF NEW TYPE WATERSOLUBLE HOST MOLECULES FOR SUPRAMOLECULAR APPLICATIONS

A. Dastan¹
E. Dalkılıç¹
B. Nisancı¹
M. Güney²

1 - Ataturk University, Science Faculty, Department of Chemistry, Erzurum, Turkey
 2 - Agri Ibrahim Cecen University, Science Faculty, Department of Chemistry, Agri, Turkey
 adastan@atauni.edu.tr

Benzocyclotrimers are compounds of increasing interest because of their applications in supramolecular chemistry.¹ These compounds are characterized by a concave and rigid structure, capable of hosting molecular guests of suitable shape and size. For these reasons, methodologies focused on the synthesis of highly functionalized benzocyclotrimers are attracting the attention of an increasing number of research groups.² In this study, we have developed practical synthesis of **9** and **10**, which are possible host for supramolecular application such as **11**, starting from **1** and **3** according to following scheme.³



References:

1. Maslak, V.; Yan, Z.; Xia, S.; Gallucci, J.; Hadad, C. M.; Badjić J. D. *J. Am. Chem. Soc.* **2006**, 128, 5887-5894.
2. Scarso, A.; Pelizzaro, R.; De Lucchi, O.; Linden, A.; Fabris, F.; *Angew. Chem. Int. Ed.* **2007**, 46, 4972-4975. Daştan, A.; Uzundumlu, E.; Balcı, M.; Fabris, F.; De Lucchi, O.; *Eur. J. Org. Chem.* **2004**, 183-192.
3. Dalkılıç, E.; Güney, M.; Daştan, A.; Saraçoğlu, N.; De Lucchi, O.; Fabris, F. *Tetrahedron Lett.* **2009**, 50, 1989-1991. Nisancı, B.; Güney, M.; Dastan, A.; Fabris, F.; De Lucchi, O. *Unpublished results.*

Acknowledgements to TUBITAK (109T232) and Ataturk University (BAP, 2009/246) for financial supports.

SYNTHESIS AND MEMBRANE-TRANSPORTING PROPERTIES OF BISAMINOPHOSPHINOXIDES

R.R. Davletshin
A.R. Garifzjanov
R.A. Cherkasov

Kazan (Volga region) Federal University, A.M. Butlerov Chemical Institute, Kazan, Russia
alchemy-rus@yandex.ru

New α -bisaminophosphinoxides were synthesized with the help of the Kabachnik-Fields reaction of a hydrophosphoryl compound, paraformaldehyde and diamine. 1,10-diamino-4,7-dioxodecan and 1,8-diamino-3,6-dioxooctan or diamines of general formula $H_2N(CH_2)_nNH_2$ were used as the amino-component of the reaction. The reaction proceeded with the formation of standard products shown in Fig. 1 for $n = 4-6$. The structures of products were established via ^1H and ^{31}P NMR spectroscopy. The synthesized compounds are presented in Table. 1.

Table 1. The structures of polysubstituted phosphinoxides obtained from diamines

$R_2P(O)CH_2N(R')-Z-N(R')CH_2P(O)R_2$			
Entry	R	R'	Z
1	$n-C_8H_{17}$	H	$(CH_2)_2O(CH_2)_2O(CH_2)_2$
2	$n-C_8H_{17}$	H	$(CH_2)_3O(CH_2)_2O(CH_2)_3$
3	$n-C_6H_{13}$	H	$(CH_2)_4$
4	$n-C_8H_{17}$	H	$CH_2CH(CH_3)(CH_2)_3$
5	$n-C_6H_{13}$	H	$(CH_2)_6$
6	$n-C_6H_{13}$	$(CH_2)_2CN$	$(CH_2)_6$

Table 2. Membrano-transport properties of the carriers (the concentration of carrier in membrane phase 0.1 M substrate concentration 0.2 M).

Entry	Metal transport flow $F \cdot 10^{-5} \text{ mol/m}^2 \text{ min}$								
	K(I)	Cs(I)	Mg(II)	Ca(II)	Sr(II)	Ba(II)	Sc(III)	Nd(III)	Sm(III)
1	1.3	1.6	18.2	46.9	16.3	62.6	56.1	63.6	79.9
2	2.4	1.9	4.6	37.5	3.9	2.1	66.3	66.0	63.9
3	1.0	1.0	7.9	18.3	4.0	2.7	36.6	99.1	75.2
4	0.9	1.1	4.0	27.1	5.8	3.9	75.6	70.1	85.6
5	0.9	0.8	5.7	17.4	2.7	1.8	27.5	128.5	93.4
6	1.6	1.3	3.2	10.3	1.8	2.4	44.0	25.5	24.9

Membrano-transport properties of the synthesized compounds have been studied. It was found that compound **5** is the excellent extractant of Nd(III). Compound **1** is excellent extractant for the nitrates of second and third group metals. All carriers are effective for calcium and elements of scandium, neodymium and samarium.

The work was supported by the Russian Foundation for the Basic Research (grant 10-03-00580).

INTERFACIAL ADSORPTION AND STRIPPING OF IONS AS A REASON OF STIMULI RESPONSIVE LUMINESCENCE OF Tb-DOPED SILICA NANOPARTICLES

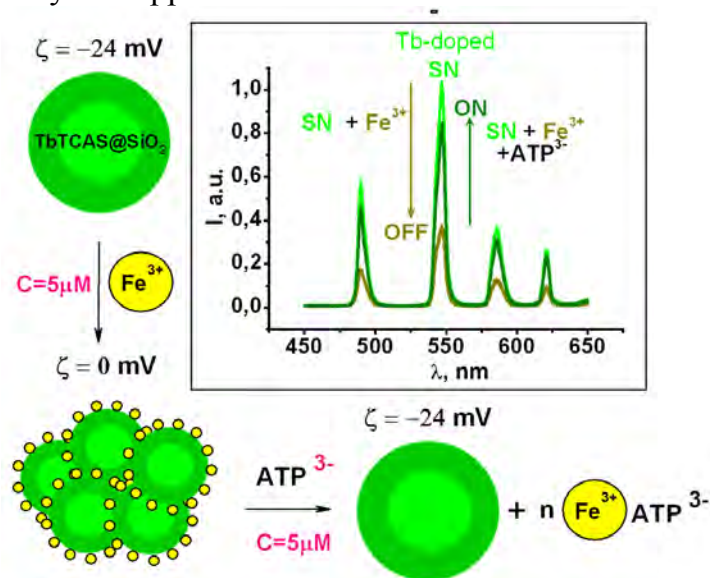
N.A. Davydov¹
V.V. Skripacheva¹
A.R. Mustafina¹
V.A. Burilov²
A.I. Konovalov¹
S.E. Soloveva¹
I.S. Antipin²

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia

2 - Kazan (Volga region) Federal University, A.M. Butlerov Chemical Institute, Kazan, Russia
kolya.davydov@inbox.ru

Silica nanoparticles (SNs) have gained much attention during recent decades due to their wide use in medicine and bioanalysis. The adsorption of metal ions and organic molecules onto silica, as well as the gaining of luminescent properties through the doping of luminophores into silica matrix and silica surface decoration are those advantages of silica nanoparticles, which provide their applicability as markers, sensors, drug delivery systems and sorbents.

Herein we introduce the “on-off-on” switching of Tb-centered luminescence as a result of reversible adsorption of Fe(III) ions at the silica/water interface of Tb-doped silica nanoparticles and the stripping effect of anions. The interfacial adsorption of Fe(III) ions results in the charge neutralization and aggregation of Tb-doped silica nanoparticles, accompanied by significant quenching of Tb-centered luminescence. The analysis of the steady state and time resolved quenching measurements reveals both static and dynamic quenching mechanisms. The addition of EDTA and some phosphates, including ATP results in the deaggregation of nanoparticles due to the complex formation with Fe(III) ions and following stripping of Fe(III) ions from the silica surface. The “off-on” switching of Tb-centered luminescence resulted from the stripping effect of biorelevant phosphates is a good basis for further bioanalytical application.



We thank RFBR (project no. 10-03-00352-a) for financial supporting.

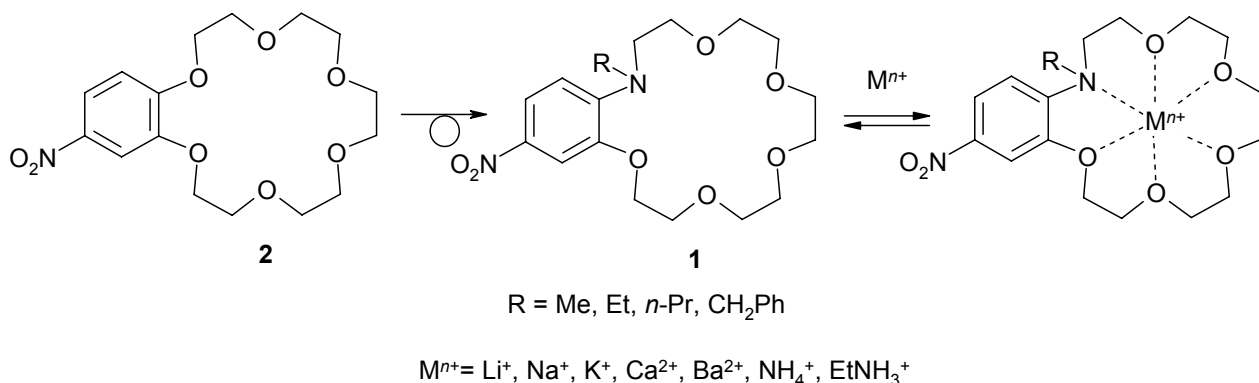
S.N. Dmitrieva¹
 M.V. Churakova¹
 N.A. Kurchavov¹
 A.I. Vedernikov¹
 A.Ya. Freidzon¹
 S.S. Basok²
 A.A. Bagatur'yants¹
 S.P. Gromov¹

SYNTHESIS AND HOST-GUEST COMPLEXES OF NITRO DERIVATIVES OF N-ALKYLBENZOAZA-18-CROWN-6 ETHERS

1 - Photochemistry Center, Russian Academy of Sciences, Moscow, Russia

2 - A.V. Bogatsky Physicochemical Institute, National Academy of Sciences of Ukraine, Odessa, Ukraine
 dmitrieva@photonics.ru

A series of *N*-alkyl(nitrobenzo)aza-18-crown-6 ethers **1** with the macrocycle nitrogen atom conjugated with the benzene ring is synthesized. The synthesis is based on stepwise transformation of the macrocycle of easily available nitrobenzo-18-crown-6 ether **2**. The complexation properties of these compounds are compared with those of the nitro derivatives of benzo- and *N*-phenylaza-18-crown-6 ethers using ¹H NMR spectroscopy and quantum-chemical DFT calculations.



The stability constants for the crown ether complexes with NH_4^+ , EtNH_3^+ , Li^+ , Na^+ , and K^+ are determined using ¹H NMR titration in MeCN-d_3 . The complexation capacity of *N*-alkyl(nitrobenzo)aza-18-crown-6 ethers is much higher than that of *N*-(4-nitrophenyl)aza-18-crown-6 ether and *N*-alkyl(nitrobenzo)aza-15-crown-5 ethers, and is comparable to (or higher than) the similar characteristics of nitrobenzo-18-crown-6 ether. The results can be used for the design of promising chromoionophores with the great optical response to a complexation with metal and ammonium cations.

This study was supported by the Russian Foundation for Basic Research and the Russian Academy of Sciences.

ZINC PHTHALOCYANINE IN SUPRAMOLECULAR COMPLEXES

A.V. Lobanov¹
G.S. Dmitrieva²
G.G. Komissarov¹

1 - Semenov Institute of Chemical Physics RAS, Moscow, Russia
2 - Lomonosov Moscow Institute of Fine Chemical Technology
(Technical University), Moscow, Russia
avlobanov@mail.ru

Zinc phthalocyanines (ZnPc) generates rare long-lived (0.1-2 ms) triplet excited states. The dye absorb the red part of the visible spectrum (660-700 nm) and are exclusive stable. To control association and to influence on photonics and affinity of ZnPc directionally it is promising to include it in a variety of supramolecular systems and nanoparticles.

We obtained supramolecular complexes of ZnPc with plasma proteins, monolamellar liposomes of phosphatidylcholine, micelles of detergents (sodium dodecylsulfate, cetyltrimethylammonium chloride, Triton X-100), hydrophilic polymers (polyvinylpyrrolidone, polyvinyl alcohol, polyethyleneglycol), adsorption of ZnPc on micro- (40-100 μm) and nanosized (60-200 nm) silica and ZnPc nanoparticles and their composites. Stability parameters of these systems and their photophysical properties according to the composition were determined. Optical and luminescent properties of ZnPc essentially depend on the nature of the local environment. For a number of complexes photosensitizing activity in $^1\text{O}_2$ generation, reactive oxygen radical forms and H_2O_2 was shown. Mechanism of this process depends on the pH. Activity of ZnPc decreases at its association due to the triplet-ground state interaction and triplet-triplet annihilation: $^3\text{ZnPc}^* + ^3\text{ZnPc}^* \rightarrow ^1\text{ZnPc}^* + ^1\text{ZnPc}$. This feature is useful for diagnostic methods in the absence of phototoxic effects. However, for photodynamic therapy the association of ZnPc should be suppressed. Thus, ZnPc-ZnPc and ZnPc-carrier interaction leads to a change of the HOMO-LUMO transition energies and the orbital nature of the radiative state of ZnPc. It is shown that many photochromic biologically active substances in different relative amounts can act as energy donors and electron acceptors.

Some novel ZnPc supramolecular and nanosized complexes have been studied by laser flash photolysis method. Triplet decay kinetics of ZnPc was recorded and photochemically active samples were found.

The work was supported by Grant of President of the Russian Federation for State support of young Russian scientists - Candidates of sciences No MK-227.2011.3, RAS Presidium Programs No 3, No 25, Project of International Science and Technology Center No 3910 and Grant of support of Leading Scientific Schools No NSh-65059.2010.3.

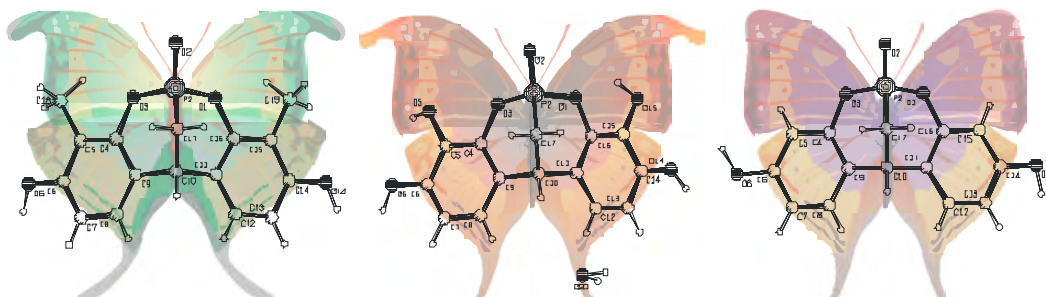
NEW CRYSTAL STRUCTURES OF PHOSPHORUS-CONTAINING BICYCLIC COMPOUNDS BASED ON RESORCINOL AND ITS DERIVATIVES

A.B. Dobrynin
Yu.M. Sadykova
I.A. Litvinov
A.R. Burilov

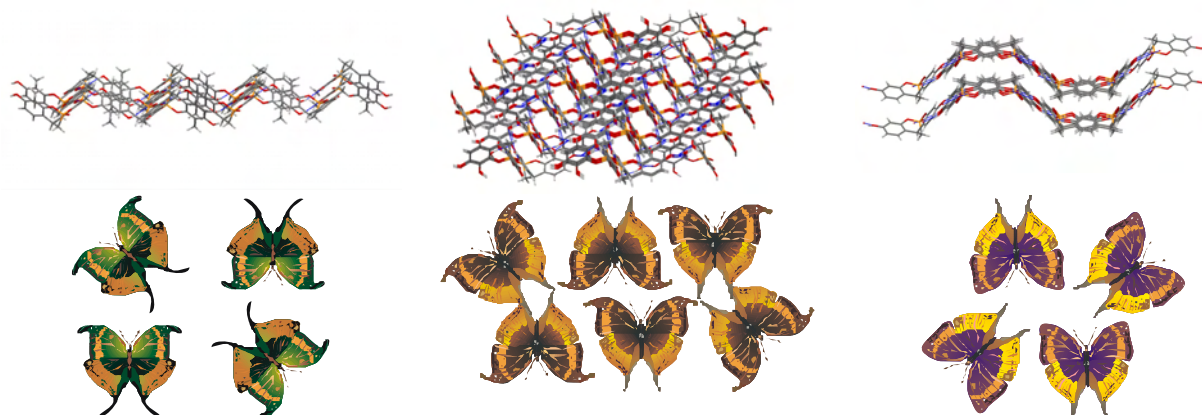
A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
aldo@iopc.ru

New phosphonate compounds with rigid framework were obtained by the by condensation of 2-ethoxyvinylidichlorophosphonate with resorcinol and its derivatives in dioxane. Should be noted that these compounds have several hydroxyl groups, and these compounds interest for further functionalization to the synthesis of new organometallic and macrocyclic compounds. The CCDC have only one compound with a similar bicyclic fragment.

Thus, it was interesting to carry out the structural studies of these compounds, as well as to study the effect of the hydroxyl groups in these heterocycles in crystalline.



Molecules of new phosphonates look like a butterflies.



X-ray analysis was shown these compounds have the rigid framework. Plane fragments is deployed to each other. Phosphoryl groups are equatorial. Conformation of heterocycles is "C-sofa". Hydroxyl groups form multiple classical hydrogen bonds OH...O-type with the phosphoryl group. These interactions lead to the formation of 2- and 3-dimensional supramolecular structures.

The financial support from the Ministry of Science and Education of Russian Federation within FTP "Scientific and scientific-pedagogical personnel of the innovative Russia" (Governmental Contract No 14.740.11.1027) is gratefully acknowledged.

SELF-ORGANIZATION OF OLIGOPEPTIDES THIN FILMS ARE ADVANCED MATERIALS FOR MOLECULAR RECOGNITION OF ORGANIC VAPORS

I.G. Efimova¹
M.A. Ziganshin¹
V.V. Gorbachuk¹
S.A. Ziganshina²
A.P. Chuklanov²
A.A. Bukharaev²

1 - Kazan (Volga region) Federal University, Kazan, Russia
2 - Zavoisky Physical-Technical Institute of KSC of RAS, Kazan, Russia
iefimova@ksu.ru

Ability of molecules peptides to self-organizing with formation tubular or layered nanostructures with various functional features has caused considerable interest to them in the last some years.

Research objective is studying of processes of the directed self-organizing nano-structured films of and change of morphology of a film surface as a result of their interaction with organic vapors (guest).

In present study receptor properties the thin layer of oligopeptides L-alanyl-L-valine (AV), L-valyl-L-alanine (VA) and L-leucyl-L-leucyl-L-leucine (LLL) were estimated using the quartz crystal microbalance technique (QCM). The morphology of thin films of oligopeptides on surfaces of the HOPG (Highly Oriented Pyrolytic Graphite) was studied using the atomic force microscopy (AFM).

It was observed that sorption ability of oligopeptides AV, VA and LLL decrease with increase molecular size of organic guests.

It was found that sorption of a relatively large and/or hydrophobic molecules are caused an irreversible change in the initially flat dipeptides surface morphology, with the formation of nanoislands with varying topology.

It was shown that micro- and nanocrystals formed on the surface of the thin film tripeptide LLL prepared from solution in methanol.

It was found that the sorption of organic compounds which able to effective binding with the tripeptide, leads to significant deformation of microcrystals LLL on the surface of thin film.

The data obtained in the present study will allow to create a fundamental reserve for the solve of a problem of controllable self-organizing of oligopeptide that is necessary for making new biocompatible nanomaterials with the useful properties for bionanomedicine, new biocatalytic systems and intelligence systems for recognition of smell and taste.

This work was supported by programs RFBR № 09-03-97011-p_volga_region and Government contract №P2345

N.A. Epifanova
E.V. Popova
S.V. Kharlamov
Sh.K. Latipov
S.F. Vasilevsky
S.E. Solovieva
I.S. Antipin

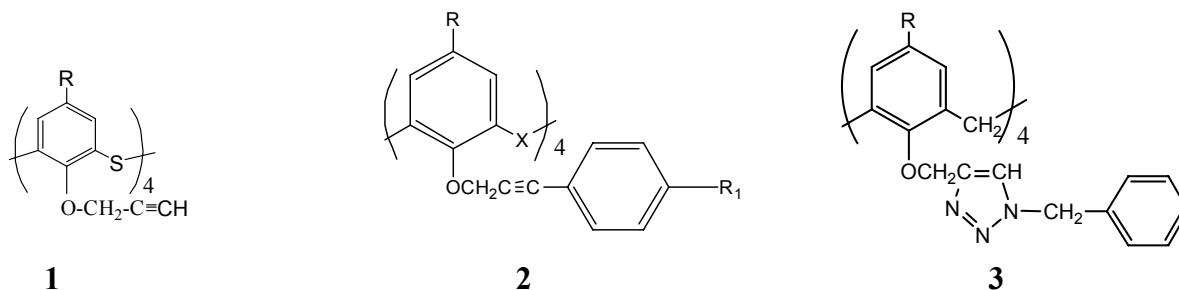
THIACALIX[4]ARENES WITH TRIPLE BONDS ON THE LOWER RIM: SYNTHESIS AND REACTIVITY

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
epifanova_nat@mail.ru

(Thia)calix[4]arenes are useful platforms for obtaining of three-dimensional structures – building blocks for construction of supramolecular systems. They are well-known as molecular receptors for bounding of different type guests: metal ions, organic substrates and metal complexes. Multiple bonds make (thia)calix[4]arene able to form “click-chemistry” products, which could be used for making of new generation biologically active compounds, modification of surface of nano-size particles, selective complexing agents and building blocks for obtaining of metal-organic structures (MOF's), probes for biomedical applications.

In the present work alkylation reactions thiacalix[4]arenes by propargyl bromide in the presence of alkali metal carbonates were systematically studied. Regularity of different stereoisomeric forms formation in dependence of used base nature were established. It was shown, that classical alkylation with using of propargyl bromide gives the possibility to obtain *tert*-butyl-thiacalix[4]arene and thiacalix[4]arene derivatives (**1**) with triple bonds at the lower rim in different conformations in one step.

(Thia)calix[4]arenes with propargyl groups were used in Sonogashira cross-coupling (**2**) as well as in “click-chemistry” (**3**) reactions.



Structure and stereoisomeric forms of new compounds were characterized with the use of 1D and 2D NMR, IR spectroscopy and mass-spectrometry.

The work was supported by the Russian Foundation for Basic Research (grant no. 10-03-00728).

SUPRAMOLECULAR COMPOUNDS OF METAL COMPLEXES WITH MACROCYCLE CAVITANDS CUCURBIT[*n*]URILS

V.P. Fedin
E.A. Kovalenko

Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk,
 Russia
 cluster@niic.nsc.ru

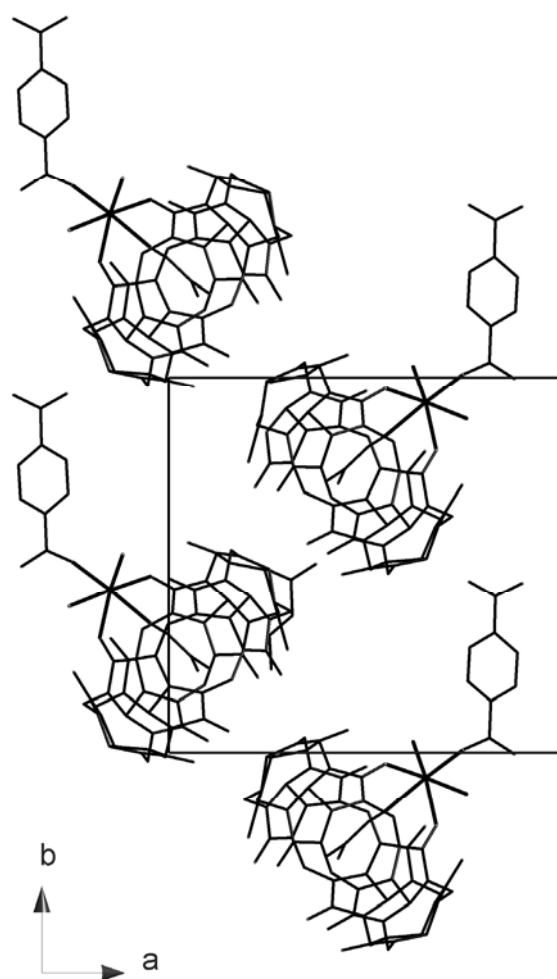
Our research focuses on the chemistry of nanosized complexes and extended solids made of molecular mono- or polynuclear metal complexes and macrocyclic cavitands cucurbit[*n*]uril (CB[*n*]). The deliberate synthesis of large complexes by linking together smaller ones, which are stable in solution under relevant reaction conditions, is a challenge for inorganic chemists. Metal complexes as molecular building blocks have been selected for the following reasons:

the coordination chemistry of metal complexes has turned out to be very rich field with respect to structural chemistry and reactivity;

the complexes are of interest not only with regard to their unique structure and reactivity but also in view of their relevance to biochemical processes, and potential uses in catalysis and material science.

Compounds

$[\text{Ca}(\text{H}_2\text{O})_2(\text{dmf}@CB[6])(\text{bdc})]$ (I) and $[\text{Ca}(\text{H}_2\text{O})_3(\text{dmf}@CB[6])]\text{Cl}_2$ (II) were synthesised by heating (95 °C) of mixture calcium chloride, cucurbit[6]uril (CB[6]) in DMF/H₂O. They are characterized by X-ray analysis, IR- spectroscopy, TGA and elemental analysis. The photoluminescence was studied. According to X-ray analysis metal atom is coordinated by oxygen atoms of cucurbituril. DMF is situated inside macrocycle cavity. The crystal structures of these compounds can be described as parket like packing (see Figure as example for I).



E.A.K. thanks the MK-1029.2011.3 for a fellowship.

M.V. Fomina¹
 A.I. Vedernikov¹
 N.A. Lobova¹
 V.Yu. Rudyak¹
 L.G. Kuzmina²
 T.G. Vershinnikova³
 V.B. Nazarov³
 V.G. Avakyan¹
 M.V. Alfimov¹
 J.A.K. Howard⁴
 S.P. Gromov¹

SYNTHESIS, STRUCTURE AND SPECTRAL PROPERTIES OF 4-(2-NAPHTHYL)PYRIDINE AND THEIR PSEUDOROTAXANE COMPLEXES

1 - Photochemistry Center of the RAS, Moscow, Russia

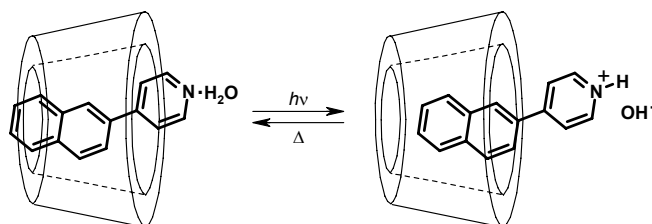
2 - N.S. Kurnakov Institute of General and Inorganic Chemistry of the RAS, Moscow, Russia

3 - Institute of Problems of Chemical Physics of the RAS, Chernogolovka, Moscow Region, Russia

4 - Chemistry Department, Durham University, South Road, Durham DH1 3LE, UK

fomina@photonics.ru

In order to investigate the structure and the stability of complexes of 4-(2-naphthyl)pyridine (**1**) with β -cyclodextrin (β -CD) and 2-hydroxypropyl- β -cyclodextrin (HP- β -CD), we synthesized **1** and its derivatives, naphthylpyridinium perchlorate (**2**) and 1-methyl-4-(2-naphthyl)pyridinium perchlorate (**3**). The spontaneous and photoinduced protonation of **1** in solutions and in complexes with β -CD and HP- β -CD were studied by absorption and fluorescence spectroscopy.



The structure and stability of the complexes ($\log K = 1.5\text{--}2.3$) of **1**, its protonated form **2**, and quaternized derivative **3**, with β -CD and HP- β -CD were studied by ^1H NMR. It was shown that irrespective of the solution pH, compound **1** resides in the cyclodextrin cavity. The structures of salt **3** and pseudorotaxane complex **1**@ β -CD were determined by X-ray diffraction analysis. According to spectral data, pK_a of **1** in water is 5.12, which promotes protonation of nitrogen atom in the excited state. As a consequence, the fluorescence spectrum exhibits only the protonated form. The formation of inclusion complex of **1** with HP- β -CD prevents its protonation, which is a prerequisite for the existence of fluorescence of the non-protonated form of **1**. Quantum chemical simulation of the protonation and complexation of **1** was performed. On the basis of results, reversible photoinduced mechanical motion of **1** in the HP- β -CD cavity was suggested.

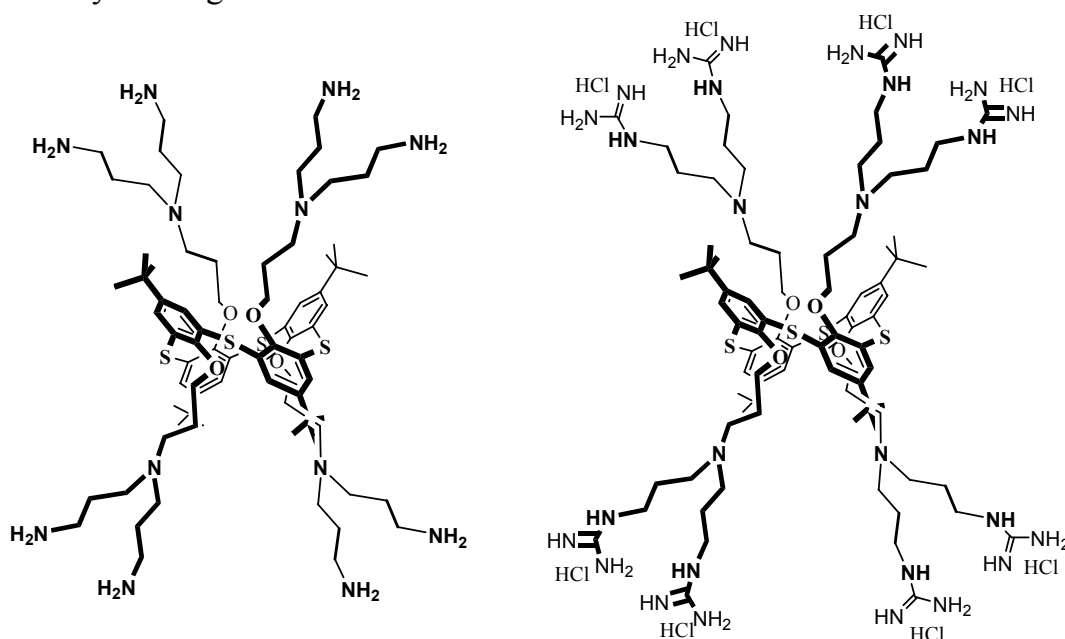
This study was supported by the RFBR and the Russian Academy of Sciences.

SYNTHESIS AND COMPLEXATION ABILITIES OF HYPERBRANCHED STRUCTURES BASED ON THIACALIX[4]ARENE: TOWARDS BIOMACROMOLECULES

A.V. Galukhin
O.A. Mostovaya
I.S. Antipin
A.I. Konovalov
I.I. Stoikov

A.M. Butlerov Chemical Institute, Kazan (Volga Region) Federal
University, Kazan, Russia
and _galuhin@mail.ru

Hyperbranched macromolecules functionalized by polydentate fragments are widely used for highly effective molecular recognition of various biologically relevant compounds, including biopolymers. Dendrimers based on *p*-*tert*-butylthiacalixarene have such interesting properties as high concentration of binding sites, highly developed surface and porosity. Thiacalixarene derivatives' ability for molecular recognition of biologically relevant molecules' surface is provided by conformational mobility of binding fragments (dendrimer's "branches") and spatial organization of functional groups, forming complementary binding sites.



In this work various dendrimers based on thiacalixarene in *1,3-alternate* configuration were synthesized. Structures of obtained compounds were characterized by 1D and 2D NMR – spectroscopy, IR-spectroscopy, mass-spectroscopy and elemental analysis. Complexation abilities of synthesized macrocycles with DNA of salmon sperm and calf thymus DNA were investigated by complex of spectroscopic methods: UV- and fluorescent spectroscopy, dynamic light scattering method.

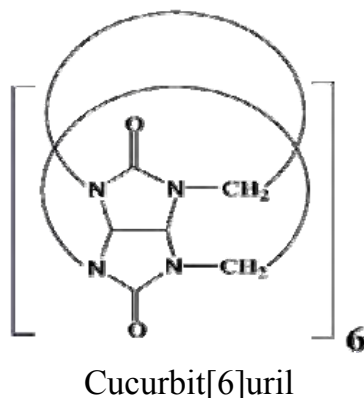
The financial support from Federal Program "Research and scientific-pedagogical cadres Innovative Russia" in 2009-2013 years (№ P1295 on 9 June 2010), RFBR (09-03-00426, 10-03-92661-NSF) and the Program of the President of the Russian Federation for the State support of young Russian scientists - Doctors of Sciences (MD-2747.2010.3) is gratefully acknowledged.

THE RECEPTOR PROPERTIES OF CUCURBIT[6]URIL TOWARD VAPORS OF ORGANIC SUBSTANCES

Sh.F. Galyaltdinov¹
A.V. Gerasimov¹
M.A. Ziganshin¹
V.V. Gorbachuk¹
V.P. Fedin²

1 - Kazan Federal University, A.M. Butlerov Institute of Chemistry,
Kazan, Russia
2 - Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the
Russian Academy of Sciences, Novosibirsk, Russia
Shamil.Galyaltdinov@ksu.ru

The receptor properties of solid cucurbit[6]uril toward vapors of volatile organic substances were studied. Thermogravimetry combined with differential scanning calorimetry and mass-spectrometry was used to determine stoichiometry and thermostability of host-guest inclusion compounds. Guest vapor sorption isotherms and desorption kinetics by cucurbit[6]uril were determined using static headspace gas chromatography.



The results of thermogravimetry and desorption kinetics indicate a weak and reversible binding of studied guests. Sorption isotherms of alcohols and nitriles, benzene and cyclohexane by cucurbit[6]uril have a shape, which is intrinsic for microporous sorbents and can be described by Langmuir and BET equations. On the other hand, sorption isotherm of toluene has a threshold by activity, which is usually observed for clathrate forming receptors as calixarenes. Increase of molecular sizes of guest molecules leads to a strong decrease of sorption capacity of cucurbit[6]uril. It was found that the selectivity of cucurbit[6]uril is essentially higher than that of zeolites.

This work was supported by RFBR (№11-03-01215) and BRHE program (REC-007).

**HYDRATION EFFECT ON RECEPTOR PROPERTIES
OF BETA-CYCLODEXTRIN AND ITS ABILITY TO
ENCAPSULATE ORGANIC GUESTS**

A.K. Gatiatulin
M.A. Ziganshin
V.V. Gorbachuk

A.M. Butlerov Chemical Institute, Kazan Federal University, Kazan,
Russia
agatiatu@ksu.ru

Hydrophilic receptors have a special distinction from hydrophobic ones by the presence of cooperative hydration effect, which is favorable for binding of hydrophobic substrates [1, 2]. In the present work, simultaneous TG/DSC/MS analysis was used to study the dependence of receptor properties of solid beta-cyclodextrin (BCD) on its hydration.

The composition of clathrates prepared by saturation of dry (less than 0.2 mol H₂O per mol BCD) and prehydrated (up to 12 mol H₂O per mol BCD) host with vapors of aliphatic alcohols, nitriles, organochlorine and aromatic compounds were determined. Their values were compared with data from vapors sorption isotherms, obtained using gas chromatographic headspace analysis. It was shown that the hydration of BCD increases its sorption capacity for the hydrophobic guests and decreases - for hydrophilic ones.

Besides, guest encapsulation by BCD was studied together with guest exchange in solid BCD phase. These processes were found to be selective for guest molecular composition.

References:

- (1) Gorbachuk V.V.; Ziganshin M.A.; Solomonov B.N. *Biophys. Chem.* **1999** 81 107-123.
(2) Gorbachuk V.V.; Mironov N.A.; Solomonov B.N.; Habicher W.D. *Biomacromol.* **2004** 5 1615-1623.

This work was supported by RFBR (№11-03-01215) and program BRHE (REC-007).

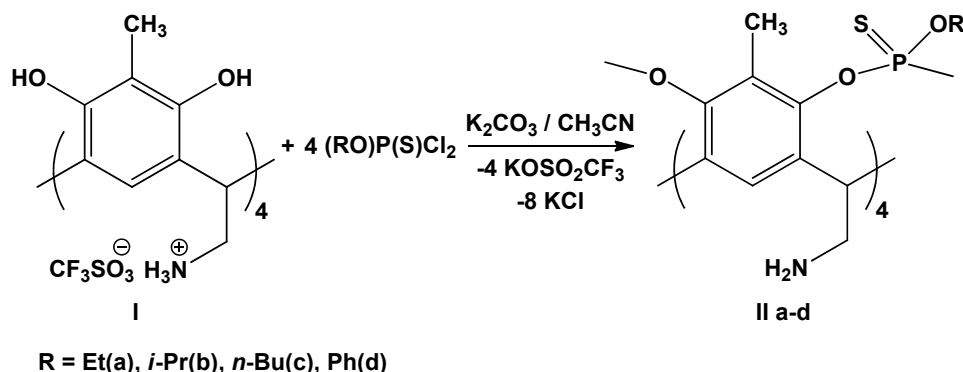
SYNTHESIS OF NOVEL PHOSPHOCAVITANDS BASED ON NITROGEN-CONTAINING RESORCINARENES

A.S. Gazizov
N.I. Kharitonova
A.R. Burilov
M.A. Pudovik

A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan
Scientific Center of Russian Academy of Sciences, Kazan, Russia
agazizov@iopc.ru

Cavitands are extremely interesting and versatile molecular receptors, the complexation properties of which have been extensively studied in the solid state, in solution, and in the gas phase. The propensity of phosphoryl group to bind cationic species is well known and the molecular design of preorganized structures containing this powerful binding group has been the subject of many recent investigations. Thus, phosphorylated cavitands derived from resorcin[4]arene, which combine an aromatic lipophilic cavity with phosphorylated binding sites, are particularly attractive compounds for design of molecules able to bind metal and ammonium cations.

Earlier [1] we have reported synthesis of nitrogen-containing resorcin[4]arene **1**. Herein we report synthesis of novel types of resorcinarene-based phosphorylated cavitands **2** bearing aminogroups on the lower rim of the molecule, in close proximity to the macrocyclic ring. Although reaction of calixarene **1** with various phosphorylating agents differs significantly from those reported in literature for unsubstituted resorcinarenes [2], we have succeeded in isolating target compounds **2** with moderate to high yields.



References:

- [1]. Gazizov A.S., Burilov A.R., Khakimov M.S., Kharitonova N.I., Pudovik M.A., Kononov A.I. / Reaction of α -aminoacetals with 2-methylresorcinol. // Russ.J.Gen.Chem., 2009, V.79, pp.1573-1574.
- [2]. Nifant'ev, E.E., Maslennikova, V.I., Merkulov, R.V. / Design and Study of Phosphocavitands A New Family of Cavity Systems // Acc. Chem. Res., 2005, V.38, pp.108-116.

This work was supported by Russian Foundation for Fundamental Research (grant no 11-03-00416-a).

**MOLECULAR RECOGNITION OF ORGANIC
VAPORS BY VARIOUS GENERATION OF
ORGANOPHOSPHORUS DENDRIMER**

A.V. Gerasimov¹
M.A. Ziganshin¹
V.V. Gorbachuk¹
V.I. Kovalenko²

1 - KFU, A.M. Butlerov Institute of Chemistry, Kazan, Russia
2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, KSC,
RAS, Kazan, Russia
alexander.gerasimov@ksu.ru

Dendrimers are well applicable for the elaboration of sensors, and as nanoparticle catalysts. Having tightly packed end groups, dendrimers of higher generations are selective to the size and shape of guest molecules with a preference to the smaller and less branched guests. In this respect, dendrimers are more selective than liquid or rubbery polymers, which do not have a special molecular recognition compared with ordinary liquid solvents.

In present work the sorption capacity for 30 volatile guests, binding reversibility, guest desorption kinetics and guest exchange, glass transition behavior and ability to be plasticized with guest were studied for phosphorus dendrimers of the first (G_1), second (G_2), third (G_3) and fourth (G_4) generation with core $>P(S)-$, spacer unit $p-(-O-C_6H_4-CH=N-N(CH_3)-)$, branch unit $-P(S)<$ and terminal group $p-(-O-C_6H_4-CHO)$ using quartz crystal microbalance sensor, FTIR microspectroscopy, atomic force microscopy, simultaneous thermogravimetry and differential scanning calorimetry combined with mass-spectrometry of evolved vapors. The dendrimers were found to have a different selectivity for different homological series of guests, high glass transition points without plasticization with guest even at high temperatures and saturation levels, moderate guest-binding irreversibility and ability both for effective guest exchange and independent guest sorption. These properties constitute an advantage of the studied dendrimers as receptor materials in various applications.

This work was supported by RFBR 11-03-01215 and Federal Program "Research and scientific-pedagogical personnel of Innovative Russia" for 2009-2013 (State number P2345).

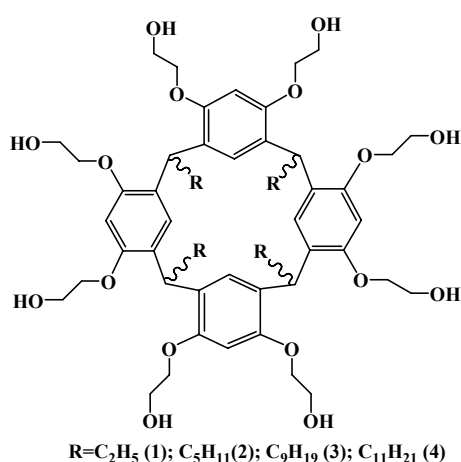
SELF-ASSOCIATION OCTA-2-ETHYLATED CALIX[4]RESORCINOLS IN WATER-ORGANIC SOLVENTS

E.M. Gibadullina¹
 T.N. Pashirova¹
 A.R. Kayupov¹
 E.P. Zhiltsova¹
 A.R. Burilov¹
 L.Ya. Zakharova¹
 W.D. Habicher²
 A.I. Konovalov¹

1 - The Institution of Russian Academy of Sciences, A.E. Arbuzov
 Institute of Organic and Physical Chemistry of Kazan Scientific Center
 of Russian Academy of Sciences, Kazan, Russia
 2 - Dresden University of Technology, Institute of Organic Chemistry,
 Drezden, Deutschland
 elmirak@iopc.ru

Self-assembly processes have been employed successfully to build with accuracy molecular assemblies and supramolecular arrays formerly unattainable using conventional chemistry. Earlier [1] we carried out the synthesis of such type compounds by acid-catalized condensation of 1,3-bis(2-hydroxyethoxy)benzene with various aliphatic aldehydes.

In this paper, we report tensiometry and dynamic light scattering studies of solvent (water-DMFA (30% and 50% vol. DMFA), water-DMSO (30% and 50% vol. DMSO), water-THF (5% vol. THF)) and temperature effects on aggregation properties of new amphiphilic octa-2-hydroxyethylated calix[4]resorcinols with hydrophobic substitutions –



C₂H₅ (1), –n-C₅H₁₁ (2), –n-C₉H₁₉ (3) and –n-C₁₁H₂₃ (4) on the lower “rim”. For all investigated compounds critical concentration of association (CCA) and the sizes of their aggregates were determined. It was shown that surface-activity of compounds 1-4 depends on their structure. Compound 2 is only surface-active at 25°C in such solvents as water-DMFA (30 % and 50 % vol.), water-DMSO (30 % and 50 % vol.). Compound 4 exhibits surface-active properties at 50°C in water-DMFA (50 % vol.) solution. In all investigated systems the sizes of aggregates depend on solvent and concentration of calixarenes. It is established that in water-DMFA and water-DMSO solutions size of

aggregates with increasing concentration in the range of 0.1÷0.2 mol/L. In water-THF (5 % vol.) solutions concentrational changes of the sizes of aggregates depend on structure of investigated compounds.

References:

1. Kasymova E.M., Kaypov A.R. et al. *Russ. J Gen.Chem.* 2007, 77, 1395.

This work was supported by the Russian Foundation for Basic Research (grant no. 11-03-00416a).

SYNTHESIS OF LANTHANUM(III) AND NEODYMIUM(III) HETEROLEPTIC COMPLEXES WITH TETRAKIS-MESO-(3-BROMOPHENYL)-PORPHYRIN AND TETRA-(15-CROWN-5)-PHTHALOCYANINE

K.A. Kamarova¹
K.P. Birin²
Yu.G. Gorbunova¹
A.Yu. Tsivadze²

1 - N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, Russia

2 - A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia
kirill.birin@gmail.com

Sandwich-type lanthanide complexes with porphyrins and phthalocyanines are found to be attractive objects for molecular recognition, molecular information storage applications, non-linear optics and formation of supramolecular architectures. The synthetic route for preparation of heteroleptic lanthanide (porphyrinato)(phthalocyaninates) developed so far is complicated a multistep procedure.

Recently we have developed a simplified regiospecific procedure allowing to prepare heteroleptic early lanthanide (porphyrinato)(phthalocyaninates) of [Por]Ln[Pc]Ln[Por] type in high yields^[1,2]. The aim of the present work is investigation of steric influence of porphyrin *meso*-substituent onto selectivity of the synthesis and the yields of obtained complexes.

It was found that introduction of bromo-substituent in *meta*-position of porphyrin *meso*-aryl group results in decrease of yields of heteroleptic triple-decker complexes Ln-*m*TD (Fig. 1). Formation of co-products with *ca.* 5% yields was detected. Despite the formation of Ln-*m*DD and Ln-*m*TD* the desired triple-decker complexes Ln-*m*TD remain the main products of the interaction. ¹H-NMR data of La-*m*TD revealed hindered rotation of porphyrin *meso*-aryl group and its statistic arrangement.

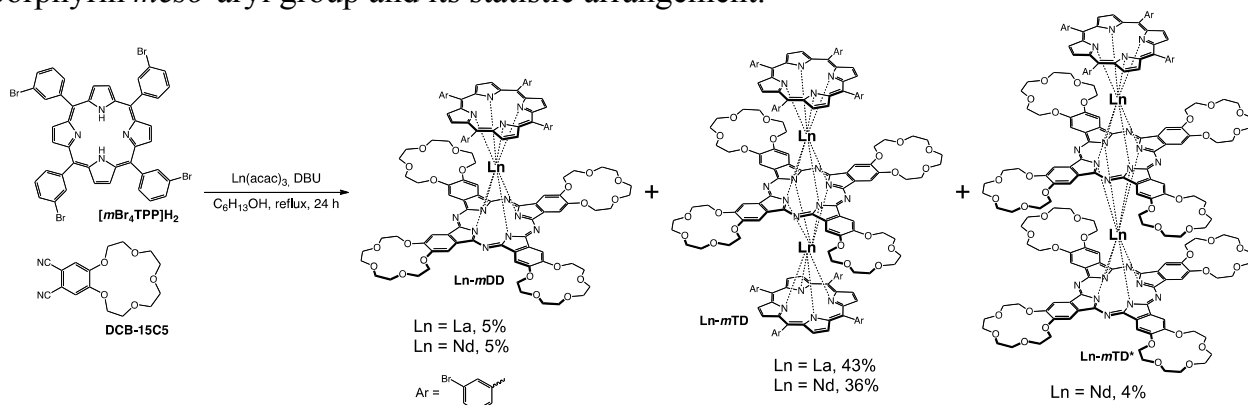


Fig. 1. Synthesis of heteroleptic lanthanide sandwich-type (porphyrinato)(phthalocyaninates).

References:

¹ Birin, K.P.; Gorbunova, Yu.G.; Tsivadze, A.Yu. *Macroheterocycles* 2010, 3, 4, 210-217.

² Birin K.P., Gorbunova Yu.G., Tsivadze A.Yu. *Inorg. Chem.* 2011, submitted.

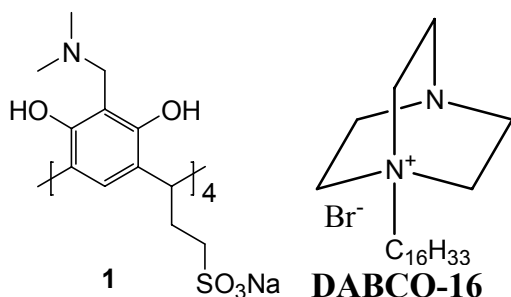
The authors are grateful to Foundation of Russian President for support of young scientists and leading scientific schools (grants MK-212.2010.3, NSh-3835.2010.3), RFBR (grant 11-03-00968) and Russian Academy of Sciences for financial support.

NOVEL SELF-ASSEMBLING SYSTEM BASED ON CALIX[4]RESORCINE AND CATIONIC SURFACTANT

R.R. Kashapov¹
 T.N. Pashirova²
 S.V. Kharlamov³
 A.Yu. Ziganshina⁴
 S.S. Lukashenko²
 E.P. Zhiltsova²
 L.Ya. Zakharova²
 Sh.K. Latypov³
 A.I. Konovalov⁵

1 - Kazan State Technological University, Petroleum and Petrochemistry, Kazan, Russia
 2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Laboratory of Highly Organized Structures, Kazan, Russia
 3 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Laboratory of Radiospectroscopy, Kazan, Russia
 4 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Laboratory of Calixarene Chemistry, Kazan, Russia
 5 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Laboratory of Chemistry and Physics of Supramolecules, Kazan, Russia
 kashapov@iopc.ru

The self-organization in the binary system based on the calix[4]resorcinol with sodium sulfonatoethylene groups on the lower rim and aminoalkylated moieties on the upper rim (**1**) and cationic surfactant 4-aza-1-hexadecyl-azoniabicyclo[2.2.2]octane bromide (**DABCO-16**) has been investigated. The data obtained by the various methods suggest that two different associative modes are realized in the binary system under the fixed **1** concentration



and the varied surfactant concentration. Surface tension versus **DABCO-16** concentration plot demonstrates a breakpoint at 0.4 mM, which is lower as compared to single **DABCO-16** cmc of 1 mM and single **1** cmc of ca. 10 mM. The close values of breakpoints are revealed by methods of conductometry, potentiometry and NMR self-diffusion. Beyond ca. 0.4 mM of **DABCO-16**,

mixed aggregates enriched by **1** are proved to be formed due to electrostatic forces at first stage of the association. Second breakpoint is observed under the conditions of higher surfactant concentration of ca. 5mM, which is assumed to indicate the formation of mixed micelles enriched by **DABCO-16** molecules through conventional surfactant aggregation mode mainly contributed by hydrophobic effect. The solubilization study with the use of hydrophobic dye Orange OT demonstrated that only mixed aggregates enriched by **DABCO-16** is capable of binding the organic probe, while mixed system where the surfactant is a minor component shows no binding capacity towards Orange OT. This finding can be used for design of nanocontainers with controllable guest-release properties.

This work was supported by the Russian Foundation for Basic Research (grant 10-03-90416-Ukr_a).

**SUPRAMOLECULAR SYSTEMS BASED ON
HYDROPHOBICALLY MODIFIED
POLYETHYLENEIMINE AND
O-2-HYDROXYETHYLATED CALIX[4]ARENES**

T.N. Pashirova¹
T.M. Gabbasova¹
R.R. Kashapov¹
E.P. Zhiltsova¹
A.R. Kayupov²
E.M. Kasymova²
A.R. Burilov²
L.Ya. Zakharova¹
A.I. Konovalov³

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry,
Laboratory of Highly Organized Structures, Kazan, Russia
2 - A.E. Arbuzov Institute of Organic and Physical Chemistry,
Laboratory of Organoelemental Synthesis, Kazan, Russia
3 - A.E. Arbuzov Institute of Organic and Physical Chemistry,
Laboratory of Chemistry and Physics of Supramolecules, Kazan,
Russia
pashirova@iopc.ru

In this work, aggregation properties and catalytic activity of systems based on individual compounds (dodecyl-modified polyethyleneimine with a molecular weight of 25000 (PEI) and o-2-hydroxyethylated calix[4]resorcinols with hydrophobic chains n-C₅H₁₁ (CR₁) and n-C₁₁H₂₃ (CR₂) on the "lower rim") and their mixed compositions towards hydrolysis of 4-nitrophenyl-O-butylchloromethylphosphonate (NBCP) were investigated in the water-dimethylformamide solution (50 vol.% DMF) at 50 °C. Tensiometry method shows that all these compounds decrease the surface tension at the air-water interface. Critical association concentrations (CAC) are 0.04 M for PEI, 0.3 mM for CR₁, and 0.15 mM for CR₂. Sizes of aggregates in the water-DMF (50 vol. %) solution at 50 °C were determined by dynamic light scattering (DLS). PEI forms aggregates with the sizes of 10 and 90-120 nm at CAC and above. The size of CR₁ is 180 nm, while CR₂ form two kinds of aggregates with radiuses of 80 and 200 nm. Conductometry and DLS methods revealed that the values of CAC and the sizes of mixed aggregates are different from those for individual systems based on PEI and CR. This indicates the formation of mixed PEI-CR₁ and PEI-CR₂ aggregates. CAC₁ values are 0.019 M for PEI-CR₁ system and 0.007 M for PEI-CR₂. CAC₂ for both mixed systems equals 0.1 M. The spectrophotometric study of the kinetics of the hydrolysis of NBCP showed that the mixed PEI-CR systems demonstrate a higher catalytic activity than a system based on PEI. It should be noted that the acceleration for the mixed PEI-CR₂ system increases only in the case of additives of CR₂ at concentration above CAC.

This work was supported by the RFBR (project No 09-03-00572-a)

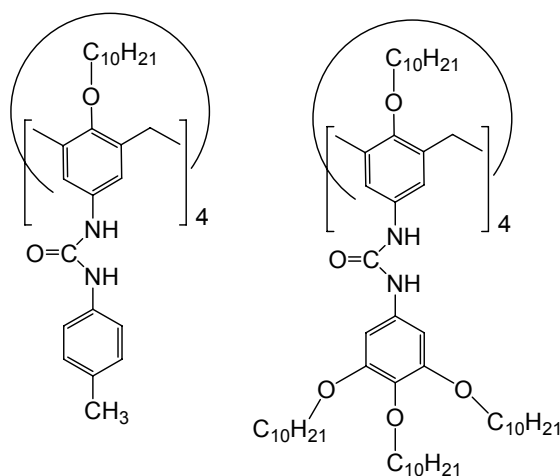
SOLID-PHASE EXCHANGE OF GUEST IN MOLECULAR CAPSULES AND THEIR THERMAL STABILITY

Kh.R. Khayarov¹
M.A. Ziganshin¹
M.O. Vysotsky²
V. Bohmer²
V.V. Gorbachuk¹

1 - A.M. Butlerov Chemical Institute, Kazan Federal University, Kazan, Russia

2 - Abteilung Lehramt Chemie, Fachbereich Chemie, Pharmazie und Geowissenschaften, Johannes Gutenberg-Universität, Mainz, Germany
 agatiatu@ksu.ru

In this work, we studied the solid-phase exchange of guests encapsulated by calixarenes **I** and **II**, and the thermal stability of molecular capsules formed by calixarene **I**.



The thermal stability parameters of molecular capsules formed by a dimer of calixarene **I** with molecules of benzene, toluene, CCl₄, fluorobenzene, and cyclohexane were obtained. The temperature range of guest loss by molecular capsules was determined. The solid-phase exchange of encapsulated the guests was observed with a combined TG / DSC analysis with mass-spectrometric determination of evolved gases and vapors. By solid-phase exchange the capsule of butane was prepared with calixarene **I**. The kinetics of toluene exchange for benzene within the molecular capsules formed by the calixarene **II** was studied by ¹H NMR spectroscopy. Exchange of encapsulated guests in solid phase of calixarene **II** was found to be faster than an exchange in solid calixarene **I** [1].

References:

- [1] M.A Ziganshin, L.S Yakimova, Kh.R Khayarov, V.V. Gorbachuk, M.O. Vysotsky and V. Böhmer / Guest exchange in dimeric capsules of a tetraurea calix[4]arene in the solid state // Chem. Comm. – 2006 – P. 3897-3899.

**CHEMICAL APPLICATIONS OF NUCLEAR
MAGNETIC RESONANCE SPECTROSCOPY FOR
MECHANISTIC AND STRUCTURAL STUDIES IN
NATIVE IMIDAZOLIUM-BASED IONIC LIQUIDS**

E.A. Khokhlova
V.P. Ananikov

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of
Sciences, Moscow, Russia
elenahkhokhlova@mail.ru

In the last decades ionic liquids have attracted continuous attention due to their unique properties and their applications in organic synthesis, catalysis, biocatalysis, extraction and dissolution processes, nanomaterials synthesis, polymerization reactions and electrochemistry¹. Unfortunately, currently mechanistic and structural studies carried out directly in ionic liquids encounter significant difficulties due to the lack of general and efficient analytical techniques such as, for example, NMR spectroscopy in regular organic solvents.²

In the present study we have developed practical NMR method to monitor chemical transformations directly in ionic liquids, to measure reaction yield and selectivity, and to determine the structure of the product.

The scope of the developed NMR method was investigated using the model reaction of dehydration of carbohydrates. The developed approach was successfully applied to study [BMIM][Cl], [BMIM][BF₄] and [BMIM][PF₆] systems using ¹H, ¹³C and ¹¹B NMR. The possibility of two-dimensional NMR measurements were demonstrated. In the past years, promising results have been reported on the dehydration of carbohydrates in ionic liquids with such catalysts as hydrochloric and sulfuric acids; metal chlorides, for example, chromium (III), aluminum (III), and tin (IV) chlorides; Amberlyst 15; boric compounds etc.³

References:

1. J.P. Hallett, T. Welton, *Chem. Rev.* **2011**, 111, 3508-3576.
2. V. P. Ananikov, *Chem. Rev.* **2011**, 111, 418-454.
3. A. A. Rosatella, S. P. Simeonov, R.F.M. Frade, C.A.M. Afonso, *Green Chem.* **2011**, 13, 754-793.

NOVEL SYNTHETIC RECEPTORS FOR ALKALI AND ALKALINE-EARTH METAL CATIONS BASED ON CROWN-CONTAINING QUINONES

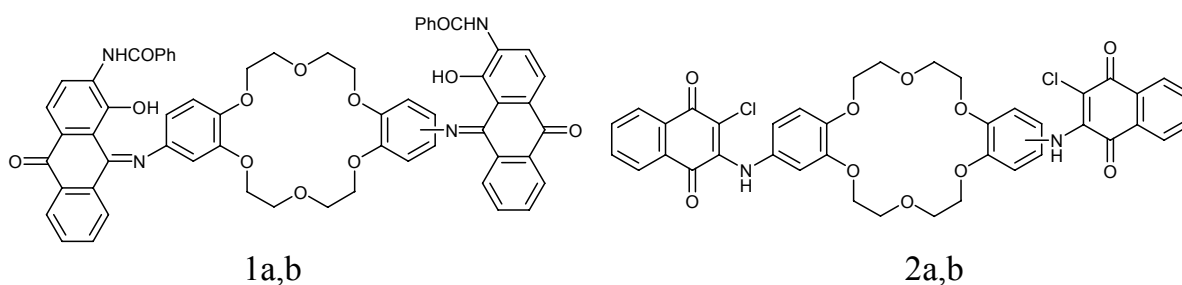
L.S. Klimenko¹
T.P. Martyanov¹
E.N. Ushakov²

1 - Yugra State University, Khanty-Mansiysk, Russia

2 - Institute of Problems of Chemical Physics, Chernogolovka, Russia

L_Klimenko@ugrasu.ru

The novel derivatives of diaminodibenzo-18-crown-6 ethers containing two anthra- or naphthoquinone chromophore fragments were synthesized. The derivatives of 9,10- anthraquinone-9-imine (1a,b) were obtained by photoirradiation of mixtures of diaminodibenzo-18-crown-6 ethers with photochromic 1-aryloxy-9,10-anthraquinones. In compounds 1a,b, the crown ether fragment is directly connected to the imine moiety of the chromophore. The crown-containing naphthoquinones 2a,b were synthesized by substitution of one of the chlorine atoms in 2,3-dichloro-1,4-naphthoquinone by arylamino group of the corresponding diaminodibenzo-18-crown-6 ether.



The complex formation of chromogenic crown ethers 1a,b and 2a,b with Group Ia and IIa metal perchlorates in MeCN and DMSO was investigated by spectrophotometric titration method. There was shown quantitative dependence of the efficiency of complex formation on the type of chromophore system and the relative spatial arrangement of the groups participating in coordination. For compounds 1a,b that are characterized by the imine–enamine tautomeric interconversion, the contribution of each of the tautomeric forms to the complex formation process was estimated. The structures of the complexes of 1a,b and 2a,b with metal cations were studied by quantum chemical simulation using DFT method.

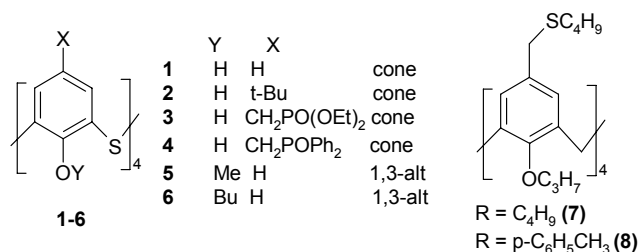
It was found that chemosensors 1a,b in MeCN effectively bind Mg^{2+} ; the complexed cation is coordinated with the imine nitrogen atom, OH-group and the carbonyl oxygen of the benzoylamino group ($\lg K = 4.4$). The other cations interact preferably with the crown ether moiety of 1a,b; in this case the complex stability constant decreases in the sequence $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Na}^+$.

G.A. Kostin
N.A. Kryuchkova
L.N. Mazalov
V.G. Torgov
A.B. Drapailo

ELECTRONIC STRUCTURE OF THIACALIX[4]ARENES ACCORDING TO DFT CALCULATIONS AND X-RAY SPECTROSCOPY

Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia
kostin@niic.nsc.ru

Thiacalixarenes (TCA) is relatively new class of macrocyclic compounds intensively studied in recent years. The replacement of the bridging CH_2 groups by electron-withdrawing sulfur atoms leads to a substantial difference between TCAs and classic calixarenes. Several features of TCA such as increased acidity of OH groups or the possibility of directly replacing them by amino and amide groups can be qualitatively explained by the inductive effects of the more electronegative sulfur atoms. The unusual regioselectivity of electrophilic substitution in TCA and its dependence on the conformation reported in Lhotak's recent papers require a quantitative description of HOMO and the charge distribution on the carbon atoms in the benzene rings.



Scheme 1

From the viewpoint of coordination chemistry, the major distinction of TCA is the presence of sulfur atoms as additional donor centers. The possibility of their participation in complexation is determined by the geometrical characteristics of thiacalixarenes, the electron density on the sulfur atoms, and the contribution of the valence electrons of sulfur to the highest occupied molecular orbitals which can be experimentally proven by X-ray

emission spectroscopy.

The DFT calculations of thiacalixarenes (Scheme 1, **1-6**) in the “cone”, “pinched cone,” and “1,3-alternate” conformations revealed that the orientation of the benzene rings relative to the mean $[\text{S}_4]$ plane through four bridging sulfur atoms played a critical role in electron density distribution (the highest occupied molecular orbital and ESP charges). In the benzene rings that form angles of approximately 90° ($84\text{--}89^\circ$) with the $[\text{S}_4]$ plane, the carbon atoms in the *meta* positions to the phenol group are the most favorable sites for an electrophilic attack. This determines the unusual regioselectivity found by Lhotak for tetraalkylated thiacalix[4]arenes in the “pinched cone” or “1,3-alternate” conformation. In the benzene rings lying at an angle of $30\text{--}50^\circ$ to the $[\text{S}_4]$ plane of tetrahydroxo thiacalix[4]arenes in the “cone” or “pinched cone” conformation, the maximum negative ESP charge and the maximum density of HOMO are located on the carbon atom in the *para* position to the phenol oxygen.

The calculated difference in the structure of HOMO between the “1,3-alternate” and “cone” conformations was experimentally confirmed by the sulfur K_β spectra of thiacalix[4]arenes. The experimentally observed decrease in the relative intensity of the short-wave band for the alternate conformers was explained by the more regular distribution of the sulfur 3p AO in the HOMO and the wider range of energies of the molecular orbitals that formed this maximum.

Change of $\text{S}2p_{3/2}$ line position in XPS spectra (TCA “cone” $\geq$ TCA “1,3 – alternate” $>$ calixarene-thioesters **7**, **8**) is similar to the shift of line in XES K_α - spectra and correlates with increase in calculated electronic density on sulfur atoms. From that point of view donor properties of bridging sulfur atoms in TCA is close to that in dialkyl sulphides and greater than diphenyl sulphide, modeling fragment Ar-S-Ar . Introduction of donor groups in upper rim in TCA **3**, **4** have only slight influence on charge state of bridging sulfur atoms.

**SUPRAMOLECULAR CATALYTIC SYSTEMS
BASED ON PLURONICS FOR THE HYDROLYSIS
OF PHOSPHORUS ACIDS ESTERS AND
CROSS-COUPLING REACTION**

Yu.R. Kudryashova
F.G. Valeeva
L.Ya. Zakharova
A.I. Konovalov

A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan
Scientific Center of Russian Academy of Sciences, Department of
Supramolecular Chemistry, Kazan, Russia
ablakova_yuliana@iopc.ru

By the methods of tensiometry, viscosity, EPR-spectroscopy, dye solubilization and dynamic light scattering the self-organization of Pluronic F127 and Synperonic F68 in water was studied at different temperatures. The two critical association concentrations and bimodal size distribution were determined. The smaller particles are unimers (non aggregated individual molecules of block-copolymers) with effective hydrodynamics diameter of 8 nm. The larger aggregates are intermolecular micelles ($D_h = 40$ nm). At the temperature above 30°C the formation of Synperonic F68 aggregates was shown by the solubilization of the Orange OT. Due to insolubility in water, Orange OT can be used as sensitive indicator of micellization.

Both block-copolymers have been used as catalytic additives in hydrolysis of phosphorus acids esters and Suzuki cross-coupling (Scheme 1). Catalytic effect of block-copolymers in hydrolysis was monitored by spectrophotometry. The yield of products in the cross-coupling reaction was determined by H^1 NMR-spectroscopy and chromatomass-spectrometry.

In the presence of Pluronics, a slight inhibition (up to two times) of the hydrolysis of substrates 1, 2 reaction was observed. In water under aerobic conditions and 25°C, the yield of cross-coupling products was varied from 60 to 80%.

This work was supported by the RFBR (grant 0-03-90416-Ukr_a).

BENZOTHIACROWN ETHERS: SYNTHESIS AND STRUCTURE OF THEIR COMPLEXES WITH PALLADIUM(II)

N.A. Kurchavov¹
 S.N. Dmitrieva¹
 N.I. Sidorenko¹
 A.I. Vedernikov¹
 A.Ya. Freidzon¹
 A.A. Bagatur'yants¹
 L.G. Kuz'mina²
 T.M. Buslaeva³
 S.P. Gromov¹

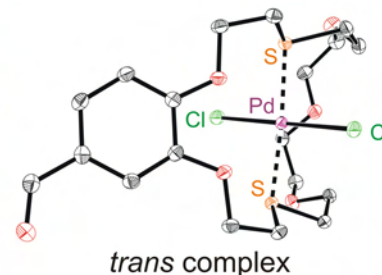
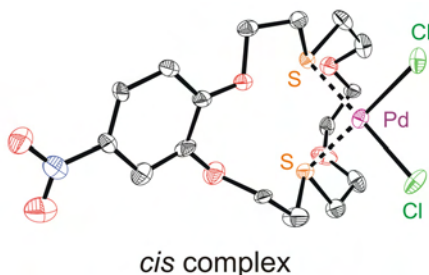
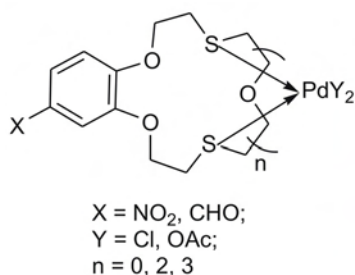
1 - Photochemistry Center, Russian Academy of Sciences, Moscow, Russia

2 - N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia

3 - Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia

kurch@photonics.ru

A synthesis of benzodithiacrown ethers (L) with various-sized macrocycles is proposed. It is found that the synthesized macrocycles form complexes of the formula $[\text{PdLCl}_2]$ and $[\text{PdL}(\text{OAc})_2]$ with $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$ and $\text{Pd}(\text{OAc})_2$ salts.



The structure of the benzothiacrown ethers and their complexes with palladium (II) salts is studied by 1D and 2D NMR (COSY, NOESY, HMBC, HSQC, ¹³C, ¹H) methods. The electronic and geometrical structures and ¹H NMR spectra of the free crown ethers and their complexes with palladium (II) chloride are calculated by DFT. It is found that the deviation of the shape of the S₂PdCl₂ fragment from the planar square correlates with the binding energy of PdCl₂ fragment with the macrocycle. The calculated structures and spectra are used for the interpretation of the experimental NMR data.

The structures of free benzothiacrown ethers and their complexes with PdCl₂ are studied by X-ray diffraction. It is found that palladium(II) is bound to the two sulfur atoms of the macrocycle and two chloride anions and lies in the center of a S₂PdCl₂ square. In 12- and 18-membered macrocycles, the sulfur atoms in the S₂PdCl₂ fragment are in the *cis* position. In 21-membered macrocycles, the sulfur atoms in the S₂PdCl₂ fragment are in the *trans* position. These structure data agree with the NMR and theoretical data.

This work was supported by Russian Foundation for Basic Research and Russian Academy of Sciences.

**SYNTHESIS OF LIPOPHILIC
AMINOMETHYLPHOSPHINE OXIDES - EFFICIENT
CARRIERS OF RARE-EARTH ELEMENTS AND
SCANDIUM IN EXTRACTION WITH LIQUID
IMPREGNATED MEMBRANES**

**N.V. Kurnosova
A.R. Garifzyanov
R.A. Cherkasov**

Kazan (Volga region) Federal University, A.M. Butlerov Chemical
Institute, Kazan, Russia
kurnosova.nataliya@yandex.ru

A vital problem of contemporary analytical, coordination and environmental chemistry is the creation of new highly effective extractants for the separation and concentration of the mixtures of substrates of different origin, both natural and technogenic. On the basis of Kabachnik–Fields three-component reaction we performed the planned synthesis of the new aminophosphoryl compounds of the general formula $R_2P(O)CH_2R_1$ containing one or two metylenediorganylphosphinyl groups at the nitrogen atom, where $R = \text{Hex, Oct, Dec}$, $R_1 = NCH_2CH_2OCH_2CH_2OH$, $N(CH_2CH_3)C_6H_5$, $NHCH_2C_6H_5$, $(C_6H_{13})_2P(O)NHC_8H_{17}$ to create the new efficient and selective extractants for the separation and concentration of rareearth elements and scandium.

Membrane transport properties of the synthesized compounds with respect to the scandium ion and satellite elements were investigated. Research has shown that bisphosphorylated amines are more efficient carriers, than monophosphorylated analogues.

The process of membrane transport of Nd (III), Sc(III), Sm(III), Al(III) and Mg(II) in nitrate media through liquid impregnated membranes, which are the porous fluoroplastic film having thickness of 10 μm impregnated with a bis- α -(dihexyl)phosphinylmetyloctylamine solution in dichlorobenzene was investigated. It was established that the highest transfer rate is observed for Nd(III), Sc(III) and Sm(III) ions. The influence of the concentration of nitrate ion, carrier in the membrane phase and the acidity of the aqueous medium on the rate of ion transport was studied.

Optimal conditions for efficient transport of these cations were found. The possibility of separation Nd(III), Sm(III) and Sc(III) from Mg(II) and Al(III) ions was shown.

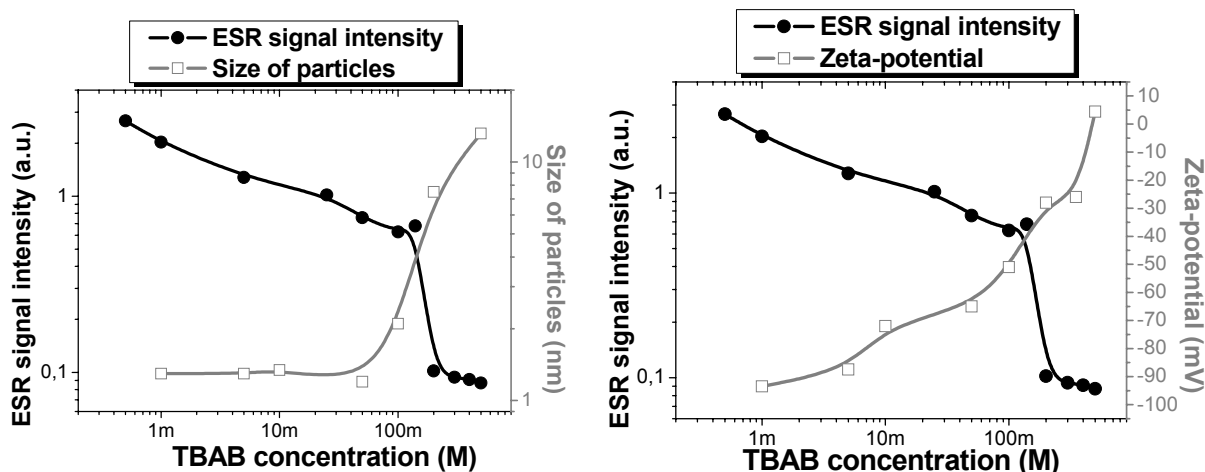
The work was supported by the Russian Foundation for the Basic Research (grant 10-03-00580).

ESR HYDROPHOBIC SPIN PROBE TECHNIQUE IN THE STUDY OF SURFACTANT AGGREGATES RECHARGE

A.I. Litvinov
F.G. Valeeva
L.Y. Zaharova
M.K. Kadirov

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan
 Scientific Center, Russian Academy of Sciences, Kazan, Russia
 zenituwka88@gmail.com

Mixed micelles of surfactants with different nature arouse great interest in science and bio-engineering, because of vast possibilities for control of their parameters and properties. Mixtures of ionic surfactant and hydrophobic electrolyte can also form mixed aggregates with properties depending on size, hydrophobicity and type of electrolyte. The mixtures of sodium dodecylsulfate (SDS) with tetramethyl ammonium chloride (TMAC), tetraethyl ammonium bromide (TEAB) and tetrabutyl ammonium bromide (TBAB) were studied by ESR spin probe technique, dynamic light scattering, and zeta-potential measurement technique. Concentration of SDS was kept at a constant level of 0,1M to ensure formation of anionic micelles. The hydrophobic spin probe 10-Me-phenothiazine (10-Me-PTZ) was used for ESR measurements. This type of probe is activated by UV and in anionic micelles has a lifetime long enough for measurements. Significant lowering of ESR signal was observed at high concentrations of electrolytes (0,5M for TBAB, 2M for TEAB), same samples revealed drastic increase of size of aggregates. Further investigations showed that zeta-potential reached zero values at these concentrations, what means the anionic surface of micelles was recharged there.



STEREOSELECTIVE [2+2]-PHOTOCYCLOADDITION IN BISSANDWICH COMPLEXES OF BISCROWNSTILBENES WITH METAL AND ALKANEDIAMMONIUM IONS

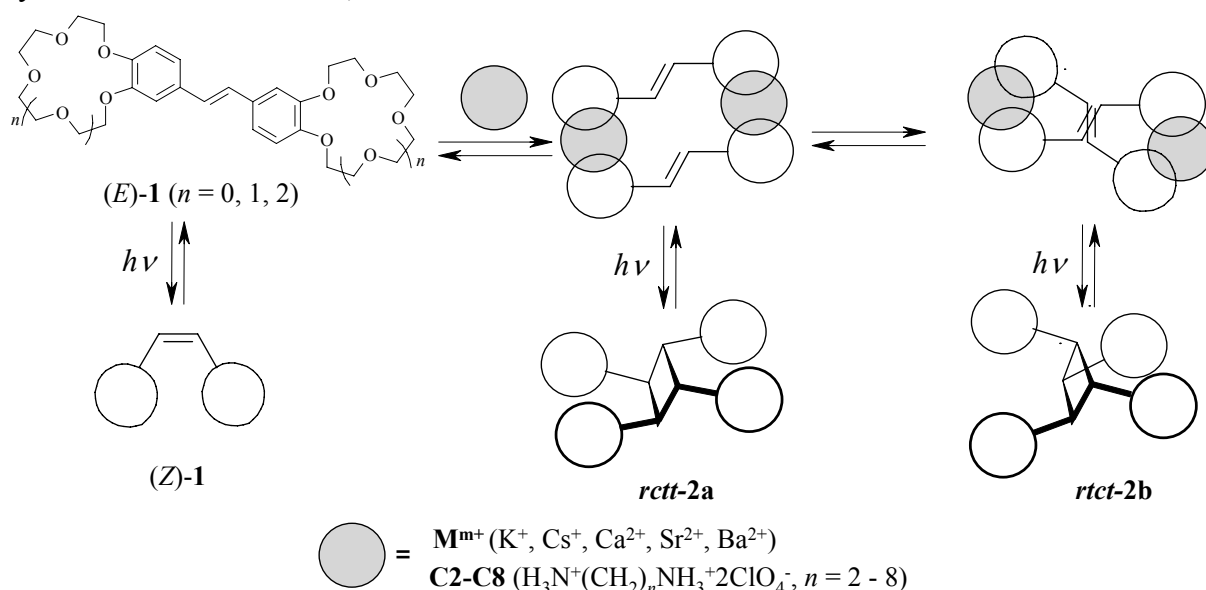
N.A. Lobova¹
A.I. Vedernikov¹
L.G. Kuzmina²
M.V. Alfimov¹
S.P. Gromov¹

1 - Photochemistry Center of the RAS, Moscow, Russia

2 - Institute of General and Inorganic Chemistry of the RAS, Moscow, Russia

lobova@photonics.ru

Bis(crown)stilbenes **1** ($n = 0 - 2$) are very simple and promising photosensitive ionophores. They can form strong complexes of various compositions with metal cations and ammonium ions. The C=C bond in the structure of stilbenes is able to a lot of phototransformations such as *trans-cis* isomerization, electrocyclization, and [2+2]-cycloaddition with formation of symmetrical cyclobutane derivatives **2a,b**.



The composition and components ratio depends on the size of crown-ether fragment in **1**, the size of metal cation and the length of diammonium ion.

Table 1. Photoproducts ratio after UV-irradiation of 1:1 mixture of bis(crown)stilbenes and salts in MeCN (from ¹H NMR data).

<i>n</i>	Cation	Photoproducts ratio (%)				
						Other
0	Ba ²⁺	0	0	66	27	7
1	Ba ²⁺	0	0	74	26	0
1	C3	6	77	5	0	12
2	Ba ²⁺	12	74	3	0	11
2	C3	0	13	84	3	0

Thus the directional phototransformation of crownstilbenes can be applied in optical sensors for cations, for information recording and storage, for the creation of molecular devices and machines.

This work was supported by the RFBR and the Russian Academy of Sciences.

UNEXPECTED CHIRAL HELICAL
SUPRAMOLECULAR STRUCTURES ON THE BASIS
OF 3-PYRROLIN-2-ONE AND
2(5H)-FURANONE DERIVATIVES

O.A. Lodochnikova¹

L.Z. Latypova²

L.S. Kosolapova²

A.R. Kurbangalieva²

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia

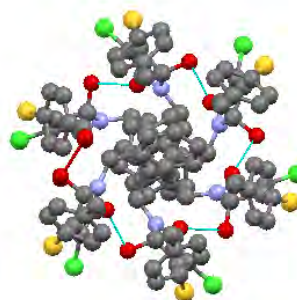
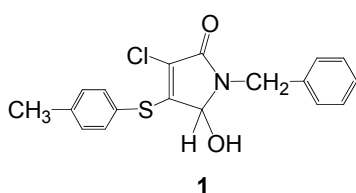
2 - A.M. Butlerov Chemical Institute at Kazan Federal University, Kazan, Russia

lod_olga@mail.ru

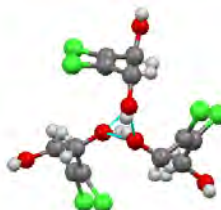
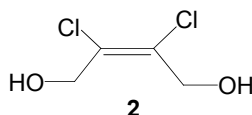
Compounds that form helical structures in the crystalline state have attracted much attention because they can be used as new materials in solid- or liquid-crystal engineering.

The crystallization of two new derivatives of 3-pyrroline-2-one and 2(5H)-furanone leads to the formation of chiral supramolecular structures. The cause of the asymmetry in the crystal - formation of the helices around the 3- or 6-fold screw axes by means of the intermolecular interactions.

Pyrrolinone **1** forms the conglomerate in the enantiomorphic space groups ($P6_5$, $P6_1$). The main supramolecular associate is the helix around the 6-fold screw axis generated by classical hydrogen bonds.



Unexpectedly, the structure of the compound **2** obtained after the reduction of 5-alcoxy-3,4-dichloro-2(5H)-furanones, which molecule is symmetrical and does not contain a chiral center, was solved in the chiral space group $P3_1$ (three independent molecules). The molecules **2** form the H-bonded helices around the screw 3-fold pseudo-axis in the crystal.



The financial support from the Ministry of Science and Education of Russian Federation (Governmental Contract No 14.740.11.1027) and RFBR № 09-03-00696-a is gratefully acknowledged.

**THE RECEPTOR PROPERTIES OF POLYMORPHS
OF *TERT*-BUTYLTHIACALIX[4]ARENE DERIVATIVE
IN "PARTIAL CONE" CONFORMATION TOWARDS
VOLATILE ORGANIC COMPOUNDS**

**K.V. Luchai
G.D. Safina
M.A. Ziganshin
V.V. Gorbachuk**

Kazan (Volga region) Federal University, A.M. Butlerov Chemical
Institute, Kazan, Russia
luch-nataliya@yandex.ru

The influence of size and presence of substituents in upper and lower rims of the macrocycle on the receptor properties of calixarenes toward different compounds vapors were widely studied. However, little attention is paid to studying of the properties of different polymorphs of calixarenes.

The aim of this work was to study the receptor properties of tetrasubstituted in lower rim *tert*-butylthiacalix[4]arene in "partial cone" conformation (calixarene **1**) in the vaporous "guest" – solid "host" systems.

The presence of polymorphic transitions in the structure of calixarene and the existence of calixarene in two polymorphic phases (α - and β -phase) were observed by powder XRD method and simultaneous TG/DSC/MS analysis.

It was shown that both phases of the studied calixarene don't form clathrates with methanol and alkanes that are stable at room temperature. The most thermally stable clathrates of calixarene **1** are formed with non-polar organic compounds. Calixarene **1** inclusion compound with pyridine has the largest stoichiometry among studied guests.

It was found that the receptor properties of solid α - and β -phases of calixarene **1** toward vaporous "guests" are different. For example, β -phase of calixarene **1** has greater sorption capacity and higher thermal stability compared to α -phase.

This work was supported by program RFBR (№ 11-03-01215) and State contract with the Ministry of Education and Science of RF (№ 14.740.11.0377).

S.T. Minzanova
O.V. Tsepaeva
V.F. Mironov
L.G. Mironova
A.V. Pashagin
G.R. Petrova
F.Kh. Ziatdinova

STRUCTURAL PECULIARITIES OF AMARANTH PECTIN POLYSACCHARIDES

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
minzanova@iopc.knc.ru

The new data concerning the physical-chemical properties and structural peculiarities of pectin polysaccharides of amaranth *Amaranthus cruentus* are offered in the report. Amaranth is non-traditional culture in the Russia and it attracts a great attention of researchers and experts in agriculture by a high content of protein with a balanced set of the essential amino acids, a high yield, a high content of vitamins and mineral salts. Rather high content of flavonoids, pectin, carotinoids and other ingredients in some sorts of amaranth allows using the last one for the industrial obtaining of a series of biologically active compounds, which are applied in medicine.

The hydrolysis and extraction processes parameters of the amaranth pectin polysaccharides under conditions of mechano-acoustical action in rotary-pulsating apparatus were optimized. Extraction was performed with 0.25% solution of oxalic acid at hydro-modulus 1 : 15, the temperature did not exceed 50 °C. The pectin yield per oven-dry weight (ODW) of raw material was 9.5%. The isolated pectin polysaccharides were established to be a highly esterified pattern (esterification degree is 65%), high molecular (molecular mass 70000 standard units). Free carboxyl groups content is 10.1%, what is the evidence of a high complexity of the amaranth pectin polysaccharides.

Structural peculiarities of the target products were investigated by IR spectroscopy and ^{13}C NMR. IR spectrum of the extracted pattern contains characteristic bands, corresponding to structural fragments of pectin polysaccharides (OH, COOH, COOR, CO, pyranose cycle). At a partial acidic hydrolysis by hydrochloric acid (20 °C, 1 hour) a water-soluble pectin fragment is formed, which is galacturonan without any neutral sugars impurities, which form a branched region of pectin. ^{13}C -NMR spectrum confirms that the polysaccharide residues are α -1,4-D-galacturonan species. The spectrum involves seven signals of different intensity [C^1 99.84; C^2 67.9; C^3 67.9; C^4 78.2; C^5 70.4, C^6 (COOH) 172.8, C^6 (COOMe) 170.78], the locations of which correspond to those in the spectrum of α -1,4-D-galactopyranosyluronan (Fig. 1). Neutral sugars, such as arabinose, galactose, xylose, are observed in supernatant by thin-layer chromatography method after polygalacturonan precipitation.

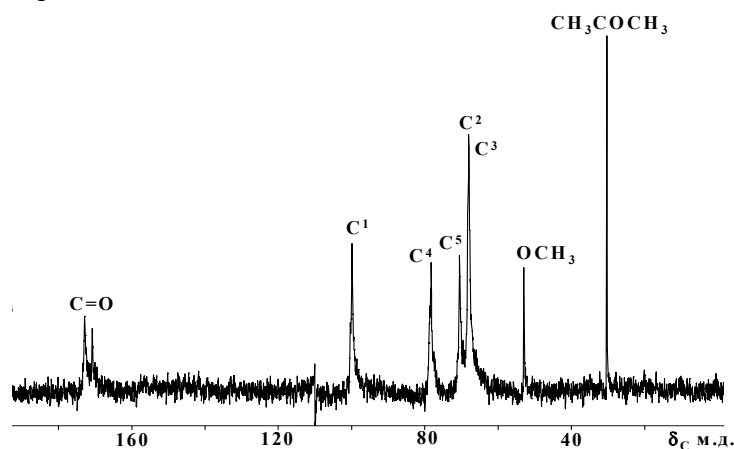


Figure 1. ^{13}C NMR spectrum fragment of pectin, obtained with extraction from amaranth.

The work is supported by the Program No. 5 of DCSM RAS.

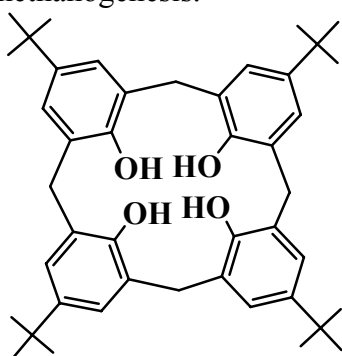
D.E. Belostotsky
V.F. Mironov
A.Z. Mindubaev
S.T. Minzanova
L.G. Mironova

INFLUENCE OF CALIXARENES ON SEWAGE SLUDGE METHANOGENESIS

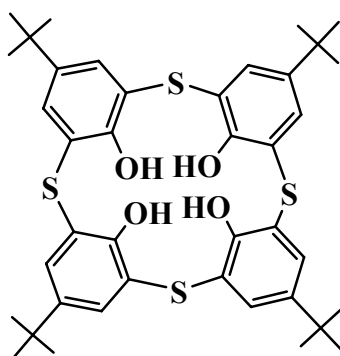
A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia
mironov@iopc.knc.ru

It's a well known fact that methanogenic microflora is highly affected by oxygen. It was thought to be interesting to estimate phenolic compounds which are used as antioxidants and free radicals catchers influence on sewage sludge methanogenesis, oxygen-centered radicals in particular. We supposed phenolic compounds to help methanogenesis process to a certain extent, reducing negative affect of oxygen. Ones of the most interesting among them are polyphenolic substances – calixarenes. Calixarenes show rather effective complexing properties towards heavy metals ions. From this point of view they could influence methanogenesis process by converting toxic metals into insoluble state.

This research show results of the using of *tert*-butyl-calix[4]arene (**1**) and *tert*-butyl-thiacalix[4]arene (**2**) in concentration of $4 \cdot 10^{-4}$ mol·l in sewage sludge methanogenesis process. These substances are poorly soluble, so we used a surfactant “triton X-100” that does not affect methanogenesis.



(1)



(2)

Anaerobic treatment was held in laboratory scale fermenters. The gas formation kinetics is shown on fig. 1, fig. 2. The influence on microflora was discovered to differ drastically. E.g., calixarene brings no harm. Specific gas yield turned out to be 22 ml per 1 ml of substrates, averaged (compared to 23 ml per 1 ml of substrates without synthetic substances).

The presence of thiocalixarene strongly inhibits methanogenesis process (specific gas yield was 1 ml per 1 ml of substrate, averaged). Numbers are averaged through three takes.

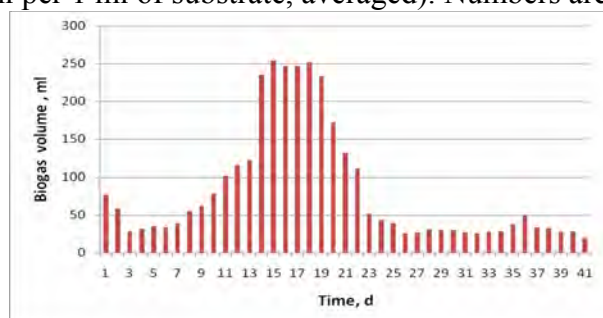


Fig. 1. Gas formation kinetics with calixarene added.

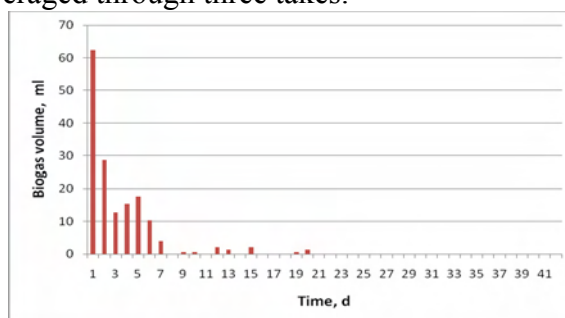


Fig. 2. Gas formation kinetics with thiocalixarene added.

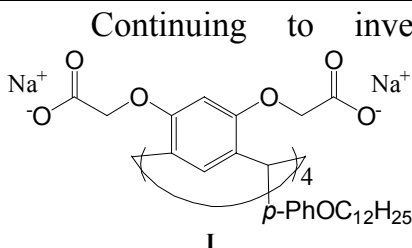
Thus, the calixarene type has a significant impact on its biological behavior towards methanogenes.

This research is supported by the Program N 3 of RAS.

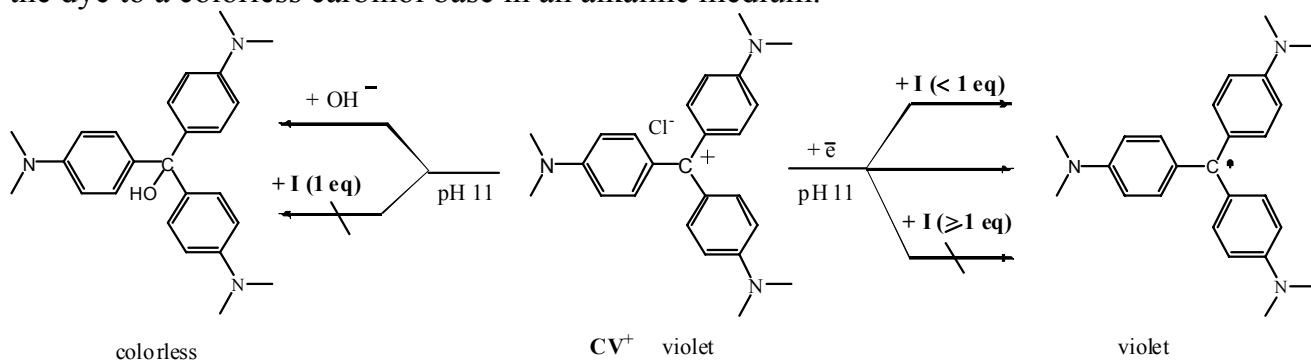
STABILIZATION OF CHARGED FORM OF CRYSTAL VIOLET AND REVERSIBLE BINDING IN THE REDOX PROCESSES WITH AGGREGATES OF ANIONIC MACROCYCLE IN AQUEOUS SOLUTIONS

D.A. Mironova
J.E. Morozova
V.V. Yanilkin
V.V. Syakaev
E.Kh. Kazakova
A.I. Konovalov

A.E. Arbuzov Institute of Organic and Physical Chemistry Russian Academy of Science, Kazan, Russia
mironovad@iopc.ru



Continuing to investigate the properties of chromogenic systems dye-calix[4]resorcinarene [1], the stabilization of the cationic form of crystal violet (CV^+) unstable in basic conditions and the reversible binding in the redox processes by the aggregates of amphiphilic calix[4]resorcinarene **I** in aqueous solution with pH 11 has been studied. Using the FT-PGSE NMR method it has been shown that the **I** forms a nanosize aggregates in water solutions (at $C_1 = 0.1 \text{ mM}$ $R_H = 4 \text{ nm}$, at $C_1 = 2 \text{ mM}$ $R_H = 5 \text{ nm}$). Spectrophotometrically and visually the stabilization of the colored form CV^+ in the presence of macrocycle **I** was observed. It was established that macrocycle interacts with the dye preventing the oxidation of the dye to a colorless carbinol base in an alkaline medium.



In the electrochemical experiments it was shown that the anionic calix[4]resorcinarene, binding effectively CV^+ inside aggregates, prevents the CV^+ reduction up to the ratio of macrocycle/dye 1:1. Excess of CV^+ (ratio of dye / macrocycle more than 1/1) binded on the surface of the aggregates of **I** and participates in the reversible redox process.

Thus, a system **I**/ CV^+ with one equivalent of the encapsulated CV^+ is obtained. A distinguishing feature of which is in the fact that an excess of CV^+ is not associated by a separate molecules, but by a nanosize aggregates that are able to the rapid reversible binding during the redox processes.

References:

- [1] Ju. Morozova, E. Kazakova, D. Mironova, Ya. Shalaeva, V. Syakaev, N. Makarova, A. Konovalov. Investigation of Tetramethylenesulfonated Calix[4]Resorcinarene Interactions with Azo-Dyes in Aqueous Solution // J. Phys. Chem. B. – 2010. – V.114. No. 41. – 13152–13158.

Financial support was provided by the grants of the RFBR, № 10-03-00266a, and Program 7 of the Division of Chemistry and Material Science RAS.

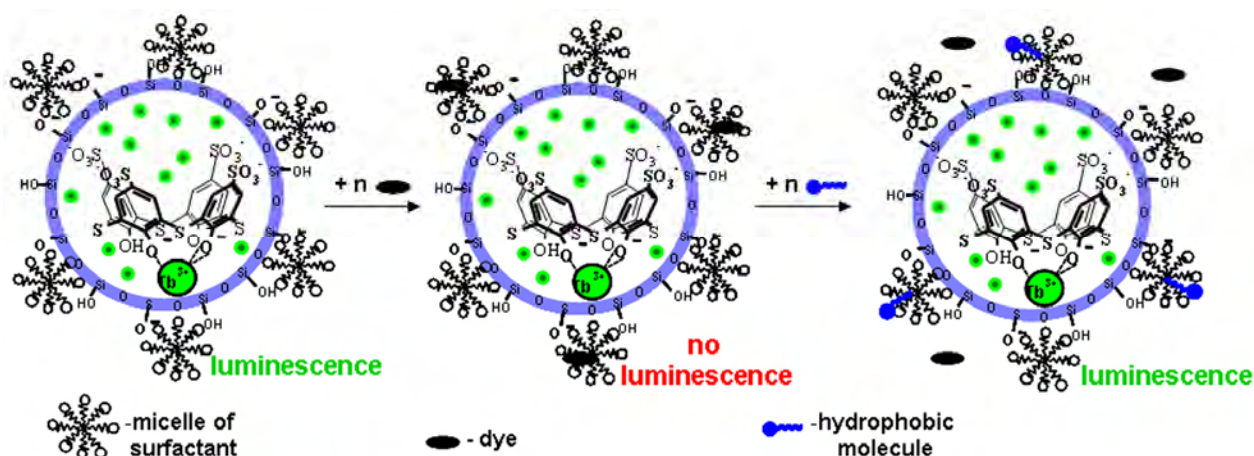
PHOTOPHYSICAL PROPERTIES OF SILICA NANOPARTICLES IN THE PRESENCE OF SURFACTANTS AND DYES

A.R. Mukhametshina¹
 O.D. Bochkova¹
 A.R. Mustafina¹
 V.V. Skripacheva¹
 V.A. Burilov²
 S.E. Soloveva¹
 A.I. Konovalov¹

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia
 2 - Kazan (Volga region) Federal University, A.M. Butlerov Chemical Institute, Kazan, Russia
 alsu_mukhamet@mail.ru

Luminescent lanthanide-doped silica nanoparticles are widely used in biochemical analyses as of biomarkers and biosensors. Lanthanides are characterized by narrow emissive bands in their spectra and a long life time of excited state that enables to distinguish the luminescent signal and a noise in biological systems. An including of lanthanides luminescent complexes in the silica matrix leads to increasing of a luminophor photostability, ensures a low toxicity, high stability and an intensive luminescence as compared with aqueous solutions of these complexes. The goal of this work is a studying of a correlation between photophysical properties of silica nanoparticles and their interactions with a substrate.

An approach was developed to determine cationic surfactant aggregation on the silica nanoparticles surface in the presence of the organic acid-base dyes on basis of the luminescent spectroscopy technique. A good correlation between emitting spectroscopy data and electrophoretic measurements is observed. Substrate responsive “smart” colloid system was obtained on the basis of dicationic surfactant modified luminescent silica nanoparticles in the presence of the organic acid-base dyes, which is capable to recognize hydrophobic anions in the micromolar concentration range. Regularities of luminescence intensity reestablishment were studied subject to the nature of hydrophobic anions.



We thank RFBR (projects N 09-03-12260 Ofi_M and 10-03-00352-a) for financial supporting.

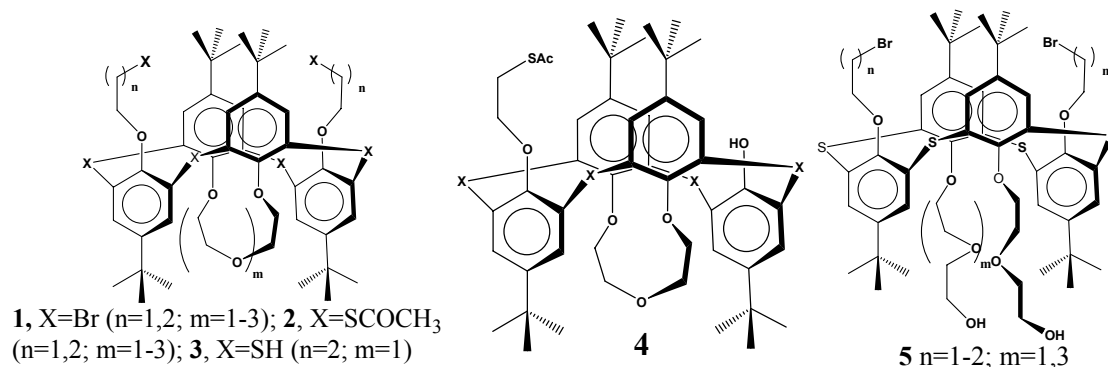
SYNTHESIS AND ALKALI EXTRACTION ABILITY OF MONOCROWN-SUBSTITUTED *P*-TERT-BUTYL(THIA)CALIX[4]ARENES

A.A. Muravev
S.E. Solovieva
S.K. Latipov
I.S. Antipin
A.I. Konovalov

Arbuzov Institute of Organic and Physical Chemistry, Laboratory of Calixarenes Chemistry, Kazan, Russia
anton_muravyov@rambler.ru

One of the promising fields of organic chemistry is the design, synthesis, and study of the properties of nanosized molecular systems, which incorporate structural blocks performing various functions, such as receptor and sensor. For example, the combination of calixarenes and crown-ether fragments in one molecule led to the formation of novel class of receptors, calixcrown ethers, which have an outstanding selectivity of recognition of alkali metal cations.

For this reason, herein, the synthetic route to the preparation of thiacalixmonocrown-ethers in *1,3-alternate* conformation was given., which have bromo- **1**, thioaceto- **2** (**4**), and mercapto- **3** groups. In order to prevent the formation of biscrown-ethers, we performed the distal substitution of hydroxyl groups of calixarene by ω -haloalcohols.



Currently new thiacalix[4]arene bromoderivatives **1** and **5** have been synthesized under Mitsunobu protocol and methods of preparation of known derivatives were improved. Bromine atoms were substituted for thioaceto-groups and, then, thiols with high yields. Finally, the alkali cation extracting ability was assessed for bromo-derivatives of thiacalixmonocrowns **1** using picrate extraction method. Structures of compounds were elucidated by 1D and 2D NMR spectroscopy, MALDI TOF MS, IR spectra, and elemental analysis.

The work was supported by the Russian Foundation for Basic Research (grant no. 11-03-00985).

**SPECTRAL PROPERTIES OF SUPRAMOLECULAR
COMPLEXES OF NAPHTHYLPYRIDINIUM
PERCHLORATE WITH CYCLODEXTRINS**

V.B. Nazarov¹
V.G. Avakyan²
S.P. Gromov²
T.G. Vershinnikova¹
M.V. Fomina²
A.I. Vedernikov²
M.V. Alfimov²

1 - Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia

2 - Photochemistry Center, Russian Academy of Sciences, Moscow, Russia

vnazarov@icp.ac.ru

Two forms of naphthylpyridine – unprotonated NP and protonated NPH^+ – have substantially various electron absorption and fluorescence spectra in water. The bands 291 and 375 nm are assigned to NP, those 315 and 480 nm belong to NPH^+ , respectively. These are used to determine a percentage of both forms at the pH change of solution. At pH=4.5 naphthylpyridinium perchlorate ($\text{NPH}^+\cdot\text{ClO}_4^-$) almost completely exists in protonated form. It means that equilibrium $\text{NP} + \text{HClO}_4 \rightleftharpoons \text{NPH}^+ + \text{ClO}_4^-$ is shifted to the right. At the addition of 2-hydroxypropyl- β -cyclodextrin (HP β CD) into solution, NP percentage is increased nearly by a factor two when compared to NPH^+ . This indicates a partial deprotonation (a shift of equilibrium to the left) of substrate included into the HP β CD cavity. The same spectral changes, although with less deprotonation effect, take place at the addition of completely methylated heptakis(2,3,6-tri-OMe)- β CD into $\text{NPH}^+\cdot\text{ClO}_4^-$ solution. It was estimated by NMR ^1H - titration that NP and NPH^+ form with HP β CD inclusion complexes of 1:1 composition. The PM3 quantum-chemical calculation [1] confirmed an opportunity of their formation. According to the calculation, deprotonation effect is due to that energetic difference between the right and left sides of equilibrium is lowered promoting the equilibrium shift to the left.

References:

1. S. P. Gromov, V. B. Nazarov, V. G. Avakyan, *et al.*, *J. Photochem. Photobiol., A*, 217 (2011) 87-99.

This work was supported by the RFBR and the Russian Academy of Sciences.

**SELF-ORGANIZATION OF
CETYLTRIMETHYLAMMONIUM BROMIDE ON
GRAPHITE/LIQUID INTERFACE**

**I.R. Nizameev
M.K. Kadirov
L.Ya. Zakharova**

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan
Scientific Center, Russian Academy of Sciences, Kazan, Russia
irek.rash@gmail.com

Cetyltrimethylammonium bromide morphology at the interface graphite/aqueous solution has been studied by AFM within the concentration range of 0.5-111 bulk critical micelle concentration (cmc = 0.9 mmol/l) and the temperature interval of 22-32°C. At this interface parallel strips of hemicylindrical surface micelles with a fixed value of period [1] are formed. Moreover, this period depends on certain parameters, and as found out, is manageable.

At concentrations below bulk critical micelle concentration parallel strips with a period of repeat 5-8.5 nm in the perpendicular direction to the strips are observed. But at concentrations above 10 cmc surface aggregates with period 12-15 nm were discovered. These aggregates are so-called precylinders, which are almost completely formed cylinders associated with the hydrophobic substrate by the tails of their constituent surfactant molecules. At intermediate concentrations (about 1-10 cmc) the hemicylinders are observed at low temperatures of the investigated temperature range, while precylinders occur at higher temperatures. Thus, it was found that there is abrupt increase in the period (called period jump) in a certain region of temperatures. This temperature range has a width of only a few degrees. Temperature of period jump growing from 26.5 to 28.5 °C with decreasing concentrations from 10 to 1 cmc.

The work gives a systematic description and explanation of the concentration and temperature dependence of the period of surface micellar strips of ionic surfactants at the hydrophobic substrate.

References:

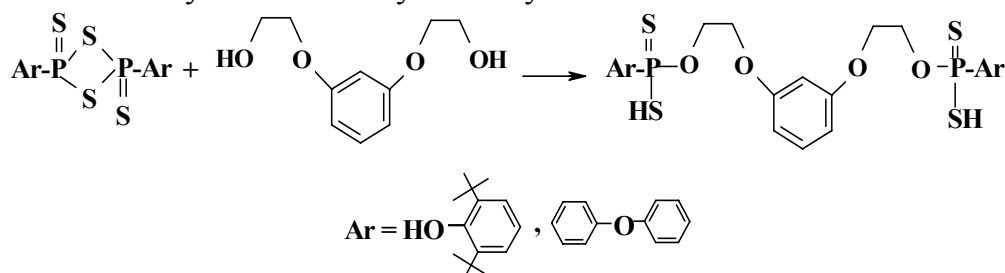
1. Manne, S.; Cleveland, J. P.; Gaub, H. E.; Stucky, G. D.; Hansma, P. K. *Langmuir* **1994**, *10*, 4409-4413

2-HYDROXYETHOXY DERIVATIVES OF RESORCINOL AND OF CALIX[4]RESORCINOLS IN THIOPHOSPHORILATION REACTIONS

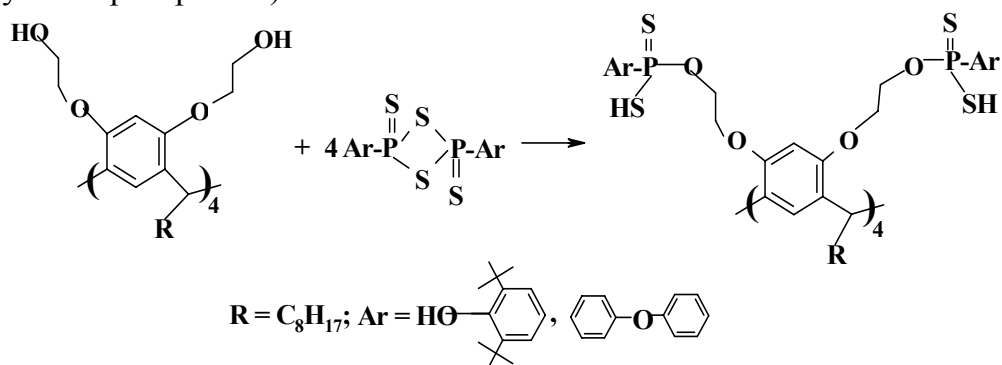
I.S. Nizamov¹
L.A. Almetkina¹
Ye.N. Nikitin¹
G.R. Sabirzyanova¹
A.R. Burilov²
M.A. Pudovik²

1 - Kazan (Volga region) Federal University, Kazan, Russia
2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia
isnizamov@mail.ru

Perdithiophosphonic acids are the new types of tetracoordinated phosphorus thioacids bearing a few dithiophosphoryl groups. We have recently obtained bisaryldithiophosphonic and perdithiophosphonic acids by the reactions of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with hydroxyphenols such as resorcinol and calix[4]resorcinols [1]. In continuation of our approach, we have tried to extend these insertion reactions into 2-hydroxyethoxy derivatives of resorcinol and of calix[4]resorcinols that contain aliphatic hydroxyl groups in contrast to aromatic ones in resorcinol and calix[4]resorcinols. It is considered of interest to compare the reactivity of resorcinol and 1,3-bis(2-hydroxyethoxy)benzene towards 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides. The reaction of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with 1,3-bis(2-hydroxyethoxy)benzene in benzene at room temperature has brought about the formation of O,O'-benzene-1,3-bis[ethoxy-2-(aryldithiophosphonic) acids. The reaction with 1,3-bis(2-hydroxyethoxy)benzene proceeds more smoothly than that of resorcinol. Bisaryldithiophosphonic acids obtained were transformed into the corresponding diammonium salts or cyclic trithioanhydrides by the treatment of iodine or MeCN.



We have now found that octa(2-hydroxyethoxy)tetraoctyl[1₄]metacyclophane react with 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides at 20-70 °C to give corresponding octakis(aryldithiophosphonic) acids.



References:

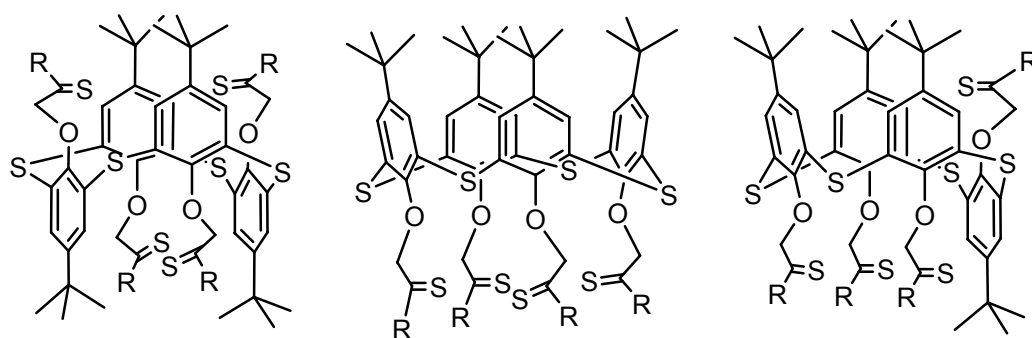
[1] Burilov A.R., Nizamov I.S., Almetkina L.A., Martianov Ye.M., Nikitin Ye.N., Pudovik M.A., Kononov A.I. *Phosphorus, Sulfur, and Silicon*. 2011. Vol. 186. P. 894-895.

SYNTHESIS, CHARACTERIZATION AND COMPLEXATION PROPERTIES OF TETRATHIOAMIDE AND TETRATHIOESTER DERIVATIVES OF *P*-*tert*-BUTYLTHIACALIX[4]ARENE IN DIFFERENT CONFORMATIONS

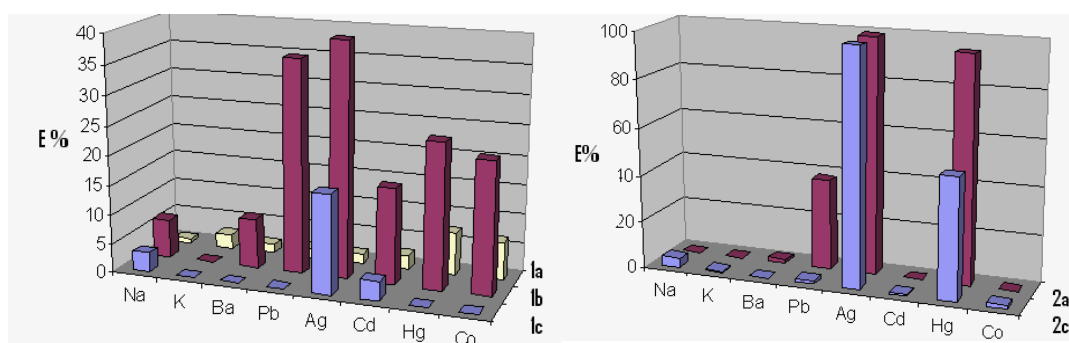
O.A. Omran

Majmaah University, College of Science in Zulfi, Saudi Arabia
omran2002@mailcity.com

Synthesis of *p-tert*-butylthiacalix[4]arene tetrathioesters and tetrathioamides in three different conformers (*cone*, *partial cone* and *1,3-alternate*). The new compounds' structures were investigated by IR, ^1H NMR, ^{13}C NMR and X-ray crystallography. Their complexation properties towards different metal cations (Na^+ , K^+ , Ba^{2+} , Ag^+ , Pb^{2+} , Co^{2+} , Hg^{2+} and Cd^{2+}) have been investigated by picrate extraction.



1a-c R = OC_2H_5 and **2a-b** , R = $\text{N}(\text{C}_2\text{H}_5)_2$



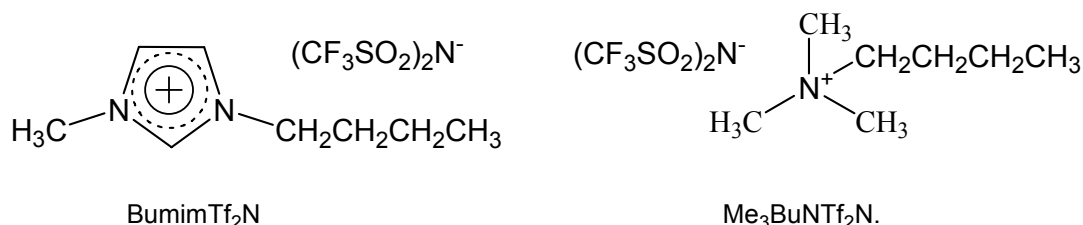
EXTRACTION SYSTEMS BASED ON IONIC LIQUIDS AND DERIVATIVES OF P-TERT-BUTYLTHIACALIX[4]ARENE

P.L. Padnya
I.I. Stoikov
I.S. Antipin

Kazan (Volga Region) Federal University, A.M. Butlerov Chemical Institute, Kazan, Russian Federation
padnya.ksu@gmail.com

Extraction - one of the most important methods of isolation and separation of compounds widely used in technology and analysis. It uses organic solvents that have a number of drawbacks: flammability, explosiveness, toxicity, etc.

Ionic liquids; molten organic salts which are liquid at room temperature may serve as interesting alternatives to classical solvents may. They are nonflammable, thermally stable and non-toxic; most ionic liquids are immiscible with water and practically almost all conduct electricity perfectly.



For the selective extraction of metal ions into ionic liquids, an appropriate complexing agent is required. In this respect, synthetic receptors such as calix- and thiocalixarenes that have proved themselves in the solvent extraction of nuclear waste are of great interest. Thus, this study is aimed at the synthesis and structure determination of new thiocalix[4]arene derivatives containing charged fragments at the lower rim. To increase the solubility of the synthesized thiocalix[4]arenes in ionic liquids, a technique for introducing charged fragments into their structure has been developed.

This work was supported by the Federal Program "Research and scientific-pedagogical cadres Innovative Russia" for 2009 - 2013 years (№ p1107 from 26 August 2009), the Russian Foundation for Basic Research (09-03-00426-a) and the grants program of the President of the Russian Federation for state support of young Russian scientists - Doctors of Science (MD-2747.2010.3).

**HOST-GUEST COMPLEXES OF FLUORESCENT
DYES WITH CUCURBITURILS**

N.Kh. Petrov

D.A. Ivanov

S.P. Gromov

Photochemistry Center, RAS, Moscow, Russia

npetrov@photonics.ru

Photophysical properties of aqueous solutions of 3,3'-diethyl-thiacarbocyanine iodide (dye **1**) and of 4-[(*E*)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethylpyridinium perchlorate, styryl dye (dye **2**), were studied in the presence of cucurbit[n]urils (CB[7]) by means of fluorescence spectroscopy.

The encapsulation of dye **1** by CB[7] (1:1 complexes) lead to changes in absorption spectrum and in a 5-fold increase of its fluorescence quantum yield. The binding constant of 1:1 complexes of dye **1** with CB7 has been determined to be $3 \cdot 10^4 \text{ M}^{-1}$ [1].

The encapsulation of dye **2** in CB[7] results in shift of maximum of absorption spectrum to long-wavelengths from 383 nm to 406 nm and in a 5-fold increase in the fluorescence of dye **2** upon increasing the CB7 concentration from 0 to $1.6 \cdot 10^{-5} \text{ M}$ [2]. The dependence of the fluorescence intensity of solution on the concentration of CB[7] allows the estimation of the 1:1 complex binding constant, that is about 10^6 M^{-1} . The average fluorescence lifetime increases from 145 to 352 ps upon the addition of CB[7]. The comparison of quantum-chemical calculations with experimental data confirms that in the host cavity dye **2** rotates as a whole with CB[7].

References:

1. N.Kh. Petrov, D.A. Ivanov, D.V. Golubkov, S.P. Gromov, M.V. Alfimov, Chem. Phys. Letters 2009, 480, 96–99.
2. D.A. Ivanov, N.Kh. Petrov, E. A. Nikitina, M.V. Basilevsky, A.I. Vedernikov, S.P. Gromov, and M.V. Alfimov. J. Phys. Chem. A 2011, 115, 4505–4510.

Support from the Russian Foundation for Basic Research and the Russian Academy of Sciences is gratefully acknowledged.

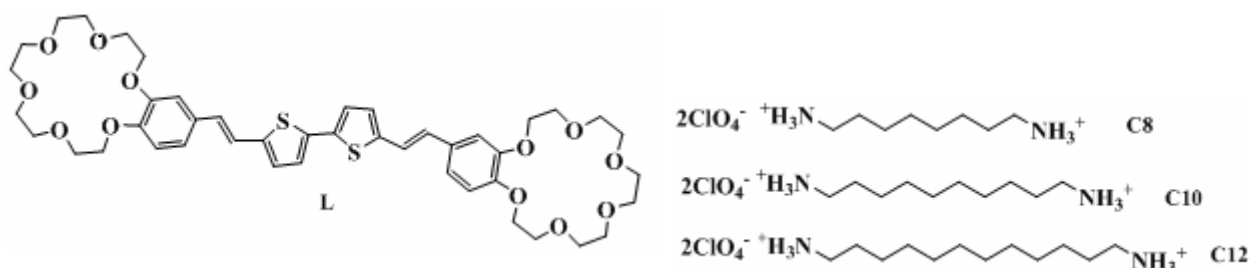
COMPLEX FORMATION OF 18-CROWN-6-CONTAINING BITHIOPHENE WITH DIAMMONIUM CATIONS

Zh.S. Petrova¹
 E.V. Lukovskaya¹
 O.A. Fedorova¹
 Yu.V. Fedorov²
 A.A. Bobileva¹
 A.V. Anisimov¹

1 - Moscow State University, Chemistry Department, Moscow, Russia
 2 - N.A. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, Russia
 zhanna.petrova.msu@gmail.com

Thiophenes and benzothiazoles presently are actively investigated among the range of crown ether compounds. Ionophoric crown ethers are capable to modify significantly electronic and optical characteristics of an entire coupled system, which allows using them as optical sensors for metal cations and ammonia ions. The latter offer a wide range of opportunities for practical applications, for example in fine tuning of supramolecules photochemical properties, hence the assortment of ammonium compounds is much larger in comparison with inorganic substrates.

In the present study, stoichiometry and complexation constants of thiophene-containing crownated ligand (**L**) with diammonium salts containing 8, 10 and 12 methylene groups were determined and possibility of their spontaneous organization into supramolecular ensembles was investigated.



The logarithms of complexation constants of the ligand **L** with diammonium salt cations determined by means of spectrophotometric titration amounted to 5.16 ± 1.55 , 5.36 ± 0.145 , and 5.10 ± 0.108 respectively. Formation of 1:1 complexes was confirmed with by means of mass spectroscopy with electrospray ionization (ESI). The NMR spectrum of the complex does not contain signals of the protons from free ligand. During investigation of complexation by means of ^1H NMR spectroscopy it was identified that the signals from the protons of methylene bridges of diammonium salts shift towards stronger fields by a substantial amount (~ 0.2 - 0.25 ppm) on complexation with the ligand. Such phenomena can be explained by anisotropic effects occurring when methylene chain of diammonium is arranged along the chromophoric molecule of the ligand, and equilibrium between monocomplexes exists in the solution of diammonium salt and ligand, where one crown ether fragment after the other bind ammonium groups. Also the formation of complex composition 2:2 was studied.

The work was financially supported by RFBR grant № 09-03-00550.

SILICA NANOPARTICLES WITH Eu (III) - CENTERED LUMINESCENCE

M.V. Pinus¹
S.V. Fedorenko¹
V.A. Burilov²
A.R. Mustafina¹
A.I. Konovalov¹

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia

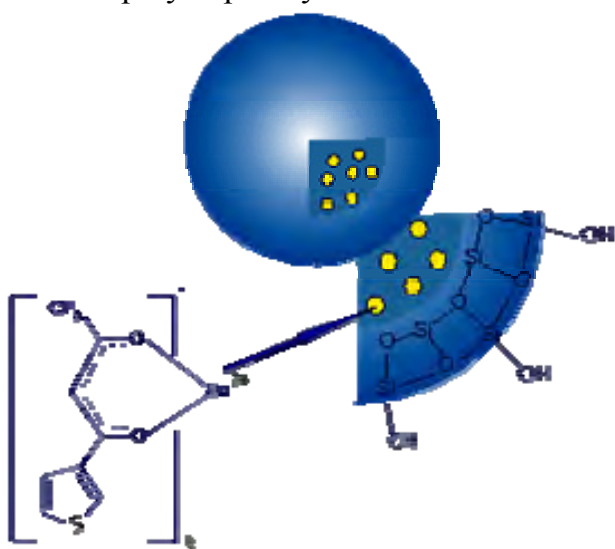
2 - Kazan (Volga region) Federal University, A.M. Butlerov Chemical Institute, Kazan, Russia

maripinus@gmail.com

Luminescent probes for biomolecular analysis and recognition are of great importance and have been widely applied in bioanalysis, medicine and biotechnology. The development of various lanthanide-doped fluorescent silica nanoparticles and novel bioanalytical techniques has greatly improved the detection and recognition of biotarget. These efforts are focused to enhance the sensitivity and stability in detecting chemical and biological species. The other possible application of fluorescent silica nanoparticles is the development of three-dimensional architectures as a basis of photonic crystals.

The fluorescent silica nanoparticles of different sizes (from 280 nm to 480 nm) with europium(III) thenoyltrifluoroacetone complex and phosphine oxide adducts as dopants were prepared. Their synthesis is based on the use of Stober procedure. The analysis of the size and polydispersity of the obtained nanoparticles reveals that the structure and amount

of luminophore included inside the polymer matrix greatly affects the size and size distribution of the obtained nanoparticles. The photophysical properties of the silica particles in aqueous solutions were studied by the fluorimetry method. The location of dye molecules in the silica matrix was investigated by the quenching measurements.



We thank RFBR (projects N 10-03-00352-a) for financial supporting.

**PHOTOPHYSICS AND PHOTOCHEMISTRY OF
BISPHENOLS - β -CYCLODEXTRIN INCLUSION
COMPLEXES IN AQUEOUS SOLUTIONS**

I.P. Pozdnyakov¹
V.A. Salomatova¹
V.F. Plyusnin¹
N.M. Bazhin¹
F. Wu²
N. Deng²

1 - Institute of Chemical Kinetics and Combustion, Novosibirsk,
Russia

2 - Department of Environmental Science, Wuhan University, P. R.
China, Hubei

pozdneyak@kinetics.nsc.ru

Bisphenols (BPs) are important industrial chemicals, being widely used as the monomers for production of polycarbonate plastics and epoxy resins. BPs are also believed to be a kind of suspected endocrine disruptors and highly toxic chemical compounds so the development of methods of water purification from BPs is urgently needed. Cyclodextrin complexation has recently emerged as a new catalytic technology complement to the photochemical treatment approaches for removal contamination in solution and in solid state.

In this work nanosecond laser flash photolysis (266 nm, 6 ns, Nd:YAG laser) and time-resolved fluorescence (280 nm, 800 ps, EPLED-280) techniques were used to study mechanistic aspects of aqueous photochemistry of two PBs - bis(4-hydroxyphenyl)ethane (BPE) and 4,4-Bis(4-hydroxyphenyl)valeric acid (DPA) as well as their inclusion complexes (1:1) with β -CD. For all systems the primary photochemical process was found to be photoionization with formation hydrated electron – phenoxyl radical pair. Optical properties and main decay channels of these species were determined.

Inclusion of BPs in cyclodextrin cavity leads to great increase of photoionization and fluorescence quantum yield as well as fluorescence lifetime due to decreasing of relaxation processes in the singlet excited state of complexed BPs. Enhancement of BPs photodegradation in inclusion complexes with β -CD could have a potential application to the technological processes of water purification.

The work was supported by the RFBR (grants 09-03-00330, 11-03-00268) and the Program of Integration Projects of Siberian Branch of Russian Academy of Sciences 2009-2011 (grant 70).

SYNTHESIS OF DISUBSTITUTED BY MERCAPTO GROUPS CALIX[4]ARENES AND THEIR CONJUGATES WITH IRON(II) TRIS-DIOXIMATES

T.A. Rovnova¹
S.K. Latipov¹
Y.Z. Voloshin²
S.E. Solovieva¹
I.S. Antipin¹
A.I. Konovalov¹

1 - Arbuzov Institute of Organic and Physical Chemistry, Laboratory of Calixarene Chemistry, Kazan, Russia

2 - Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia

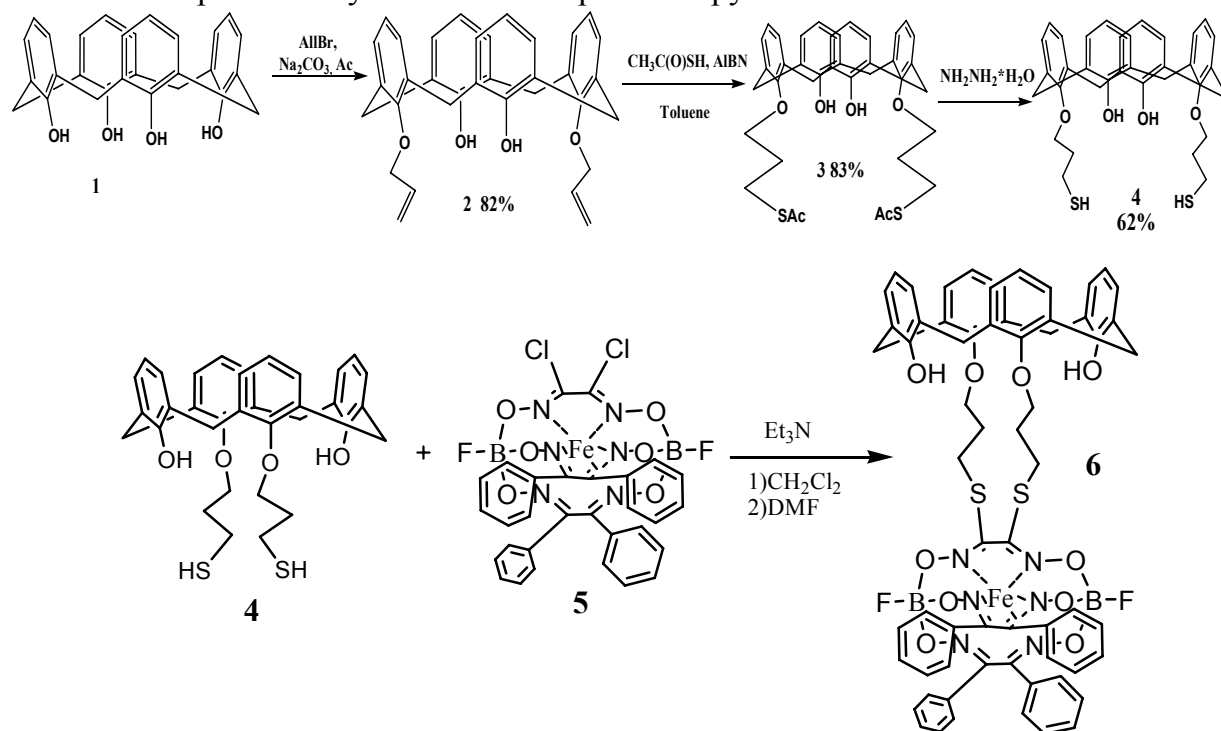
lekksa330@list.ru

Calix[4]arenes (CAs) are easily obtained in one step and represent convenient molecular frameworks for the design of three-dimensional structures with various spatial arrangements of functional groups on their basis. Calixarenes with narrow rim mercapto-substituents are potential precursors for further modification with various functional groups and can be immobilized on a solid surface, giving rise to sensors for heavy metal ions.

Tris-dioximate clathrochelates are the macrobicyclic compounds with a metal ion encapsulated in a three-dimensional macropolycyclic ligand cavity. These complexes demonstrate unique thermodynamic and kinetic stabilities and have unusual redox and photochemical properties.

Combination of two macrocyclic frameworks mentioned above makes it possible to design nanosized molecular structures, which can represent interest for the creation of nanostructural materials for sensors. Earlier, we have synthesized and characterized the conjugates of unsubstituted parent CA and clathrochelate.

Herein, we report on the successful synthesis of calixarene-clathrochelate conjugates **6** linked by sulfur atoms. In order to obtain them, we performed the consecutive synthesis of terminal disubstituted allyl- **2**; thioaceto-**3**; and mercapto-**4** calixarenes, which was further reacted with iron(II) tris-dioximate **5**. The compounds obtained were characterized by MALDI TOF spectrometry and ¹H NMR spectroscopy.



The work was supported by RFBR grant no. 11-03-00985.

**APPLICATION OF *TERT*-BUTYLCALIX[6]ARENE
POLYMORPHIC TRANSITIONS FOR ORGANIC
COMPOUNDS MIXTURES ANALYSIS**

**G.D. Safina
M.A. Ziganshin
V.V. Gorbachuk**

Kazan (Volga region) Federal University, A.M. Butlerov Chemical
Institute, Kazan, Russia
safina_goulnaz@mail.ru

Application of supramolecular receptors in determination of mixed guest is a difficult task for scientists dealing with vapor recognition. Using guest responsible structural changes of calixarenes and their clathrates is a perspective route to solve this problem.

The aim of this work is development of system for quantitative analysis of organic compounds mixtures using polymorph transitions of *tert*-butylcalix[6]arene.

It was observed that decomposition of *tert*-butylcalix[6]arene clathrates with some guests carry out throw a metastable guest-free phase formation upon elimination of guests from their clathrates. The metastable phase formation is attended by a large exothermic DSC peak without mass loss above the temperature range of clathrate on TG-DSC experiment. Decomposition curves of clathrates of this host with second group of guests have no endothermic peak at all temperature range. That's mean no metastable phase formation is take place. It was found that the polymorphic structures formation of *tert*-butylcalix[6]arene clathrates with organic compounds vapors can be used to determine the content of components in binary mixtures of guests from these two groups. Dependences of thermal effects of clathrates decomposition on the content of components in benzene/c-hexane, chloroform/tetrachloromethane mixtures were established by simultaneous TG/DSC/MS analysis.

This work was supported by program RFBR (№ 11-03-01215-a) and State contract with the Ministry of Education and Science of RF (№ 14.740.11.0377).

AQUEOUS PHOTOCHEMISTRY OF SUPRAMOLECULAR COMPLEX BETWEEN DIPHENOLIC ACID AND β -CYCLODEXTRIN

V. Salomatova¹
I. Pozdnyakov¹
V. Plyusnin¹
F. Wu²
N. Deng²
N. Bazhin¹

1 - Institute of Chemical Kinetics and Combustion, Novosibirsk,
Russia
2 - Department of Environmental Science, Wuhan University, P. R.
China, Hubei
salomatova@kinetics.nsc.ru

Diphenolic acid (4,4'-bis(4-hydroxyphenyl)valeric acid, DPA) is industrially important chemical, which is widely used in production of alkyd resin, phenol-formaldehyde resins, printing-inks, adhesives and coatings. DPA is a close structural analog of widely known endocrine disruptor – bisphenol A and so DPA potentially can exhibit estrogenic activity and toxicity in environment. The development of photochemistry methods of water purification from industrial pollutants is believed to have a great potential.

In the previous work authors observed that DPA forms stable 1:1 inclusion “host – guest” complex with β -cyclodextrin (β -CD) molecule and such complexation leads to increase of quantum efficiency of DPA UV - photodegradation.

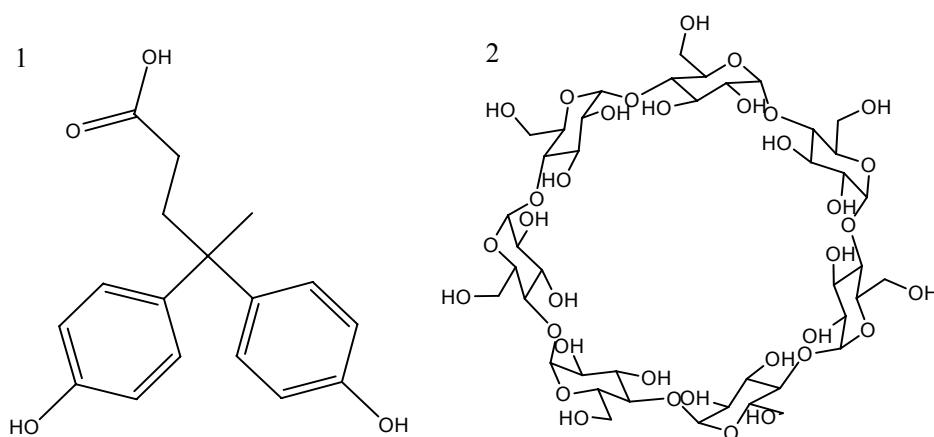


Figure 1. Chemical structures of (1) DPA and (2) β -CD

In this work time-resolved fluorescence (280 nm, 800 ps, EPLED-280) and nanosecond laser flash photolysis (266 nm, 6 ns, Nd:YAG laser) techniques were used to study photophysics and photochemistry of DPA and its inclusion complex with β -CD. For both systems the primary photochemical process was found to be photoionization with formation hydrated electron – phenoxyl radical pair. Inclusion of DPA in cyclodextrin cavity leads to great increase of photoionization (from 0.01 to 0.04) and fluorescence quantum yield (from 0.01 to 0.13) as well as fluorescence lifetime of complexed DPA due to decreasing of the quenching rate of the singlet excited state by solvent molecules.

The work was supported by the RFBR (grants 09-03-00330, 11-03-00268) and the Program of Integration Projects of Siberian Branch of Russian Academy of Sciences 2009-2011 (grant 70).

PROPERTIES OF NANOSIZED FILMS ON THE BASIS OF AMPHIPHILIC MOLECULES OF XANTHENE DYE AND POLY[CARBOXYETHYL- 3(DODECYL) AMINOCROTONATE]

E.V. Seliverstova¹
N.Kh. Ibrayev¹
S.E. Kudaibergenov²

1 - Karaganda State University named after E.A. Buketov, Institute of
Molecular Nanophotonics, Karaganda, Kazakhstan
2 - Institute of Polymer Materials and Technology, Almaty,
Kazakhstan
genia_sv@mail.ru

The properties of the mixed monolayers consisting of amphiphilic molecules of aminocrotonate (poly[carboxyethyl-3(dodecyl) aminocrotonate]) and decyl ether of eosin on the water-air interface were investigated.

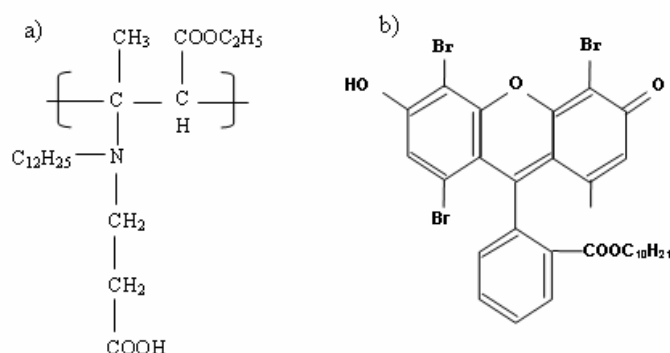


Figure. Structural formula of aminocrotonate (a), eosin decyl ether (b)

The investigated monolayers were formed by spreading onto subphase surface in Langmuir-Blodgett through. The finding data from measurements, the analysis of isotherms of surface pressure – the average area per a molecule and molecules geometry calculation have allowed to evaluate orientation of molecules in dyes monolayer and in the mixed films with molecules of aminocrotonate. It is ascertained that aminocrotonate forms pristine closely packed monolayer with the orientation of hydrophobic fragment of monomer unit perpendicularly to water phase. The dye isotherm is typical for liquid state. Addition of aminocrotonate leads to more dense packing of dye molecules in a monolayer. Is shown, that the structure of films depends and on initial spatial geometry of dyes molecules.

Influence of dye concentration on absorption and fluorescence spectra of mixed solid films prepared by Langmuir-Blodgett technique is investigated. Absorption and fluorescence spectra of samples show an dimers absorption shoulder, and the increase of dye concentration leads to growth of films optical density and "red" shift of spectrum maximum.

FLUORESCENT SENSOR PROPERTIES OF CROWN-CONTAINING 4-PYRAZOLINIL-1,8-NAPHTHALIMIDE DERIVATIVES

A.N. Sergeeva
P.A. Panchenko
O.A. Fedorova
Yu.V. Fedorov

INEOS RAS, Moscow, Russia
antonina@ineos.ac.ru

During the last years much attention has been paid to the design, synthesis and characterization of photochemical molecular devices, which combine chromophore signaling moieties and receptor groups capable of binding of molecules and ions. These devices can find applications in many disciplines such as clinical and environmental sciences, analytical chemistry and biochemistry. In the present paper we report synthesis and sensor properties of two novel crown containing 4-pyrazolinylnaphthalimide derivatives (**1a**, **1b**).

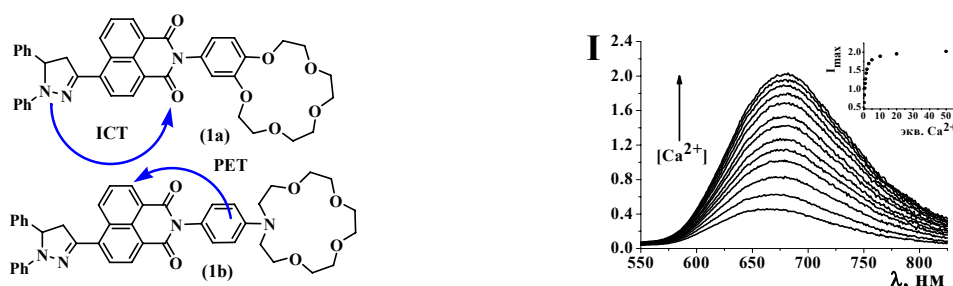


Fig. 1. Chemical structure of naphthalimides (**1a**, **1b**). The changes in fluorescence of (**1b**) in the presence of a graduated amount of Ca(ClO₄)₂ in CH₃CN solution. C_L = 2·10⁻³ mol·l⁻¹, λ_{ex} = 490 nm. The inset shows fluorescence intensity at 664 nm versus equivalents of Ca²⁺.

Complex formation of (**1a** – **b**) with alkaline-earth metal cations in acetonitrile solutions was observed by absorption and emission spectroscopy. It was shown that the binding of Mg²⁺ cations with compound (**1a**) containing *N*-benzo-15-crown-5-ether substituent resulted in fluorescence quenching. Compound (**1b**) containing azacrown ether moiety in *N*-aryl fragment forms strong complex with Ca²⁺ cations, which leads to increase the fluorescence quantum yield (fig. 1). The observed spectral effects were attributed to the occurrence of ICT and PET processes.

Acknowledgments to RFBR program (09-03-00041, 09-03-93116), GDRI "SUPRACHEM" and Russian Ministry of Education and Sciences for financial support.

G.R. Shaikhutdinova

I.P. Romanova

A.V. Bogdanov

L.I. Musin

M.I. Valitov

I.P. Nizamiev

D.G. Yakhvarov

V.F. Mironov

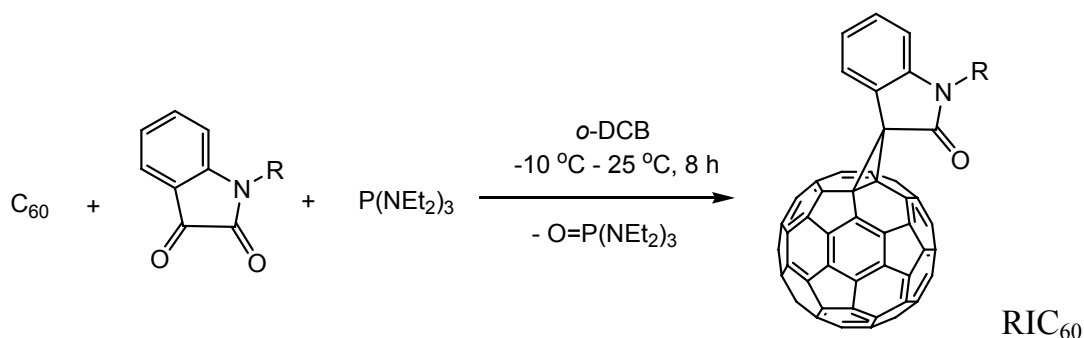
O.G. Sinyashin

INDOLINONE SUBSTITUTED METHANOFULLERENES - A NEW ACCEPTORS FOR BULK HETEROJUNCTION SOLAR CELLS

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan
Scientific Centre of Russian Academy of Sciences, Kazan, Russia
gshaikhu@iopc.ru

Organic solar cells, as alternatives to conventional inorganic photovoltaic devices based on Si, have a number of potential advantages, such as lightweight, flexibility and low cost fabrication of large areas. At the same time the cells efficiency has reached 5%–7%, which is low for commercial power generation. It is considered that one of the causes of slow progress in the organic photovoltaics is small amount of fullerene derivatives, which were investigated as an electron acceptor in the photoactive layer.

We report first organic solar cells based on the new type of the methanofullerenes, namely indolinone substituted methanofullerenes. These compounds were obtained by the reaction in a three-component system fullerene - isatin - tris(diethylamino)phosphine. In contrast to synthetic reaction of known methanofullerenes, the three-component system doesn't require heat or irradiation and leads only to the formation of 6,6-closed monoadducts. The yield of title compounds is about 50% in regard to the amount of fullerene even in not optimized conditions. The indolinone substituted methanofullerenes are attractive because addend strikes a blow for light harvesting by methanofullerene molecule alongside with the fullerene sphere.



The first organic solar cells based on the indolinone substituted methanofullerenes obtained improved power conversion at 2 %.

The work is supported by the Russian foundation for the Basic Research (grants 09-03-00259-a) and by the Program No. 6 of the Division of Chemistry and Material Sciences of Russian Academy of Sciences.

**THE RECEPTOR PROPERTIES OF DENSE AND
POROUS PHASES OF
TERT-BUTYLCALIX[6]ARENE TOWARD VOLATILE
ORGANIC COMPOUNDS AND GASES**

R.I. Sinichkina
G.D. Safina
M.A. Ziganshin

A.M. Butlerov Chemical Institute, Kazan Federal University, Kazan,
Russia
rada.sin@yandex.ru

The application of calixarenes porous phase for binding and transportation gaseous compounds is a perspective way of research of this type of macrocyclic receptors.

The aim of this work is to study the receptor properties of dense (α -phase) and porous (β 0-phase) polymorphs of *tert*-butylcalix[6]arene toward vaporous organic compounds and gases.

The products of saturation of both polymorphs with *n*-butane, *n*-pentane, *n*-hexane were studied by simultaneous TG/DSC/MS analysis.

The porous phase of calixarene was prepared by heating of saturated clathrates of *tert*-butylcalix[6]arene with benzene and tetrachloromethane in vacuum up to 150°C for 1 hour.

Table 1. The composition of inclusion compounds of *tert*-butylcalix[6]arene and alkanes, mol guest per mol host.

Guest	α -phase	β 0-phase obtained from the clathrate with CCl ₄	β 0-phase obtained from the clathrate with C ₆ H ₆
<i>n</i> -butane	0,09	0,82	0,90
<i>n</i> -pentane	1,09	0,89	1,15
<i>n</i> -hexane	0,01	0,94	1,12

It was found that the porous β 0-phases of calixarene form stable clathrates with all the guests studied. The dense α -phase of calixarene bound only *n*-pentane, table 1. It was also found, that the porous β 0-phase of calixarene obtained from the clathrate with C₆H₆ possesses larger capability toward alkanes than that of obtained from the clathrate with CCl₄, table 1.

Present work was supported by program RFBR (№ 11-03-01215) and State contract with the Ministry of Education and Science of RF (№ 14.740.11.0377).

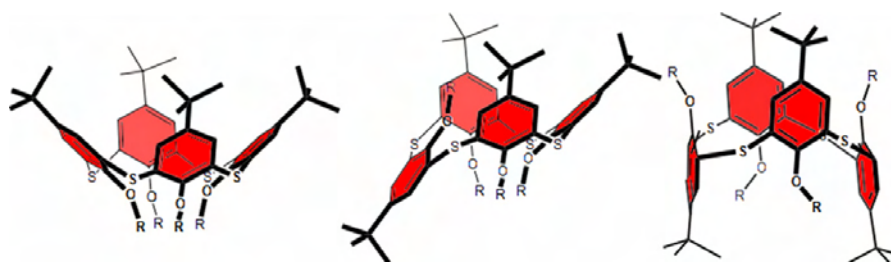
DESIGN OF NOVEL P-TERT-BUTYLTHIACALIX[4]ARENE DERIVATIVES FUNCTIONALIZED WITH MULTIPLE SPATIALLY ORGANIZED HYDROXYL AND AMIDE FRAGMENT

R.R. Sitdikov
I.I. Stoikov
I.S. Antipin

Kazan (Volga Region) Federal University, A.M. Butlerov Chemical
Institute, Kazan, Russia
Ruzal.Sitdikov@ksu.ru

Specific recognition in biological systems (i.e. peptides, DNA) is often achieved by formation of multiple hydrogen bonds with target substrate according to "hand and glove" principle. Groups such as amide and hydroxyl are perfect proton donor moieties. Spatial arrangement of such groups on the lower rim of macrocycle may allow the creation of highly specific receptors, capable of forming multiple hydrogen bonds with proton acceptor groups of target substrate.

The macrocyclic platform of *p*-tert-butylthiacalix[4]arene has attracted attention due to the ease of synthesis of its stereoisomers with tetrasubstituted receptors. Varying macrocycle's configuration leads to significant changes in geometry of binding sites and number of functional groups which are capable of interacting with target substrate. We have introduced 1',1'-dimethyl-2'-hydroxy-, 1'-ethyl-1'-hydroxymethyl-2'-hydroxyethylamido-carbonyl, dopamide and glucosamide fragments as preorganized proton donor moieties.



Compounds were characterized by a variety of physical methods: NMR ^1H , ^{13}C , IR- and X-Ray spectroscopy, MALDI-TOF mass-spectrometry and dynamic light scattering, complexation with anions was studied by UV-vis method.

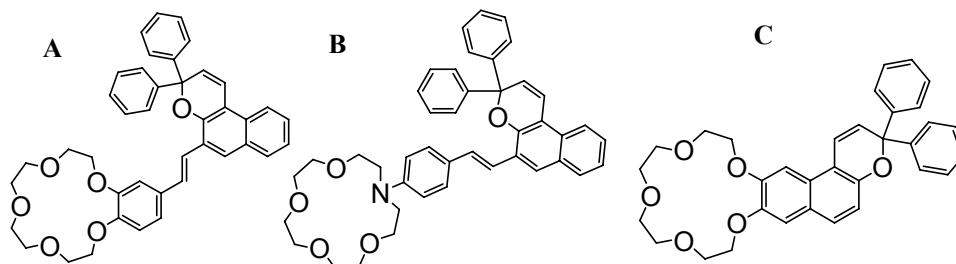
This work was supported by the Federal Program "Research and scientific-pedagogical cadres Innovative Russia" for 2009 - 2013 years (№ p1107 from 26 August 2009), the Russian Foundation for Basic Research (09-03-00426-a) and the grants program of the President of the Russian Federation for state support of young Russian scientists - doctors of science (MD-2747.2010.3).

CATION COMPLEXATION, PHOTOCHROMISM AND FLUORESCENCE OF CROWN-CONTAINING NAPHTHOPYRANS

A.B. Smolentsev¹
 E.M. Glebov¹
 V.V. Korolev¹
 S.V. Paramonov²
 O.A. Fedorova²

1 - Institute of Chemical Kinetics and Combustion SB RAS,
 Novosibirsk, Russia
 2 - Nesmeyanov Institute of Organoelement Compounds RAS,
 Moscow, Russia
 s_art@ngs.ru

Photochromism is defined as a reversible photoinduced phenomenon in which a photosensitive compound is converted to another isomer having a different absorption spectrum. Photochromic molecules containing macrocyclic moiety have attracted much interest in molecular chemistry as components of functional materials. Examples of potential applications of these compounds include: photoswitching transport through membranes, optical information storage, photoswitching extraction of metal cations.



Scheme 1

Crown-containing naphthopyrans (chromenes) A, B, C (scheme 1) and their crownless analogues were used in the work. All studied compounds, upon UV irradiation, yield open colored forms. Then in the course of dark reaction open form of chromenes turns into colorless closed form. Moreover, naphthopyrans A and B, upon UV irradiation, undergo irreversible geometrical isomerisation.

All studied crown-containing compounds form host-guest complexes with Mg^{2+} , and Ba^{2+} cations. The presence of metal cations in the solution leads to partial destabilization of the photoinduced form of C and consequently decreases its lifetime. Nevertheless, complexation doesn't effect on the spectroscopic and kinetic properties of the colored forms of A and B.

Naphthopyran B fluoresces with maxima at 530 nm. It's remarkable that only trans-isomer of B is fluorescent, while cis-isomer is not. For this reason trans-cis isomerisation of B leads to disappearance of fluoresce. The presence of metal cations in the solution also leads to significant decrease of fluorescence quantum yield of B.

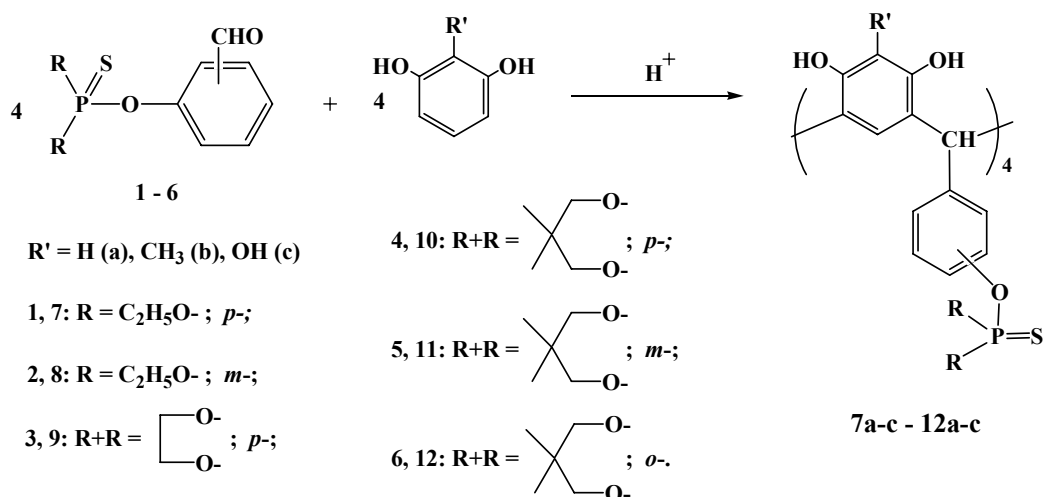
This work was supported by the Russian Foundation of Basic Research (grants №11-03-00268 and №09-03-00283).

SYNTHESIS AND REDOX PROPERTIES OF TRANSITION METAL COMPLEXES ON THE BASIS OF NEW CALIX[4]RESORCINOLS WITH THIOPHOSPHORYL-CONTAINING FRAGMENTS

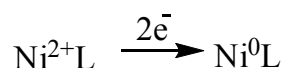
V.I. Sokolova¹
V.V. Khrisanforova¹
I.R. Knyazeva¹
T.V. Gryaznova¹
A.R. Burilov¹
Yu.G. Budnikova¹
M.A. Pudovik¹
W.D. Habicher²

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia
2 - Dresden University of Technology, Institute of Organic Chemistry, Dresden, Germany
vict.sokolova@yandex.ru

The research of new catalytic systems which combine the complex-forming properties and ability to the molecular recognition in the one molecule is the important problem in present time. Calix[4]resorcinols are unique ligands, containing the few coordination sites and having wide possibilities for the selective modification of their upper and low rim with various functional groups. We synthesized the new type of calix[4]resorcinols **7a-c** – **12a-c** with four thiophosphoryl-containing groups inserted to aromatic substituents located in methylenide bridges of the molecule by the condensation of thiophosphorylated aldehydes **1** – **6** with resorcinol and its derivatives in acidic media. The conformation of these compounds was determined by NMR methods and a single crystal X-ray diffraction study. In particular, the conformation of calixarenes **7a-c** – **9 a-c** was found to be “*flattened partial cone*” or “*chair*”, molecules **10a-c** – **12a-c** can exist in “*cone*” and “*chair*” conformations.



We obtained the new submicro-sized complexes of Ni in the low oxidation state on the basis of thiophosphorylated calix[4]resorcinols **7a-c** – **12a-c** (L) as a result of the irreversible electrochemical reduction:



The size of obtained complexes was estimated by the methods of DLS and AFM.

This work was supported by Russian Foundation for Fundamental Research (grant № 11-03-00416-a).

SUPRAMOLECULAR POLYMER P LIPASE SYSTEMS : STRUCTURE AND FUNCTION

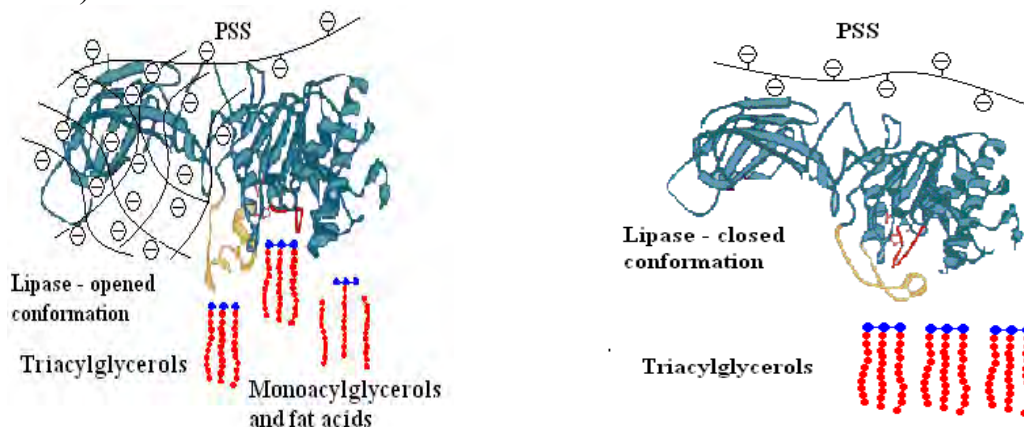
D.O. Solovyeva
S.Yu. Zaitsev

Moscow State Academy of Veterinary Medicine and Biotechnology,
the Organic and Biological Chemistry Department, Moscow, Russia
d.solovieva@mail.ru

Supramolecular biochemical systems (SBS) based on the enzymes immobilized in the polymeric environment is one of the modern directions on the “cross-section” of polymer and biological chemistry. Such SBS have several advantages that making them more convenient for the effective applications: increase stability of the enzyme in time and to various denaturing agent; more simple and rapid separation of the reaction medium; multiple usage etc.

The aim of this study was to prepare supramolecular complexes of polymers and lipases possessing high catalytic activity for the further application as biomaterials.

It was found that the lipase activity in the complex with polystyrenesulfonate (PSS) was higher than the control on 17% and 15% at ratios of 1:10 and 1:100 (lipase:PSS). The complex with polydiallyldimethylammonium chloride (PAMA) the lipase activity decreased to 94% at a ratio 1:10 (lipase:PAMA). The complex with PE-240 (copolymer based on polypropylene oxide) the lipase activity was higher than the control on 12% at a ratio 5:1 (lipase:PE-240).



a

b

Models of lipase:PSS 1:1(a) and 1:10(b) complexes with “low activity”(a) “high activity”(b).

These SBS with high lipase activity are promising for application in bioengineering and biotechnology.

The work was supported by RFBR, the Russian Ministry of Education and Science.

**THIACALIX[4]ARENES: SYNTHESIS AND
SELF-ASSEMBLED SUPRAMOLECULAR
ARCHITECTURES**

**I.I. Stoikov
I.S. Antipin
A.I. Konovalov**

A.M. Butlerov Chemical Institute, Kazan (Volga Region) Federal
University, Kazan, Russia
ivan.stoikov@mail.ru

The controlled self-assembly of macrocyclic molecules based on calixarenes in functional supramolecular entities is an interesting topic of research in the area of supramolecular chemistry and nanotechnology. Due to many possible applications, such molecule receptors can be useful as base elements in the development of sensors and as selective carriers in industrial membrane extraction technologies.

Being highly affine and convertible effectors and catalysts, the calixarenes can be considered as building blocks for constructing nanosized structures adapted for recognition specific guest molecules.

The role of calixarenes in the design, synthesis and application of nanoscale aggregates with metal cations by self-association processes is discussed. Among others, the approaches to the synthesis and modification of nanoparticles ranging from 1 nm to 1 μ m are considered with particular emphasis to the areas of their possible application in nanotechnology.

The discussion is focused on the establishment of the “structure-property” relationships that allow determining size, shape, and chemical properties of the nanoscale aggregates at the spatial structure level as well as their application.

The aggregation of metal cations and calixarenes is of special interest due to the following reasons: (i) metal cations can participate in photon absorption or emission, electron transfer, and ion exchange and (ii) synthetic receptors are able to form molecular or supramolecular architectures of predicted spatial arrangement of the active parts, among them, due to their interaction with metal cations.

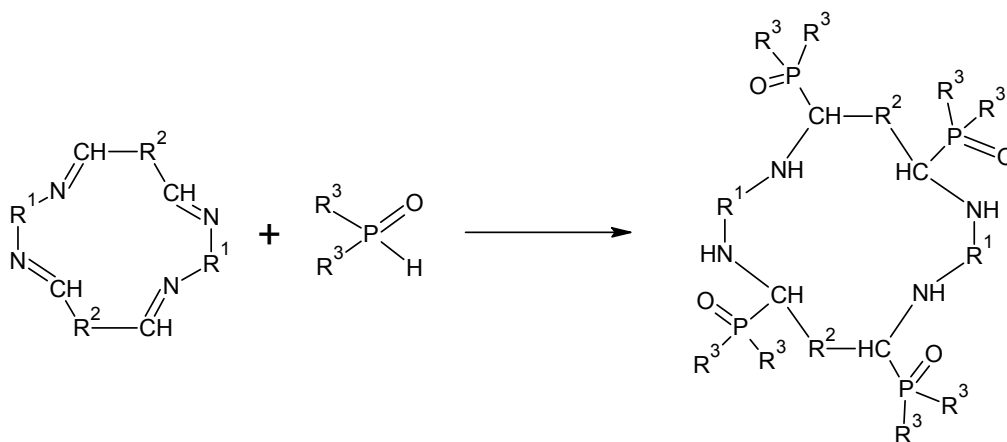
This work was supported by the Federal Program "Research and scientific-pedagogical cadres Innovative Russia" for 2009 - 2013 years (№ p1107 from 26 August 2009), the Russian Foundation for Basic Research (09-03-00426-a) and the grants program of the President of the Russian Federation for state support of young Russian scientists - doctors of science (MD-2747.2010.3).

Yu.G. Trishin
N.A. Anisimova
L.A. Tamm
L.V. Danilova
E.A. Karpova
E.A. Avdeeva

MACROCYCLIC AMINOPHOSPHORYL COMPOUNDS FOR THE SUPRAMOLECULAR SYSTEMS

St. - Petersburg State Technological University of Plant Polymers,
Department of Organic Chemistry, St. - Petersburg, Russia
trish@YT4470.spb.edu

Macrocyclic aminophosphoryl compounds containing N atom in the cycle and P=O group out cycle are not synthesized. The using these compounds as "host" molecule for the building of the supramolecular systems are unknown. We have prepared these compounds as result of reactions of macrocyclic azomethynes with hydrophosphoryl compounds.



R^1, R^2 = alkyl, cycloalkyl, aryl, heteryl; R^3 = alkyl, aryl, benzyl, alkoxy, hydroxyl

As macrocyclic azomethynes we have used cycles with various dimensions. C=N group is bonding with hard aromatic and heteroaromatic as well as flexible aliphatic structure. The substituents by phosphorus atom differ from electron withdrawing, spatial pattern and hydrophilia. The obtained phosphorylated macrocycles are tested in the supramolecular systems (included complexes, metal extracting agents, biological active compounds etc.)

This work was supported by the Russian Foundation for the Basic Research, grant 11-03-00648.

**SELF-ASSEMBLY OF Au(I)-Cu(I) AND Au(I)-Ag(I)
HETEROMETALLIC COMPLEXES: STRUCTURE
AND PHOTOPHYSICS OF THESE
SUPRAMOLECULAR AGGREGATES**

S.P. Tunik
I.O. Koshevoy

St. Petersburg State University, Department of Chemistry, Russia
stunik@inbox.ru

Growing attention to d^{10} organometallic complexes of coinage metals is stimulated by their intriguing photophysical properties and ability to form polynuclear homo- and heterometallic structural patterns due to metallophilic interaction between the metal ions. In our recent works we developed an approach to the synthesis of a novel class of alkynyl-diphosphine supramolecular complexes, which display extremely efficient phosphorescence, negligible triplet oxygen quenching and in some cases NLO properties. The general structural motif found in this type of coordination compounds may be described as “rods-in-belt” pattern, with a few dialkynyl-gold “rods” held together by M(I) ions ($M = Ag$ or Cu) and fasten with cationic $\{Au(diphosphine)\}_n$ ($n = 1, 2$) “belt” to give stable supramolecular aggregates. Self-assembly of the supramolecular complexes occurs due to formation of extended Au(I)-M(I) metallophilic network, which is responsible for bonding both inside central core and attachment of this fragment to the $\{Au(diphosphine)\}_3$ “belt”. In the case of Au-Ag complexes it was also possible to prepare closely analogous compound containing silver-dialkynyl-gold core. Depending on the length and nature of the spacers between phosphorus atoms in the diphosphine it proved to be possible to synthesize molecular aggregates of similar structural motifs containing up to 18 dialkynyl-gold rods in the central core and with molecular weight up to 14.5 kD.

The effect of metallophilic interactions and structure of the compounds under study onto their unique electronic structure and photophysical properties will be discussed in the presentation along with prospective of their application in electroluminescence devices and bioimaging.

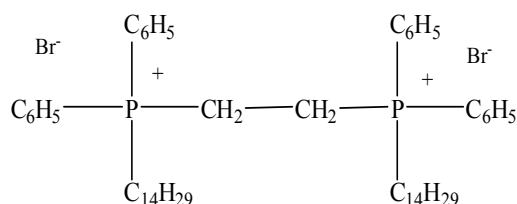
Authors acknowledge financial support from Finnish Academy of Science and Russian Foundation for Basic Research, grants 07-03-00908a

NEW GEMINI SURFACTANT WITH PHOSPHONIUM HEAD GROUPS: SELF-ORGANIZATION AND CATALYTIC ACTIVITY

G.I. Vagapova¹
G.A. Gaynanova¹
F.G. Valeeva¹
I.V. Galkina²
L.Ya. Zakharova¹
A.I. Kononov¹

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry of
 Kazan Scientific Center of Russian Academy of Sciences, Department
 of Supramolecular Chemistry, Kazan, Russia
 2 - Kazan Federal (Volga Region) University, A.M. Butlerov Institute
 of Chemistry, Kazan, Russia
 vagapovagu@iopc.ru

Gemini surfactants demonstrate a higher surface activity and a lower critical micellization concentration (CMC) values as compared to the conventional surfactants of equivalent chain length. These properties determine their wide applications in nanoscale technology, biotechnology, catalysis and solubilization processes. In our work, the aggregation behavior and catalytic activity of supramolecular systems based on amphiphilic gemini phosphonium salt ethylenedi(tetradecyldiphenylphosphonium) bromide (EDFB) and polyethylene glycol (PEG) with molecular mass 1000 were studied. This surfactant with two phosphonium head groups is of interest due to both its dimeric structure and biological activity.



By the methods of tensiometry, conductometry, pH-metry, and dynamic light scattering, the critical association concentration (CAC) and radii of aggregates were determined in the individual EDFB system and binary EDFB-PEG mixture. In the presence of PEG, the CMC value decreases from 0.08 to 0.05 mmol/l. This indicates the formation of mixed aggregates in the solution. These values are much lower than those of single head surfactants. In both systems formation of two types of aggregates were revealed. Aggregates with a diameter of 10-25 nm are formed by monomers of EDFB. Aggregates of large diameter (220-250 nm) can probably be polymer-free or polymer-bound micelles and vesicles.

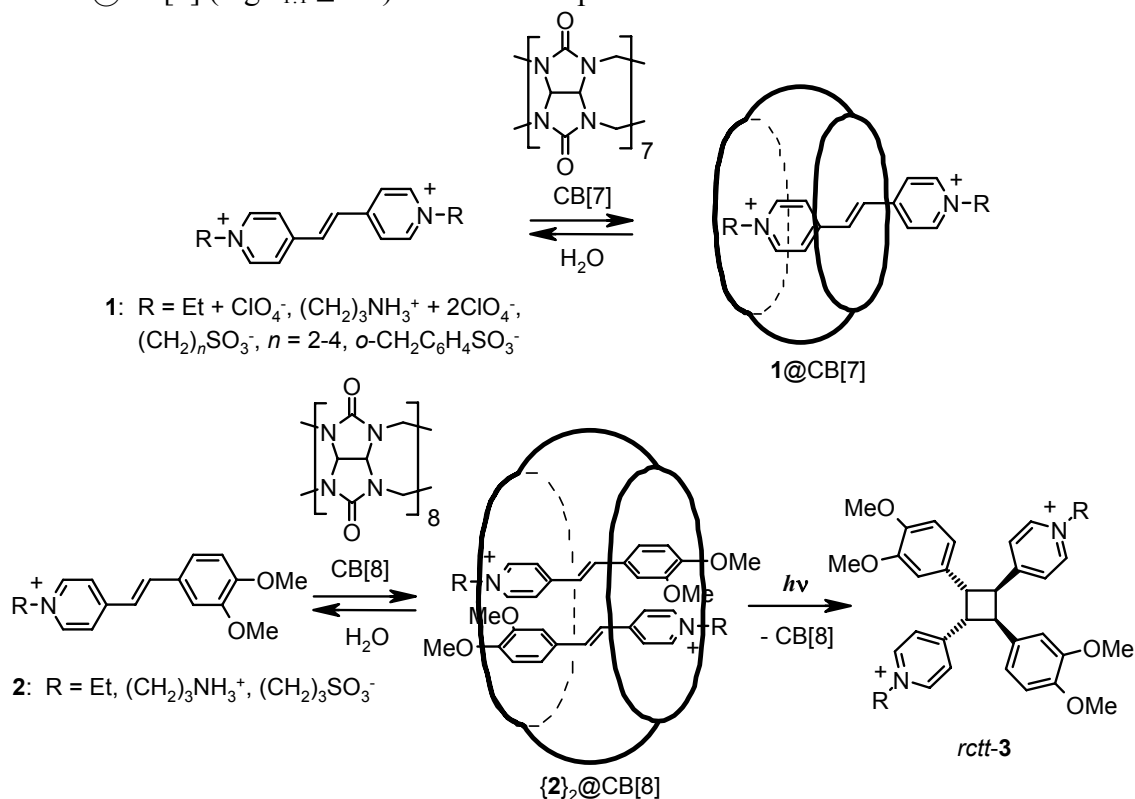
This work was supported by the Russian Foundation for Basic Research (grant № 09-03-00572-a).

PSEUDOROTAXANE COMPLEX FORMATION OF UNSATURATED COMPOUNDS WITH CUCURBIT[*n*]URILS AND THEIR PHOTOCHEMICAL PROPERTIES

A.I. Vedernikov¹
N.A. Lobova¹
L.G. Kuzmina²
S.K. Sazonov¹
M.V. Alfimov¹
S.P. Gromov¹

1 - Photochemistry Center of the RAS, Moscow, Russia
2 - Institute of General and Inorganic Chemistry of the RAS, Moscow, Russia
artem@photonics.ru

A series of unsaturated viologen analogs **1** and 4-pyridine styryl dyes **2**, which bearing various *N*-substituents, were synthesized. Complex formation features of compounds **1**, **2** with cucurbit[*n*]urils (CB[*n*], *n* = 7, 8) was studied using NMR, UV-Vis spectroscopy, and X-ray diffraction. In water, CB[7] and planar *trans* isomers of compounds **1** form relatively stable complexes **1**@CB[7] ($\log K_{1:1} \geq 3.2$) which have a pseudorotaxane structure.



Dyes *trans*-**2** and CB[*n*] also demonstrate pseudorotaxane-type complex formation. Under irradiation with visible light, **2** and their complexes with CB[7] undergo only reversible *E*-*Z* photoisomerization. With CB[8], dyes **2** are able to give both bimolecular **2**@CB[8] ($\log K_{1:1} \geq 4.0$) and termolecular **{2}₂@CB[8]** ($\log K_{2:1} \geq 2.6$) complexes. Within termolecular complexes, two organic cations are arranged according to *syn*-head-to-tail pattern thus enabling the efficient stereospecific [2+2]-photocycloaddition (PCA) reaction to proceed to form *rcctt* isomers of cyclobutane derivatives **3**. The stability of *rcctt*-**3**@CB[8] complexes ($\log K_{1:1} \geq 3.2$) is lower than that of **2**@CB[8]. This makes it possible to use CB[8] as a supramolecular catalyst in order to attain complete photoconversion of **2**. Thus, CB[8] is a photocontrolled *molecular assembler* for cyclobutanes. Such systems can be used for optical recording and storage of information, for creation of molecular machines driven by light.

This work was supported by the Russian Foundation for Basic Research and the Russian Academy of Sciences.

A.A. Yantemirova
R.V. Nosov
A.N. Yagarmina
I.I. Stoikov
I.S. Antipin
A.I. Konovalov

**THIACALIX[4]ARENES SUBSTITUTED AT THE
LOWER RIM BY CHROMOPHORE FRAGMENTS**

Department of Organic Chemistry of A.M. Butlerov Chemical
Institute, Kazan (Volga Region) Federal University, Kazan, Russia
anelia_86@mail.ru

Design and synthesis of receptor structures capable of selective binding of substrates from the bulk phase and as well as at the interface provides an opportunity for the realization of highly organized processes in artificial systems. Calixarenes are widely used as building blocks in the design of host molecules because they have a lot of advantages such as the availability of initial compounds, ability to form host-guest complexes, possibility for modification and construction of systems with several binding sites. As structural fragments for construction of binding sites for biologically important substrates, we chose ethylacetate, *N,N*-diethylacetamide fragments and secondary amide groups with chromophore substituent, which is necessary for the spectrophotometric detection of complexation.

New thiocalix[4]arenes containing 1- and 2-amidoanthraquinone and ester fragments differently substituted at the lower rim were synthesized by sequential alkylation of *p*-*tert*-butyl thiocalix[4]arene. For the synthesis of stereoisomers of *p*-*tert*-butyl thiocalix[4]arene with ester and amide fragments at the lower rim, the template effect of alkali metal cations was used. The structures of obtained macrocycles were studied by various physical methods: IR, 1D and 2D NMR spectroscopy, mass-spectrometry (ESI, MALDI-TOF). Receptor properties of the newly synthesized thiocalix[4]arene derivatives toward some biologically important substrates were studied by UV and fluorescence spectroscopy.

This work was supported by Federal Program "Research and scientific-pedagogical cadres Innovative Russia" in 2009-2013 years (№ P1295 on 9 June 2010), RFBR (09-03-00426, 10-03-92661-NSF) and the Program of the President of the Russian Federation for the State support of young Russian scientists - Doctors of Sciences (MD-2747.2010.3).

**AQUEOUS PHOTOCHEMISTRY OF
SUPRAMOLECULAR COMPLEXES OF
2,4,5-TRICHLOROPHENOXYACETIC ACID WITH
CYCLODEXTRINES**

**M.P. Yurkova
I.P. Pozdnyakov
V.F. Plyusnin
V.P. Grivin**

Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia
yurkova@kinetics.nsc.ru

2,4,5-trichlorophenoxyacetic acid (2,4,5-T) is one of the widely used herbicides. 2,4,5-T is a toxic contaminant and its introducing into the water systems leads to deterioration of drinking water. Photochemical technique is one of perspective approach of water purification. Cyclodextrin (CD) complexation has recently emerged as a new catalytic technology complement to the photochemical treatment approaches for removal contamination in solution and in solid state.

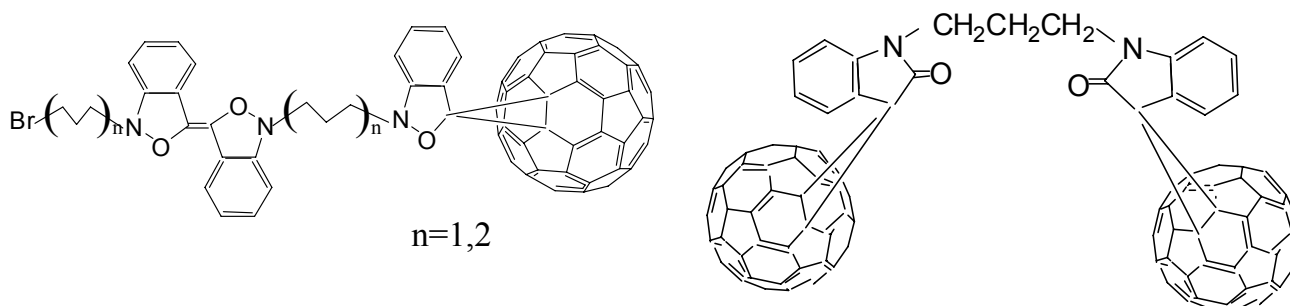
The report presents obtained data of initial stages of 2,4,5-T photodegradation by stationary and nanosecond laser (266 nm) flash photolysis techniques without and in a presence of β - and γ -CD. UV-excitation 2,4,5-T leads to its photoionization with generation of hydrated electron – cation-radical pair, that is typical feature of photochemistry of chlorophenols. Former intermediate is characterized by absorption band with maximum at 720 nm, cation-radical demonstrates absorption band with maximum at 540 nm. Quantum yield of photoionization is equal to 0.021 at excitation energy 0.25 J/cm^2 . In deoxygenated solutions the main decay channels of hydrated electron are capture by 2,4,5-T ($k = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and recombination with cation-radical. In presence of oxygen hydrated electron converts into $\text{O}_2^{\bullet -}$ radical, mainly. Cation-radical of 2,4,5-T undergoes hydrolysis by water molecule ($k = 10^7 \text{ s}^{-1}$) with generation of long-lived phenoxyl radical. The latter decays apparently in recombination reaction with formation of final photolysis products.

In the presence of β - and γ -CD formation of 1:1 inclusion complexes is observed ($K_{\text{form}} = 1100$ and 150 M^{-1} , accordingly). Complexation with γ -CD leads to increase of 2,4,5-T photodegradation rate in 1.5 times, but complexation with β -CD decrease this rate in 1.8 times. This fact could be explained by difference in photochemical activity of inclusion complexes and participation of cyclodextrines in reactions with primary photochemical species.

This work was supported by RFBR (grants 09-03-00330, 11-03-00268) and Program of integration projects of SB RAS 2009-2011 (grants № 70).

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan
Scientific Centre of Russian Academy of Sciences, Kazan, Russia
gulshat@mail.ru

We have been developed the method of the synthesis of elemental indolinonesubstituted methanofullerenes by the reaction in a three-component system fullerene-dicarbonyl compound-hexaethyltriaminophosphine. The first organic solar cells based on the indolinonesubstituted methanofullerenes appeared power conversion at 2%. To improve the methanofullerene characteristics we have been began the design of new complex fullerene derivatives having the several fulleroindolinone fragments or fulleroindolinone and indolinone dye fragments simultaneously.



The characteristics of the synthesized compounds are superior to that of known methanofullerenes and of elemental indolinonesubstituted methanofullerenes. This fact allow to suppose that these compounds are perspective for the creation of high effective organic solar cells.

The work is supported by Russian foundation for the Basic Research (grants 09-03-00259-a) and by the Program No. 6 of the Division of Chemistry and Material Sciences of Russian Academy of Sciences.

THE PROPERTIES OF A NEW PARACETAMOL-PYRIDINE SOLVATE AT LOW TEMPERATURES

B.A. Zakharov¹
A.G. Ogienko²
E.V. Boldyreva¹

1 - Institute of Solid State Chemistry and Mechanochemistry SB RAS,
Novosibirsk, Russia

2 - REC-008 "Molecular Design and Ecologically Safe Technologies",
Novosibirsk State University, Novosibirsk, Russia

b.zakharov@yahoo.com

The method of the preparation of the “glass-like” (amorphous) phase by rapid cooling of solutions in the paracetamol-pyridine system has been developed. The processes occurring on annealing of this phase have been examined by X-ray diffraction. A novel intermediate phase was observed, which is a new solvate of paracetamol with pyridine.

In the present work a new solvate has been studied by single-crystal X-ray diffraction in the temperature range 100 – 275 K. The new solvate has unusual H-bonding types (“peptide hydrogen bonds”) as compared to the structures of individual paracetamol polymorphs. This kind of hydrogen bonding becomes possible because OH-groups of paracetamol in the solvate link to the nitrogen atom of “guest” pyridine molecule. Two molecules of paracetamol in the asymmetric unit have very different geometries – in contrast with the structures of previously known solvates. Anisotropic lattice compression on cooling has been analysed, and we have found that the most compressible direction is close to the direction of “peptide” N-H...O hydrogen bonds and coincides with the direction of undulating layers in the structure, which are formed by paracetamol and pyridine solvate. In general, if compared with pure polymorphs of paracetamol, the solvate structure is less compressible.

This work was supported by grants from RFBR (09-03-00451), BRHE (RUX0-008-NO-06), by the Integration Projects No. 13 and 109 of the Siberian Branch of RAS, a FASI Grants P2529 and 16.740.11.0166 and State Contract of RF № 14.740.11.1023.

**ULTRA-LOW DOSES OF PLANT GROWTH
REGULATORS BASED ON PHOSPHORIC
MELAMINE AND PYRIMIDINES DERIVATIVES
REDUCES LIPID PEROXIDATION IN
MITOCHONDRIAL MEMBRANES**

I.V. Zhigacheva¹
E.B. Burlakova¹
S.G. Fattakhov²

1 - Institution of the Russian Academy of Sciences: Emanuel Institute of Biochemical Physics, Moscow, Russia

2 - Institution of the Russian Academy of Sciences: Arbuzov Institute of Organic and Physical Chemistry Kazan Scientific Center, Kazan, Russia

zhigacheva@mail.ru

In a wide range of concentrations (10^{-3} - 10^{-22} M) studied effect of plant growth regulators melaphen (a melamine salt of bis bis(oxymethyl)-phosphonic acid) and pyraphen (a 2,4,-triaminopyrimidine salt of bis(oxymethyl) phosphonic acid) on the intensity of lipid peroxidation (LPO) in mitochondrial membranes. To activate LPO, we used a model of “ageing”, i.e., a long-term storage of mitochondria that increased the intensity of fluorescence of the LPO products in 3 to 4 times. The introduction of the preparations into the mitochondria incubation medium results in a decrease in the LPO products fluorescence depending on a dose. Melaphen at a concentration of 10^{-12} - 10^{-13} and 10^{-18} - 10^{-21} M decreases the fluorescence intensity of LPO products to the control level. For pyraphen, we observed quite a different effect. Pyraphen at concentrations of 10^{-5} and 10^{-15} - 10^{-21} M decreases the content of LPO products in mitochondrial membranes to the control values. Moreover, 10^{-3} , 10^{-4} , 10^{-8} , and 10^{-13} - 10^{-14} M solutions of the preparation increase 1.5 times the intensity of fluorescence of LPO products in membranes of “aged” mitochondria. The obtained data show that the preparations exhibit antioxidant properties and may obviously exhibit the adaptogenic activity. Indeed, melafen at 2.5 times and pyraphen at 1.2 times stimulated the growth of sprout pea seedling roots under drought conditions. These events are great important for adaptation. The obtained concentration dependence in appearance drugs biological activity may be interpreted in terms of formation in various concentration ranges of nanoassociates of the preparation with water differing in structure (I.S. Ryzhkina, A.I. Kononov, 2009).

**APPLICATION OF POLYMORPHISM OF
SUPRAMOLECULAR RECEPTORS FOR
MOLECULAR RECOGNITION**

M.A. Ziganshin

G.D. Safina

K.V. Luchai

V.V. Gorbachuk

A.M. Butlerov Chemical Institute, Kazan Federal University, Kazan,
Russia
Marat.Ziganshin@ksu.ru

Polymorphism of solid receptors, giving the formation and collapse of metastable porous structures, can affect significantly their binding ability for vapors and gases [1,2]. Substances capable of polymorphism and/or pseudo-polymorphism can be used as new sorption materials with high sorption and adjustable selectivity, sorption capacity and thermal stability for solving problems of energy, environment and medicine.

In present study, the parameters of polymorphic and pseudo-polymorphic transitions in the phase of supramolecular receptors were determined using simultaneous thermogravimetry and differential scanning calorimetry analysis combined with mass-spectrometry of evolved vapors.

Sorption properties of supramolecular receptors in different modifications toward the vapors of organic compounds were studied with the static method of headspace gas chromatographic analysis, and quartz crystal microbalance sensor.

As the result of study the new approach to molecular recognition of vapors of some organic guests was offered, which is based on the use of polymorphism and pseudo-polymorphism of supramolecular receptors [4].

References:

1. A.V. Yakimov, M.A. Ziganshin, A.T. Gubaidullin, V.V. Gorbachuk, *Org. Biomol. Chem.*, 2008, **6**, 982.
2. L.S. Yakimova, M.A. Ziganshin, V.A. Sidorov, V.V. Kovalev, E.A. Shokova, V.A. Tafeenko, V.V. Gorbachuk, *J. Phys. Chem. B*, 2008, **112**, 15569.
3. G.D. Safina, L.R. Validova, M.A. Ziganshin, I.I. Stoikov, I.S. Antipin, V.V. Gorbachuk, *Sens. Actuators, B: Chem.*, 2010, **148**, 264.

This work was supported by RFBR №11-03-01215 and Federal Program "Research and scientific-pedagogical personnel of Innovative Russia" for 2009-2013 (Gov. contract № P2345).

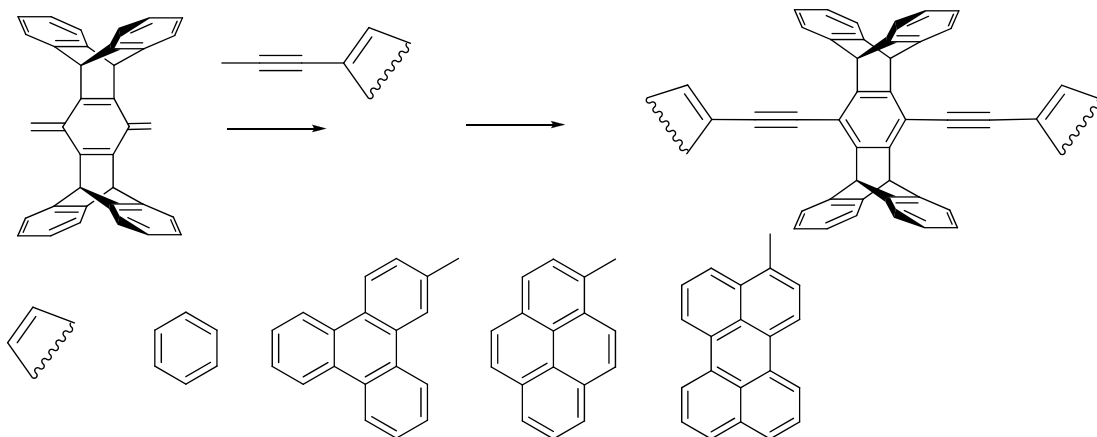
POLYARYLACETYLENE-SUBSTITUTED IPTYCENES FOR NITROAROMATES DETECTION

G.V. Zyryanov¹
P.A. Slepukhin²
I.S. Kovalev³
D. Kopchuk⁴
V.L. Rusinov⁵
O.N. Chupakhin¹

1 - Urals Federal University, Organic Chemistry Department,
 I.Ya. Postovskiy Institute of Organic Synthesis, "Sphere" Ltd.,
 Yekaterinburg, Russia
 2 - Urals Federal University, I.Ya. Postovskiy Institute of Organic
 Synthesis, "Sphere" Ltd., Yekaterinburg, Russia
 3 - Urals Federal University, Organic Chemistry Department, "Sphere"
 Ltd., Yekaterinburg, Russia
 4 - Urals Federal University, Organic Chemistry Department,
 I.Ya. Postovskiy Institute of Organic Synthesis, Yekaterinburg, Russia
 5 - Urals Federal University, Organic Chemistry Department,
 Yekaterinburg, Russia
 gvzyryanov@gmail.com

Poly-aromatic hydrocarbons (PAHs) (triphenylene, pyrene and other) are common compounds to be utilized for the visual (photoluminescent) detection of electron deficient species, including nitroaromatics.¹ Iptycenes are widely used sensing and synthetic platforms in both supramolecular and materials chemistry.² In our research we combined both elements in one molecule to obtain new chemosensors for nitroaromatic detection.

Reaction pentiptycene quinone **1** with aromatic lithium acetylenides afforded aryl-acetylene substituted pentiptycenes **2** in good yields. Sensors **2** have demonstrated the different degree of fluorescence quenching upon the titration with nitroaromatic compounds in organic solvents in a following way: increasing the size of aromatic residue in acetylene moiety results in higher quenching constants (up to 10^4 M^{-1}) due to the possible excimer formation. In those experiments beyond simple solutions of **2**, a higher concentration excimer emitting solutions of **2** as well as different fluorescence resonance energy transfer (FRET) systems were utilized.



References:

1. a) R. Wen, C.-J. Yan, H.-J. Yan, G.-B. Pan and L.-J. Wan *Chem. Commun.*, **2011**, Advance Article; b) K.-S. Fosananu and J.C. Scaiano *Photochem. Photobiol. Sci.* **2005**, 4, 817-821; c) W. Chen, N. B. Zuckerman, J. P. Konopelski, and S. Chen *Anal. Chem.* **2010**, 82, 461-465
2. J.H. Chong and M. J. MacLachlan *Chem. Soc. Rev.*, **2009**, 38, 3301-3315

This work was supported by the State Contract # 14.740.11.1020 and "Start 2011"

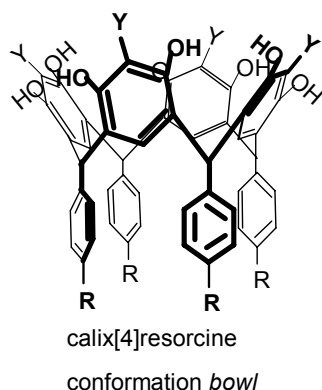
M.N. Saifutdinova¹
 E.L. Gavrilova¹
 N.I. Shatalova¹
 R.I. Tarasova¹
 A.R. Mustafina²
 A.T. Gubaidullin²
 A.R. Burilov²
 O.G. Sinyashin¹

HOST-GUEST COMPLEX FORMATION OF N-FUNCTIONALIZED CALYX[4]RESORCINES AND PHOSPHORYLACETIC ACID'S HYDRAZIDES

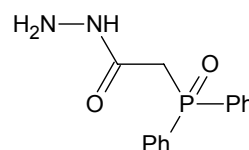
1-Department of Organic Chemistry, Kazan State Technological University, Kazan, Russia

2-A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan Scientific Center of Russian Academy of Sciences, Kazan, Russia
 shipova-marija@rambler.ru

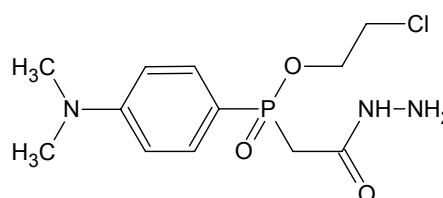
Using of supramolecular systems (including calyx[4]resorcines) for the transportation of drugs has attracted considerable attention during past years. Earlier we have published [1] the synthesis and pharmacological activity of molecular complex on the base of calyxresorcine (1) and Phosenazid (5). It is known, that hydrazides of phosphorylacetic acids possess psychotropic effects promoting the brain operation [2]. Phosenazid (5) and CAPAH (6) are the most studied which correspond to the group of phosphorylaceto hydrazides and which were recommended as tranquilizers. Here we present the host-guest complex formation of N-functionalized calyx[4]resorcines (2-4) and phosphorylacetic acid's hydrazides Phosenazid (5) and CAPAH (6). The process of complexes formation and structure of isolated compounds were studied by ³¹P, ¹H, IR, UV spectroscopy, powder X-ray diffraction and data of elemental analysis.



- 1 (R=CH₃; Y=H)
- 2 (R=NH₃⁺ Cl⁻; Y=H)
- 3 (R=NH⁺(CH₃)₂ Cl⁻; Y=H)
- 4 (R=CH₃; Y=CH₂-NEt₂)



Fosenazid 5



CAPAH 6

References:

- [1] M.N. Saifutdinova, N.I. Shatalova, E.L. Gavrilova, R.I. Tarasova, I.P. Pashina, I.I. Semina. Vestnik KSTU, Kazan, 2010, №7. – p. 294-299.
- [2] Semina I., Schilovskaya E., Tarasova R., Baychorina A. et. Phosph., Sulfur and Silicon, 1999, V. 144-146, p. 753-756.

Work at financial support of grant MK-64832.2010.3

**LOW AND ULTRA-LOW CONCENTRATIONS OF A
PREPARATION MELAPHEN POSSESS
ANTIOXIDANT PROPERTIES**

I.V. Zhigacheva¹
E.B. Burlakova¹
S.G. Fattakhov²

1 - Institution of the Russian Academy of Sciences: Emanuel Institute
of Biochemical Physics Moscow Russia
2 - Institution of the Russian Academy of Sciences: Arbuzov Institute
of Organic and Physical Chemistry Kazan Scientific Center Kazan
Russia
zhigacheva@mail.ru

Many natural and synthetic biologically active substances (BAS) exhibit activity in a range of low (10^{-10} - 10^{-4} M) and ultra-low (10^{-20} - 10^{-11} M) concentrations. The effects of ultra-low doses of BAS have a common objective feature, which is evidently accounted for by common targets. Cell membranes may be such targets. Changes in physicochemical properties of biological membranes caused by various impacts, including those of BAS, result in changes in the activity of membrane-associated enzymes and thus affect the functional state of cells.

The aim of our work is to study the influence of various concentrations of plant growth regulators melaphen (a melamine salt of bis bis(oxymethyl)-phosphonic acid) on the intensity of lipid peroxidation (LPO) in mitochondrial membranes. To activate LPO, we used a model of "ageing", i.e., a long-term storage of mitochondria that increased the intensity of fluorescence of the LPO products 3 to 4 times. The introduction of the preparation into the mitochondria incubation medium results in a decreased in fluorescence of POL, which is dose dependent. The melaphen concentrations of 10^{-3} - 10^{-6} and 10^{-8} - 10^{-11} M rendered a slight effect on the intensity of POL processes. The preparation concentrations of 10^{-7} 10^{-12} - 10^{-13} and 10^{-18} - 10^{-21} M decreased the fluorescence intensity of LPO to the control level. The obtained data show that at concentration 10^{-7} 10^{-12} - 10^{-13} and 10^{-18} - 10^{-21} M melaphen exhibit antioxidant properties. . The data obtained may be interpreted in terms of formation in various concentration ranges of nanoassociates of the preparation with water differing in structure. (I.S. Ryzhkina, A.I. Konovalov, 2009).

Section 6.

Bioorganic and Medicinal Chemistry

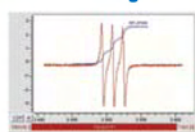
Single Measurement Quantitative EPR Spin Counting

Factory Preparation



Critical resonator properties included

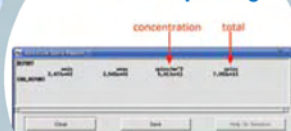
Double Integration



New tool for high precision double integration

Determine the absolute number of spins in your sample

Software Reporting



Results for further analysis

User Input



Minimum user interaction

- An easy to use high precision method
- No reference sample required
- Single measurement
- One-time factory calibration of cavity response function

● www.bruker-biospin.com

think forward

EPR Solutions

**THE ORGANOPHOSPHORUS CHEMISTRY OF
NUCLEOTIDES: NEW ADVANCES IN SYNTHESIS,
STEREOCHEMISTRY AND DESIGN OF BIOACTIVE
MOLECULES**

C.E. McKenna¹
Y. Wu¹
V.M. Zakharova¹
B.T. Chamberlain¹
B.A. Kashemirov¹
K. Oertell²
M.F. Goodman²
W.A. Beard³
V.K. Batra³
S.H. Wilson³

1 - University of Southern California, Department of Chemistry, Los Angeles, California, USA

2 - University of Southern California, Department of Biological Sciences, Los Angeles, California, USA

3 - NIEHS, Laboratory of Structural Biology, Research Triangle Park, North Carolina, USA

mckenna@usc.edu

Designed modifications of natural nucleotides (*e.g.* deoxyribonucleoside triphosphates, dNTPs) can be exploited to obtain information about the structure and function of enzymes such as nucleic acid polymerases. Such analogues usually have changed base or sugar moieties, particularly when the objective is to create a therapeutically useful inhibitor of the target enzyme. However, increasingly attention is being focussed on the effects and translational potential of modifications in the triphosphate group, the locus of chemical reactions catalyzed by polymerases. Replacement of the p_{α} -O- p_{β} bridging oxygen in dNTPs by a carbon atom (-CXY-) prevents turnover, whereas a p_{β} -CXY- p_{γ} modification generally produces a substrate with altered leaving group properties depending on the nature of substituents X and Y. The introduction of appropriate substituents enables new active site bonding interactions, not possible with the natural nucleotide, that might be exploited to aid design of novel inhibitors targeting DNA polymerases such as DNA pol β , a key base excision repair enzyme that is overexpressed in some tumors. To explore these concepts, a 'toolkit' of α,β and β,γ bisphosphonate dNTPs exhibiting a wide range of stereoelectronic properties at the CXY group (X,Y = H, F, Cl, Br, Me, N₃) has been synthesized, including the first examples of individual stereoisomers of both α,β and β,γ p-CXY-p dNTPs, and used in conjunction with NMR, X-ray crystallographic and enzyme kinetics analyses to obtain important new insights into DNA pol β mechanism and fidelity at the molecular level.

DESIGN OF MULTIVALENT DRUGS

N.S. Zefirov
V.A. Palyulin

Moscow State University, Department of Chemistry, Moscow, Russia
zefirov@org.chem.msu.ru

Design of new drug molecules is a sophisticated process involving in the first steps the application of molecular modelling and QSAR techniques, molecular docking and virtual screening. The joint application of these approaches provides deeper understanding of both structure-activity relationships and ligand-receptor interactions as well as facilitates lead finding and optimization.

Until recently the main criterion in the design of drug molecules was based on their selective interaction with one binding site of one biotarget (receptor, enzyme, etc.). Interactions with other biotargets were considered in this case as “side effects”. However sometimes simultaneous interaction of drug molecules with two (or more) different biotargets is necessary. Such compounds are considered as “multitarget drugs”.

Another approach deals with the modelling and development of drug molecules interacting simultaneously with two (or more) binding sites of the same biotarget (so called “bivalent” or “multivalent” drugs). This kind of drug molecules usually has much higher binding affinity and selectivity as compared to the molecules interacting with just one binding site.

All the approaches mentioned above were successfully used in the design of new neuroprotectors with cognition enhancing properties (including highly potent (picomolar) ones) on the basis of previously developed molecular models of all types and subtypes of glutamate receptors.

References:

N.S.Zefirov, V.A.Palyulin, Molecular Modelling of Central Nervous System Receptors, Mendeleev Commun., **2010**, 20, 243-248.

**REACTIONS OF HUMAN CHOLINESTERASES
WITH CRESYL SALIGENIN PHOSPHATE: A
TROJAN HORSE POISONING BY TRI-O-CRESYL
PHOSPHATE**

P. Masson¹
M. Liyasova²
E. Carletti³
L.M. Schopfer²
O. Lockridge²

1 - Institut de Recherche Biomedicale des Armees, Toxicology
Department, La Tronche, France

2 - University of Nebraska Medical Center, Eppley Institute, Omaha,
USA

3 - Institut de Biologie Structurale, Grenoble, France
pmasson@unmc.edu

The cabin air in jet airplanes is taken directly from heat exchangers in the engine compartment. Leaks in the engine can release jet engine oil and hydraulic fluid into the cabin air. Aircrew and passengers have complained of illness following such “fume events”. This aerotoxic syndrome is hypothesized to be caused by exposure to low doses of tricresyl phosphate (TCP), an anti-wear additive in jet engine lubricants and hydraulic fluid. Cresyl saligenin phosphate (CBDP) is the toxic metabolite of tri-ortho-cresylphosphate (TOCP), a component of TCP. Reactions of CBDP with human cholinesterases (ChE) were investigated on highly purified enzymes and in plasma samples of jet airplane passengers collected within 24 hours of completing a trip.

Exposure to TOCP in jet airplane travelers was diagnosed by detection of CBDP adduct on plasma butyrylcholinesterase (BChE) (1). The enzyme was partially purified from each plasma sample, digested with pepsin, enriched for the phosphorylated active site peptide (FGepSAGAAS) by binding to titanium oxide, and analyzed by mass spectrometry. 50% of jet airplane passengers tested were positive for exposure to TOCP. The level of exposure was very low. No more than 0.05 to 3% of plasma BChE was modified. None of the subjects had toxic symptoms. After 3 to 7 months after no airplane travel, the positive subjects were found to be negative for phosphorylated BChE (2).

Kinetics of irreversible inhibition of ChEs, BChE and acetylcholinesterase (AChE), by CBDP was investigated with pure human enzymes. Progressive inhibition under pseudo first-order conditions, displayed a biphasic time course, indicating reaction with two enzyme forms (E and E') in slow equilibrium. The bimolecular rate constants $1.6 \times 10^8 \text{ M}^{-1} \text{ min}^{-1}$ and $2.7 \times 10^7 \text{ M}^{-1} \text{ min}^{-1}$ for E and E' forms of BChE are among the highest for reaction of organophosphates with ChEs. AChE is less sensitive to CBDP than BChE with inhibition constants less than one to two orders of magnitude slower. CBDP-phosphorylated cholinesterases are non-reactivable due to ultra fast “aging” (3).

Mass spectrometry analysis showed an initial BChE adduct with an added mass of 170 Da from cresylphosphate, followed by dealkylation to a structure with an added mass of 80 Da. Mass spectrometry in ^{18}O -water showed that ^{18}O was incorporated only during the final aging step to form phospho-serine as the final “aged” BChE adduct. CBDP is the first organophosphorus agent that leads to a fully dealkylated phospho-serine BChE adduct. The X-ray structures of CBDP-inhibited BChE, the cresylphosphate intermediate and the ultimate phosphate conjugate, were solved at 2.5 Å resolution.

References:

(1) L.M. Schopfer et al., *Anal. Biochem.*, 2010, 404, 64-74; (2) M. Liyasova et al., *Tox. Appl. Pharmacol.*, 2011, in press ; (3) E. Carletti et al., *Chem. Res. Toxicol.*, 2011, June issue.

DESIGN AND SYNTHESIS OF MEMBRANE-ANCHORED BACE INHIBITORS AS POTENTIAL DRUGS FOR THE TREATMENT OF ALZHEIMER'S DISEASE

P. Linning¹
H. Schieb²
S. Weidlich¹
J. Wiltfang²
H.-W. Klafki²
H.-J. Knölker¹

1 - TU Dresden

2 - University of Duisburg-Essen

hans-joachim.knoelker@tu-dresden.de

Alzheimer's disease (AD) is a neurodegenerative disorder leading to progressive loss of memory and cognitive abilities. Currently, there is no successful treatment for AD patients. In cooperation with several partners, we are developing a novel approach for the design of potential drugs against AD. A hallmark of AD is the formation of extracellular aggregates of A β peptides, known as amyloid plaques. These plaques are generated from the membrane protein APP (amyloid precursor protein) by sequential cleavage of APP involving firstly, β -secretase (BACE), and subsequently, γ -secretase. Thus, highly efficient inhibition of the β -secretase enzyme should lead to a potential therapy for AD. Cleavage of APP takes place only when APP and β -secretase are co-internalized into the cell via endocytosis. β -Secretase is found in structural microdomains of the cell membrane, known as lipid rafts and cleavage of APP by β -secretase occurs exclusively in these lipid rafts. Based on these findings, we have designed and synthesized a modified lipophilic β -secretase inhibitor with a tripartite structure, in which each unit exhibits a well-defined function.¹

β -Secretase Inhibitor: H-Glu-Val-Asn-Sta-Val-Ala-Glu-Phe-NH₂ (GL 189)



The known β -secretase inhibitor GL 189 (Calbiochem) is a transition state inhibitor showing no effect in a cellular assay. However, linking it to a membrane anchor via a spacer of defined length, leads to a tripartite structure which locates the β -secretase inhibitor to lipid rafts. The tripartite structure is transported into the cell by endocytosis and delivered to the site of action where β -secretase is active.¹⁻³ The first results emphasized that our tripartite structures are more effective compared to non-lipophilic modified inhibitors, by several orders of magnitude – in cell culture as well as in living organisms.² Recent progress in structural design, solid-phase synthesis and activity of membrane-anchored β -secretase inhibitors on A β -generation from wild-type and Swedish-mutant APP is described.⁴

References:

1. G. Jennings, H.-J. Knölker, K. Simons *et al.*, PCT Int Appl. WO 2005/097199.
2. G. Jennings, H.-J. Knölker, K. Simons *et al.*, *Science* **2008**, 320, 520.
3. H.-J. Knölker, K. Simons *et al.*, *Nature Reviews Drug Discovery* **2010**, 9, 29.
4. J. Wiltfang, H.-W. Klafki, H.-J. Knölker *et al.*, *Chem. Eur. J.* **2010**, 16, 14412.

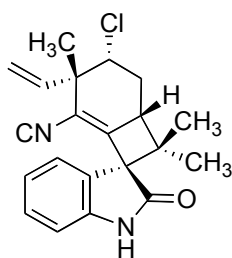
SYNTHETIC STUDIES OF OXINDOLE-CONTAINING NATURAL PRODUCTS

Colorado State University, Department of Chemistry, Fort Collins,
USA

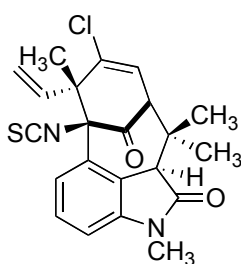
J.L. Wood

jjacjwood@gmail.com

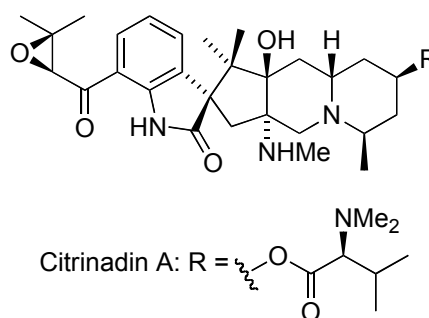
Recent efforts in our laboratories have focused on the synthesis of several oxindole-containing natural products. The evolution of synthetic strategies directed toward the welwitindolinones and citrinadins will be discussed.

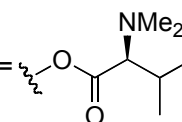


Welwitindolinone A



N-Methylwelwitindolinone C
Isothiocyanate



Citrinadin A: R = 

Citrinadin B: R = H

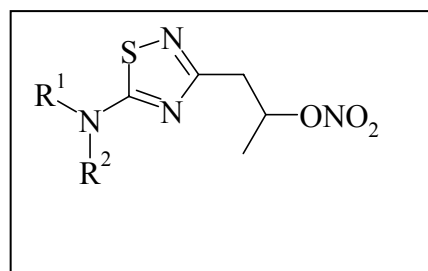
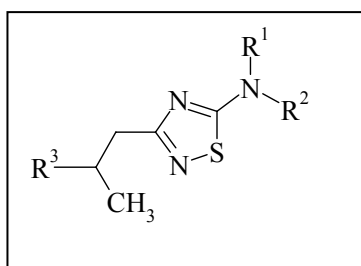
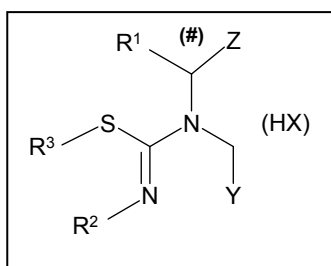
S.O. Bachurin
A.N. Proshin
V.V. Grigoriev
I.V. Serkov
L.N. Petrova
N.S. Zefirov

FOCUSED DESIGN OF MEDICINAL AGENTS FOR THE DISORDERS OF NEUROUS SYSTEM

Institute of Physiologically Active Compounds, Chernogolovka,
Russia
bachurin@ipac.ac.ru

The pronounced tendency for ageing in the main developed countries determines the strong requirement to modern medicinal chemistry of developing novel efficient drugs for such age-dependent diseases as Alzheimer's disease, parkinsonism, vascular dementia, etc. Due to the multifactorial nature of these disorders the compounds that affect more than one therapeutic target attract especial attention. In the present report the analysis of main approaches for design of «multi-target» CNS agents will be performed. Important place in this area occupy the compounds, which act on different glutamate CNS receptors, in particular, positive modulators of AMPA- (“ampakines”), and blockers of NMDA-receptors. The researches from the IPAC RAS and the organic chemistry chair of MSU undertook focused search, design and synthesis of radically new group of agents, combining in the same structure both these properties. Synthesis of original bioisosters of neuroprotective agents Dimebon and MK-801 was performed in series of isothioureia and thiadiazole derivatives. Bioscreening of focused libraries of synthesized structures revealed number of hit-compounds, and on the ground of preclinical trials the lead-compounds in these structural classes were selected.

As an alternative approach the synthesis and primary testing of compounds, containing additional NO-generating pharmacophore, was performed. It was revealed that such modification leads to a significant change in spectrum of the primary pharmaceutical activity.

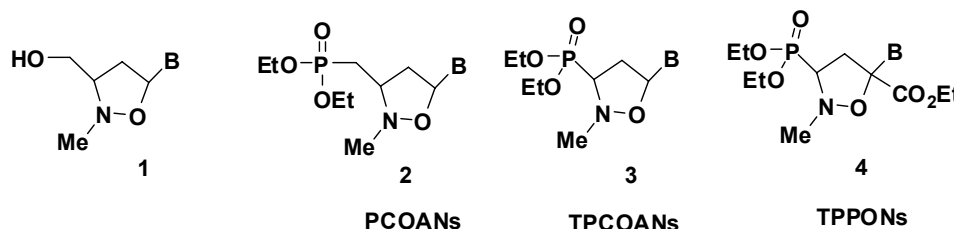


PHOSPHONATED N,O-NUCLEOSIDES: SYNTHESIS AND BIOLOGICAL EVALUATION**R. Romeo**University of Messina, Dipartimento Farmaco-chimico, Messina, Italy
gromeo@unime.it

Modification of naturally occurring nucleosides is an important research area for the development of new antiretroviral agents. In particular, heterocyclic replacement of the ribose moiety has resulted in the synthesis of new effective anti-HIV drugs.¹ In this context, we have reported the synthesis of a series of nucleoside analogues where the furanose ring has been replaced by a N,O-heterocyclic system: carbocyclic 2'-oxa-3'-azanucleosides **1** are endowed with interesting physiological activities.

Most of the nucleoside analogues possessing antiviral activities rely on phosphorylation by specific kinases; moreover, among the three successive phosphorylation steps, the first is rate-limiting. On this basis, analogues, where the phosphate moiety is changed to isosteric and isoelectronic phosphonates, have been designed; these compounds mimic the nucleoside monophosphates and are able to bypass the initial selective enzymatic monophosphorylation step.²

Recently, we have described the synthesis of the new class of phosphonated carbocyclic 2'-oxa-3'-azanucleosides (PCOANs) **2**,³ which have been shown to be potent inhibitors of RT of different retroviruses and have been proposed for ensuring a long last control of HTLV-1, an oncogen retrovirus associated with adult T-cell leukemia/lymphoma. We have also synthesized truncated phosphonated carbocyclic 2'-oxa-3'-azanucleosides (TPCOANs) **3**, where the phosphonate group is directly linked to the C-4' position of the sugar moiety. The obtained compounds exert a specific inhibitory activity on two different types of commercial RT from animal retroviruses, comparable with that of the well-known AZT, following incubation with human PBMCs crude extract.⁴



B = Ty, 5-Fu, Cy, U

Starting from these findings, to obtain derivatives more potent and more active against different virus strains, we have extended our studies to the synthesis and biological evaluation of a new class of compounds bearing a hydroxymethyl group at the anomeric carbon atom, the truncated phosphonated N,O-psiconucleosides (TPPON) **4**. To the best of our knowledge, no example of this kind of compounds has been reported in literature until now.

Preliminary studies show that β -anomers are able to inhibit the RT of different retroviruses at nM concentration, comparable to Tenofovir. Truncated phosphonated N,O-psiconucleosides represent a new template of nucleoside analogs which deserve further investigations as lead compounds for extending the current spectrum of antiviral activity of modified nucleosides, avoiding unwanted side effects.

References:

1. G. Romeo, U. Chiacchio, A. Corsaro, P. Merino, *Chem. Rev.*, **2010**, *110*, 3337-3370
2. U. Chiacchio, A. Rescifina, P. Merino, B. Macchi, E. Balestrieri, A. Mastino, A. Piperno, D. Iannazzo, R. Romeo, *J. Med. Chem.*, **2009**, *52*, 4054-4057.
3. U. Chiacchio, A. Rescifina, D. Iannazzo, A. Piperno, R. Romeo, E. Balestrieri, A. Mastino, G. Romeo, *J. Med. Chem.*, **2007**, *50*, 3747-3760
4. A. Piperno, S. Giofrè, D. Iannazzo, R. Romeo, G. Romeo, U. Chiacchio, D.G. Piotrowska, *J. Org. Chem.*, **2010**, *75*, 2798-2828

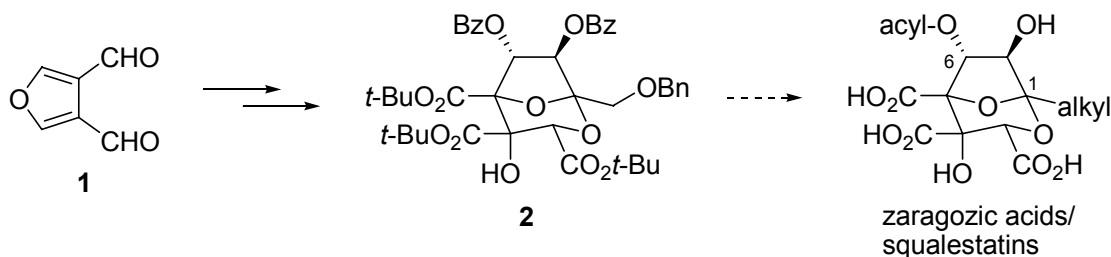
RECENT ADVANCES IN THE TOTAL SYNTHESIS OF BIOACTIVE NATURAL PRODUCTS

P.R. Metz

Technische Universität Dresden, Department of Chemistry, Dresden,
Germany
peter.metz@chemie.tu-dresden.de

The zaragozic acids/squalestatins isolated from various fungi are potent inhibitors of squalene synthase and in part *ras*-farnesyl protein transferase, too. Due to their strong physiological effects and complex molecular structure, these natural products have stimulated enormous synthetic efforts.¹

An efficient two-directional route from dialdehyde **1** to the enantiopure heterobicyclic compound **2** is presented.^{2,3} Triester **2** offers itself as a fully substituted general intermediate for naturally occurring zaragozic acids/squalestatins and unnatural analogs. The application of **2** to the formal synthesis of zaragozic acids A and C and the first total synthesis of zaragozic acid D is discussed.⁴



References:

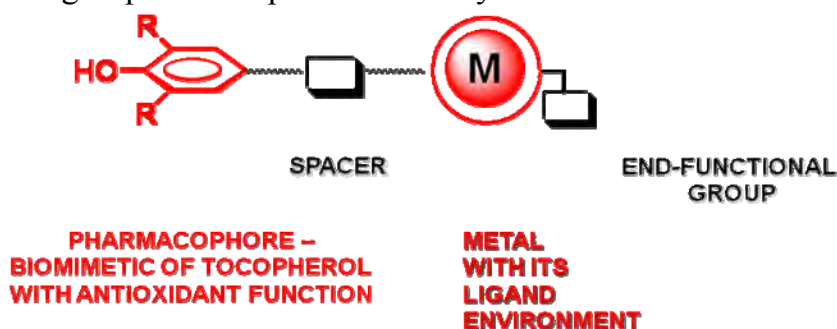
- ¹ Recent reviews: a) S. Nakamura, *Chem. Pharm. Bull.* **2005**, 53, 1-10; b) A. Armstrong, T. J. Blench, *Tetrahedron* **2002**, 58, 9321-9349; c) N. Jotterand, P. Vogel, *Curr. Org. Chem.* **2001**, 5, 637-661.
- ² Prior model study: Y. Wang, S. Gang, A. Bierstedt, M. Gruner, R. Fröhlich, P. Metz, *Adv. Synth. Catal.* **2007**, 349, 2361-2367.
- ³ Y. Wang, O. Kataeva, P. Metz, *Adv. Synth. Catal.* **2009**, 351, 2075-2080.
- ⁴ Y. Wang, P. Metz, *Chem. Eur. J.* **2011**, 17, 3335-3337.

A NOVEL STRATEGY IN BIOORGANOMETALLIC CHEMISTRY FOR THE DESIGN OF PROTECTORS AGAINST OXIDATIVE STRESS

E.R. Milaeva

Moscow State Lomonosov University, Organic Chemistry Department,
Moscow, Russia
milaeva@org.chem.msu.ru

A novel approach for the design of drug candidates for the therapy of oxidative stress induced pathological states is presented. The novel bioconjugable membrane active compounds consist of pharmacophore - 2,6-dialkylphenol, biometal (Fe, Mn, Cu, Cu, Ni, Zn), end-functional group for transport and affinity.



The synthesis, physico-chemical properties and physiological activity of novel compounds will be discussed. The compounds perform the properties of multitarget agents and act in $H\cdot$, H^+ and e^- transfer processes. The biological activity has been evaluated in the *in vitro*, *ex vivo*, *in vivo* experiments in peroxidation of lipids in mitochondria, neurons, liver and brain homogenates, liposomes and lipids structural fragments, as well as in enzymatic reactions (xanthin oxidase, lipoxygenase, catalase, superoxide dismutase, cytochromes P450). The activity in oxidation reaction, solubility (logD), blood-brain barrier penetration (PAMPA, PAMPA BBB), has been studied. The novel membrane-active compounds are perspective candidates as protectors against oxidative stress, mito- and neuroprotectors.

References:

1. E.Milaeva. Metal-based antioxidants – potential therapeutic candidates for prevention the oxidative stress (Review). *Current Topics in Med.Chem.* 2011, vol. 12 (in press).
2. *Bioinorg. Chem. & Appl.* 2010, ID 165482.
3. *Applied Cat. B: Env.*, 2011, 101, 417-425.
4. *Inorg. Chim. Acta*, 2010, 363, 1455–1461.
5. *Inorg. Chem.* 2010, 49, 488–501.
6. *Macroheterocycles*. 2010, 3, 139-144.
7. *J. Catal.*, 2010, 270, 153-162.
8. *Dokl. Chem.*, 2010, 432, 629-631; 2008, 419, 62–64.
9. *Talanta*. 2009, 78, 126-131.
10. *Heteroatom Chem.*, 2009, 20, 70-80; 2008, 19, 490-494; 562-568.
11. *Eur. J. Med. Chem.* 2008, 43, 327-335.
12. *J. Inorg. Biochem.* 2008, 102, 1348–1358.
12. *Cat. Comm.* 2007, 8, 2069-2073.
13. *J.Organomet. Chem.* 2007, 692, 5339-5344.
14. *Mol. Phys.* 2007, 105, 2185-2194.
15. *Russ. Chem. Bull.* 2007, 737-743, 744-750; 800-803.

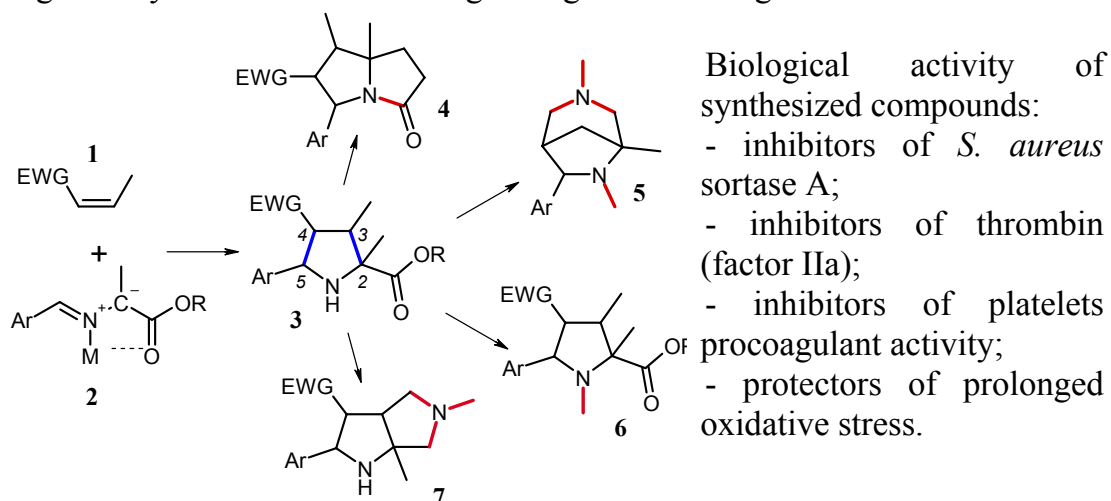
This work was supported by RFBR (08-03-00844, 09-03-00090, 09-03-12261, 10-03-01137, 11-03-01134); Program 9 RAS "Medicinal Chemistry"; Russian State Program (02.513.12.0033); NATO PDD(CP)-(CBP.NR.NRCLG 982211, 983167), (CBP.EAP.CLG 983239).

APPLICATION OF 5-ARYLPYRROLIDINE-2-CARBOXYLIC ACID SCAFFOLD FOR DESIGN OF BIOLOGICALLY ACTIVE COMPOUNDS

M.V. Lomonosov Moscow State University, Department of Chemistry,
Moscow, Russia
kudr@org.chem.msu.ru

K.V. Kudryavtsev

Interaction of electron-deficient olefins (**1**) and azomethine ylides (**2**) is an efficient strategy for synthesis of functionalized derivatives of 5-arylpyrrolidine-2-carboxylic acids (**3**) [1-6]. Synthesized compounds contain 5-arylproline molecular scaffold with particular physico-chemical characteristics providing effective interactions with different biological targets and structural modifications potential. Subsequent intra- and intermolecular functional groups condensations in compounds (**3**) lead to pyrrolizidinones (**4**), 3,6-diazobicyclo[3.2.1]octanes (**5**), diverse N-substituted 5-arylprolines (**6**), octahydropyrrolo[3,4-*b*]pyrroles (**7**). Novel small-molecule compounds classes (**3-7**) with promising activity were identified during biological screening.



Structure-activity relationships (SARs) and structural modifications directed to the innovative drugs development will be discussed in the report.

References:

1. K.V. Kudryavtsev, M.Yu. Tsentalovich, A.S. Yegorov, E.L. Kolychev. Highly Diastereoselective Synthesis of Chimeras of Proline and Glutamate // *J. Heterocyclic Chem.*, **2006**, v. 43, p. 1461-1466.
2. K.V. Kudryavtsev, N.V. Nukolova, O.V. Kokoreva, E.S. Smolin. Stereoselective Synthesis of Functional Derivatives of 2-(2-Carboxyethyl)pyrrolidine-2-carboxylic Acid // *Russ. J. Org. Chem.*, **2006**, v. 42, p. 412-422.
3. K.V. Kudryavtsev, M.L. Bentley, D.G. McCafferty. Probing of the *cis*-5-Phenyl Proline Scaffold as a Platform for the Synthesis of Mechanism-Based Inhibitors of the Staphylococcus aureus Sortase SrtA Isoform // *Bioorg. Med. Chem.*, **2009**, v. 17, p. 2886-2893.
4. K.V. Kudryavtsev. Synthesis of Bridged Heterocycles from *cis*-Pyrrolidine-2,4-dicarboxylic Acids: I. 3,6-Diaza-bicyclo[3.2.1]octanes // *Russ. J. Org. Chem.*, **2010**, v. 46, p. 372-379.
5. K.V. Kudryavtsev. Efficient Synthesis of Functionalized Diazacyclopenta[*c*]pentalene with Multiple Intermolecular Interactions in Crystal // *Heterocycles*, **2011**, v. 83, p. 323-330.
6. K.V. Kudryavtsev, E.V. Trofimova, A.O. Borisova. Pyrrolidine-2,3,4-tricarboxylic Anhydrides: I. Organocatalytic Synthesis and Fusion of Pyrrole Ring by the Action of *p*-Fluorobenzylamine // *Russ. J. Org. Chem.*, **2011**, v. 47, p. 556-562.

DNA - "RECOGNIZING" LIGANDS. DESIGN AND RESULTS

A.V. Garabadzhiu¹
D.V. Ovchinnikov²

1 - St. Petersburg State Institute of Technology (Technical University),
St. Petersburg, Russia

2 - St. Petersburg State Institute of Technology (Technical University),
Dep. of Organic Chemistry, St. Petersburg, Russia
rvwp98@gmail.com

The branch of synthetic organic chemistry, based on the design, synthesis and study of medical and biological properties of low molecular weight ligands that specifically bind to DNA is tightly related to tumor chemotherapy.

Historically, first, it was hypothesized that the target of actinomycin D, well-known antitumor antibiotic of natural origin is DNA. This was confirmed by the molecular genetic studies and served as a starting point in developing the whole branch of the chemistry of biologically active compounds, able to form stable reversible complexes with DNA. Compounds of this type have found application in medical practice as drugs - antineoplastic, antiviral, including anti-HIV drugs that cause the differentiation of tumor cells, as well as inducers of interferon synthesis.

The key task in the design of DNA "recognizing" ligands is the problem of creating compounds specific to certain nucleotides sequences. This, in turn, supposed "blocking" of the genome regions with that nucleotide sequence up to complete suppression of gene expression.

The strategy of synthesis of DNA complexones assumed design of ligands of two types, differed in terms of synthetic complexity, the nature of DNA binding, a type of "recognition" of the nucleotide sequences of biopolymers. We proceeded from the assumption that increasing the specificity of ligand binding to DNA can be achieved through combining in one molecule of several groups that are capable of independent interaction with DNA that are specific to different nucleotides and their sequences, including interacting with DNA by different mechanisms. Synthesis and study of simple ligands containing fragments that are specific only to the GC-rich regions of DNA (the derivatives of phenoxy (thio) zines, acridines, carbazoles, coumarins) or only to AT-rich regions (polybenzimidazole derivatives, indoles, polypyrrolcarboxamides) have shown the limitations of the ligands of this kind. DNA binding constants of the latters were in the range of $10^5 - 10^7 \text{ mol}^{-1}$, whereas those for the majority of enzymes lay in the region of $10^{10} - 10^{13} \text{ mol}^{-1}$. Developing of polyfunctional DNA ligands had allowed not only to expand the binding(recognition) site on biopolymers' surface, but also greatly enhance the affinity of ligands to DNA which is characterized by the binding constant of about $10^8 - 10^9 \text{ mol}^{-1}$. One of the promising approach in polyfunctional DNA ligands design is introducing alkylating/chelating fragments or creating ampholitic functionality.

Breakthrough in the study of therapeutic aspects of "recognition" happened with the discovery of RNA - interference, which is the suppression of gene expression by means of special short double-stranded RNA molecules. The specificity of the latter is so large that they are able to discern the point (1-2 nucleotide) defects in the DNA molecule. Opportunities of this kind are regarded as one of the most important discoveries in molecular oncology in the past decades, and open up broad prospects in developing anti-cancer therapy. Success of RNA interference and possibility of computer assisted predicting(using PASS programm) open new perspectives in the design of DNA "recognizing" ligands, to establish the relationship between the structure, affinity to biopolymers and the cytotoxicity level.

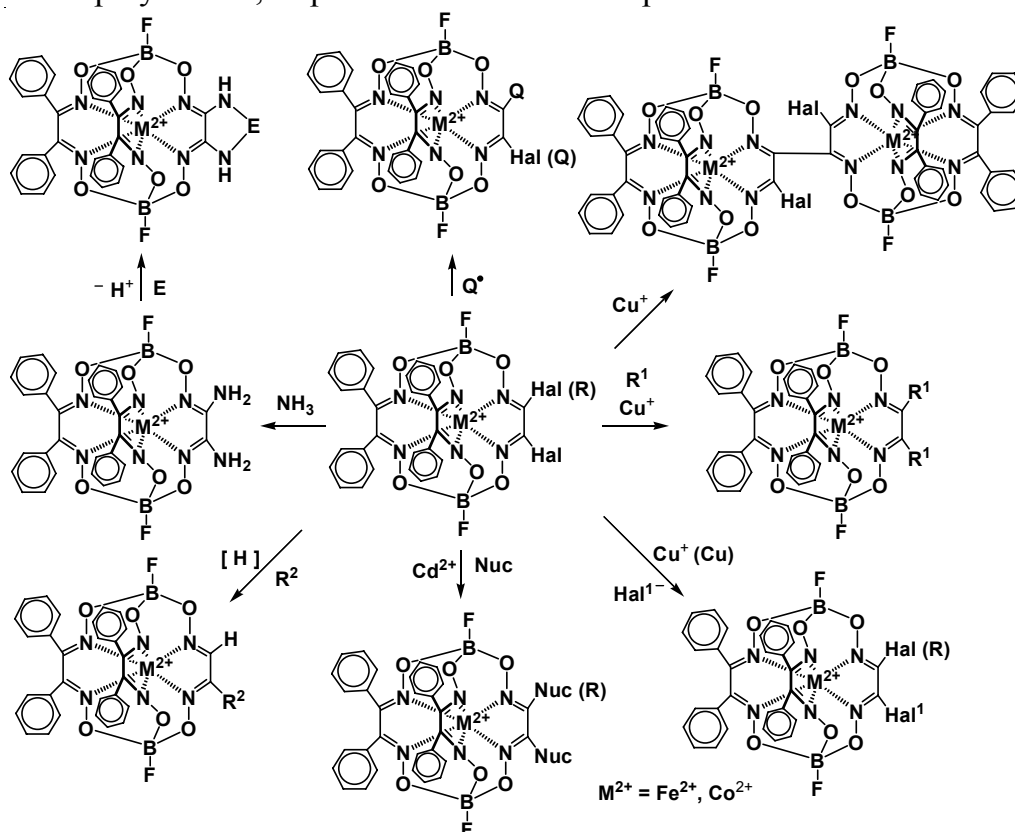
ORGANIC REACTIONS OF THE METAL-CENTERED QUASI-AROMATIC CAGES AND THEIR POTENTIAL FOR THE DESIGN OF THE TOPOLOGICAL DRUGS

Y.Z. Voloshin¹
O.A. Varzatskii²
Y.N. Bubnov¹

1 - Nesmeyanov Institute of Organoelement Compounds RAS,
Moscow, Russia

2 - Vernadskii Institute of General and Inorganic Chemistry NANU,
Kiev, Ukraine
voloshin@ineos.ac.ru

The following organic reactions of the polyene macrobicyclic *d*-metal complexes (clathrochelates) as the metal-centered quasi-aromatic systems and the perspectives of their practical application in biochemistry and medicine will be discussed: cadmium-promoted nucleophilic substitutions of the reactive halogen-containing clathrochelate precursors with N,O,S,C-nucleophiles¹; copper(I)-promoted substitution reactions of these precursors and unexpected dehalogenation – reduction processes at a clathrochelate framework²; copper-promoted halogen exchange at the *vic*-dihalogen-substituted macrobicyclic α -dioximate frameworks; copper(I)-promoted coupling of the clathrochelate precursors giving the new C–C conjugated bis-clathrochelate molecular scaffolds; free-radical addition – elimination reactions of polyene macrobicyclic framework as a novel approach to its functionalization³; electrophilic substitutions of the deprotonated amine-functionalized macrobicyclic ligands with 1,2-dicarbonyl compounds resulting in an extension of their polyene system⁴; the potential of the metal clathrochelates for the design of the topological and allosteric drug candidates and the results of their *in silico* and *in vitro* testing as the transcription inhibitors of the T7 RNA polymerase, Topoisomerase I and HIV protease⁵.



References:

- (1) (a) O.A.Varzatskii, Y.Z.Voloshin and others, *Polyhedron* **28**, 2009, 3431; (b) Y.Z.Voloshin, O.A.Varzatskii and others, *Eur. J. Inorg. Chem.*, 2010, 5401; (c) O.A.Varzatskii, Y.Z.Voloshin and others, *Inorg. Chem. Comm.*, 2011, INOCHE-S-11-00346. (2) Y.Z.Voloshin, A.S.Belov and others, *Inorg. Chim. Acta*, 2011, in press. (3) M.A.Vershinin, A.B. Burdukov, I.V.Eltsov and others, *Polyhedron* **30**, 2011, 1233. (4) M.A.Vershinin, A.B.Burdukov and others, *Inorg. Chim. Acta* **366**, 2011, 91. (5) (a) Y.Z.Voloshin, O.A.Varzatskii and others, *Proc. 9th EUROBIC*, 2008, 71; (b) Y.Voloshin, O.Varzatskii and others, *Proc. 10th EUROBIC*, 2010, 29.

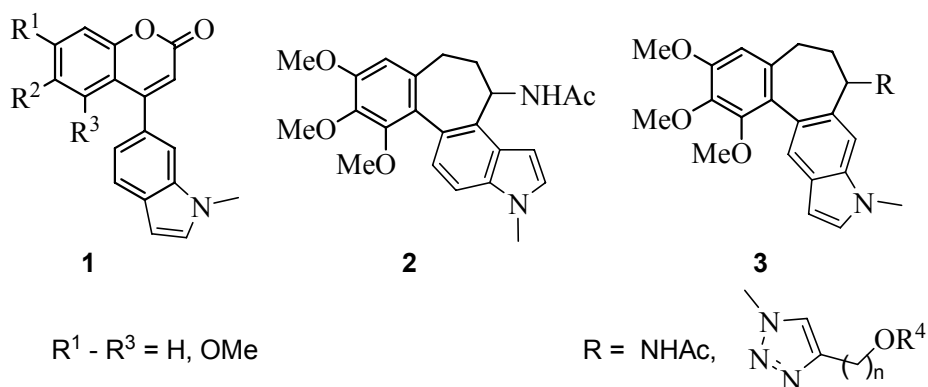
The authors gratefully acknowledge support of the RFBR (grants 09-03-00540, 09-03-00688, 11-03-00986, 11-03-90458) and RAS (programs 6, 7 and P7).

SYNTHESIS AND BIOLOGICAL EVALUATION OF NEW COUMARIN- AND COLCHICINE-TYPE TUBULIN ASSEMBLY INHIBITORS

N.S. Sitnikov¹
S. Combes²
I.P. Beletskaya³
J. Velder⁴
H.G. Schmalz⁴
A.Yu. Fedorov¹

1 - Nizhnii Novgorod N.I. Lobachevsky State University, Department of Organic Chemistry, Nizhnii Novgorod, Russia
2 - University d'Aix-Marseille, Saint-Jerome Faculty, Marseille, France
3 - M.V. Lomonosov State University, Department of Chemistry, Moscow, Russia
4 - University of Koln, Department of Chemistry, Koln, Germany
afnn@rambler.ru

A range of indole-containing coumarins and allocolchicinoids **1** - **3** was synthesized:



Coumarins **1** inhibit *in vitro* microtubule assembly with a substoichiometric mode of action and exhibit excellent cytotoxic activity against HBL100 epithelial cell line. Colchicinoids **2** - **3** manifest antitumor activity at nanomolar or even subnanomolar concentration range (Burkitt-like lymphoma cells), along with particularly low unspecific cytotoxicity as determined by LDH-release measurements.

This work was supported by Russian Foundation for Basic Research (09-03-00647-a), German Academic Exchange Service (A-08-79551), Council for grants under the President of Russia (MD-5606.2010.3) and Federal Purpose Program for Dr. Science 2011

**TARGET SYNTHESIS OF BIOLOGICALLY ACTIVE
COMPOUNDS IN THE SERIES OF
FUNCTIONALIZED QUATERNARY PHOSPHONIUM
SALTS**

I.V. Galkina¹
E.V. Tudryi¹
L.M. Yusupova²
F.S. Levinson²
M.Kh. Lutfullin³
M.Sh. Shakurov³
M.P. Shulaeva⁴
O.K. Pozdeev⁴
S.N. Egorova⁵
V.I. Galkin¹

1 - Kazan Federal University, A.M. Butlerov Chemical Institute,
Kazan, Russia
2 - Kazan State Technological University, Kazan, Russia
3 - Kazan State Academy of Veterinary Medicine, Kazan, Russia
4 - Kazan State Medical Academy, Kazan, Russia
5 - Kazan State Medical University, Kazan, Russia
vig54@mail.ru

Probably, there are not too many branches of organic chemistry, which are so closely related to creation of biologically active compounds for medicine and agriculture, as it is in the chemistry of organophosphorus compounds. At the last years a grate volume of information has been appeared in patent literature concerning high biological activity of quaternary phosphonium salts. So, elaboration of new medicines on the basis of fuctionalized quaternary phosphonium salts is an actual task.

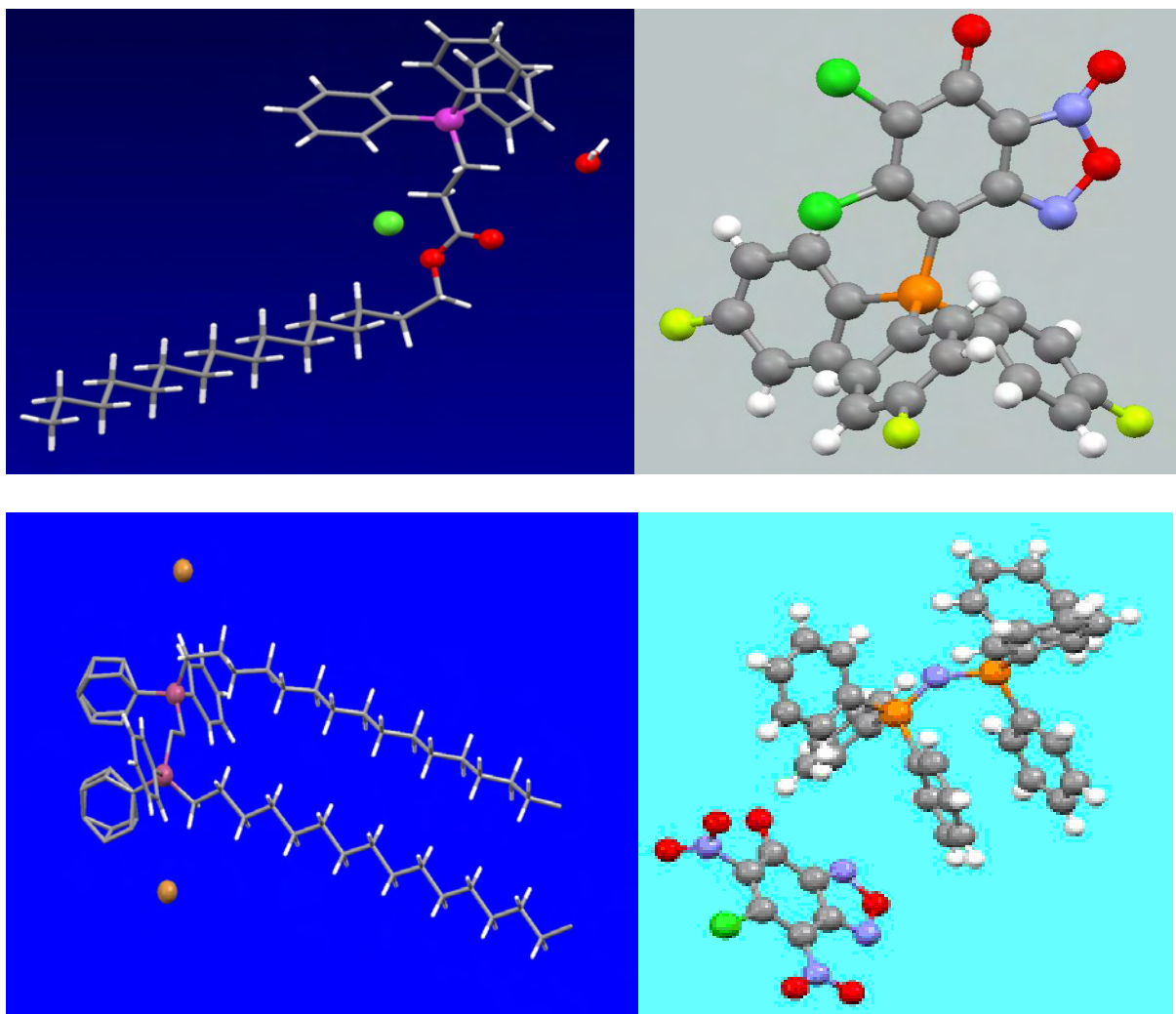
Thereupon, elaboration and perfection of methods of the directed organic synthesis of new medical products in the frameworks of biomimetic approach, consisting in imitation of structure or function of more complicated natural biological molecules and final creation of artificial biosimilar molecules-models, become more and more actual.

In this work the following results on the basis of biomimetic approach have been obtained:

- The effective method of synthesis of quaternary phosphonium salts with the higher alkyl radicals, analogues of components of natural cellular membranes, has been elaborated on the basis of tertiary phosphines and carboxylate phosphobetaines. The antibacterial and antifungal activity of the synthesized compounds concerning pathogenic microflora has been studied;
- Reactions of phosphorylation and amination of biologically active nitrogen-containing heterocycles (substituted benzofuroxans and -furazans) by tertiary phosphines and various amines have been spent. The products obtained possess by high biological activity in relation to pathogenic microflora of the human and animals, and they are NO generators in vivo and in vitro. Stable NH and OH radicals have also been isolated in these reactions;
- Synthesis of different metallocomplexes on the basis of carboxylate phosphobetaines (analogs of amino acids betaines) with a wide series of biogenic metals to obtain structural models of enzymes biocenters has been elaborated.

As a research result, 137 new compounds have been obtained, the structure of more than 70 key molecules has been confirmed by X-ray analysis, 47 compounds among the synthesized products have shown exclusively high biological activity concerning pathogenic microflora.

On the basis of most perspective compounds the concrete antibacterial, antifungal and antiparasitic preparations have been elaborated, which have been protected by 7 patents of the Russian Federation.



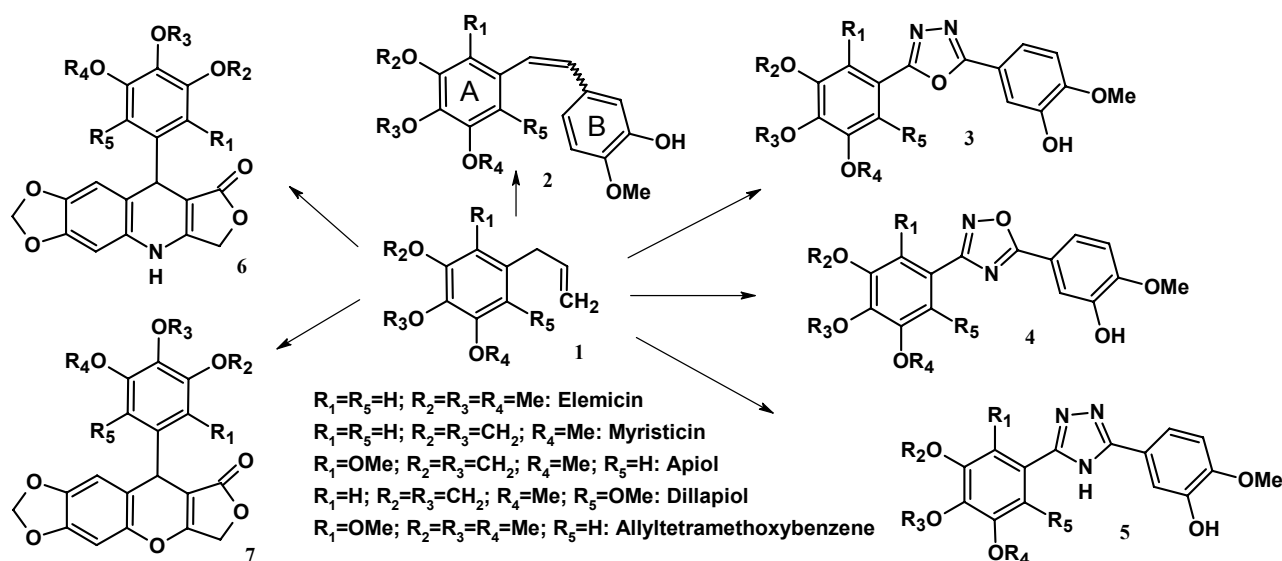
We are grateful to Prof. O.N. Kataeva, Dr. D.B. Krivolapov, and Prof. I.A. Litvinov (A.E. Arbuzov Institute of Organic and Physical Chemistry of the Russian Academy of Sciences) for X-ray investigations.

PLANT POLYALKOXYBENZENE MODIFICATION - THE APPROACH TO HIGH EFFECTIVE ANALOGS OF NATURAL ANTIMITOTIC DRUGS

V.V. Semenov¹
N.B. Chernysheva¹
D.V. Tsyganov¹
M.N. Semenova²

1 - N.D. Zelinsky Institute of Organic Chemistry
2 - Institute of Developmental Biology RAS
vs@zelinsky.ru

A number of natural plant-derived cytostatics with possible chemotherapeutic value in cancer contain diverse polyalkoxybenzene fragments. However in many cases the source plant material is unavailable in Russia. We have synthesized heterocyclic derivatives of natural polyalkoxybenzenes to obtain readily available compounds with high antiproliferative activity. The CO₂ seed extracts of parsley and dill varieties featuring a high content of allylpolyalkoxybenzenes (**1**) served as a starting material. The compounds (**1**) were isolated in large scale (5–40 kg) using both industrial and IOC pilot plant devices. The key building blocks for target synthesis, i. e., polyalkoxybenzoic aldehydes, acids, and nitriles, were obtained in high yields (70–90%) by isomerization, ozonation, and oxidation reactions.



We have synthesized novel polyalkoxyaryl derivatives of natural antimitotic compounds combretastatin (**2–5**) and podophyllotoxin (**6, 7**). The biological activity of **2–7** has been evaluated *in vivo* using a phenotypic sea urchin embryo assay and *in vitro* by conventional procedures including NCI cytotoxicity test on 57 human cancer cell lines and inhibition of purified tubulin polymerization.

It was found that molecules **2–7** displayed promising antimitotic tubulin destabilizing effects along with the cytotoxicity against a panel of human cancer cell lines. The most potent derivatives exhibited higher antiproliferative activities than those of the respective parent natural products currently in clinical trials.

FUCOIDANS – A PLATFORM FOR NEW DRUGS DISCOVERY

N.E. Nifantiev¹

N.E. Ustyuzhanina¹

N.A. Ushakova²

M.E. Preobrazhenskaya²

M.I. Bilan³

A.I. Usov³

A.A. Grachev¹

A.S. Shashkov⁴

A.G. Gerbst¹

1 - N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Laboratory of Glycoconjugate Chemistry, Moscow, Russia

2 - V.N. Orekhovich Research Institute of Biomedical Chemistry, Russian Academy of Medical Sciences, Moscow, Russia

3 - N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Laboratory of Plant Polysaccharides, Moscow, Russia

4 - N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Laboratory NMR Spectroscopy, Moscow, Russia

nen@ioc.ac.ru

Natural polysaccharides fucoidans were found in many species of brown seaweeds and in some echinoderms. Fucoidans often consist from selectively O-sulfated α -L-fucopyranose residues linked through (1 $\rightarrow$ 2)-, (1 $\rightarrow$ 3)- and (1 $\rightarrow$ 4)-linkages with the presence of branched points that makes difficult their detail structural characterization. At the same time these biopolymers exhibit very interesting profile of biological activity. Particularly, they may effectively inhibit microbial and viral adhesion to host cells, angiogenesis development, P- and L-selectin mediated inflammation, blood coagulation and some other biological processes. It should be noted that the structure of fucoidans differ absolutely from human ligands involved in the development of above listed diseases and processes, thus the pharmacophore fucoidan fragments are the efficient mimetics of these human ligands and thus can be considered as potential drugs.

To assess structures of pharmacophore fucoidan fragments we conduct systematic synthesis of corresponding short and long chain linear and branched selectively and per-O-sulfated oligofucosides and study their NMR and conformational characteristics and biological properties. Obtained results will be summarized in this lecture.

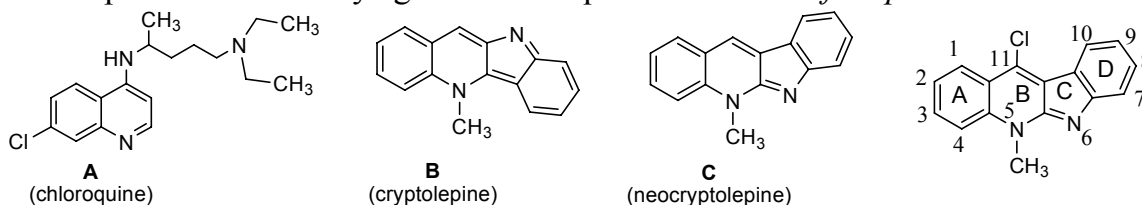
Selected publications: E.A. Khatuntseva, N.E. Ustuzhanina, G.V. Zatonskii, A.S. Shashkov, A.I. Usov, and N.E. Nifantiev, "Synthesis, NMR and conformational studies of fucoidan fragments. Part 1.", *J. Carbohydr. Chem.*, 19 (2000) 1151-1173; N.E. Ustuzhanina, V.B. Krylov, A.A. Grachev, A.G. Gerbst, N.E. Nifantiev, "Synthesis, NMR and Conformational Studies of Fucoidan Fragments. VIII.", *Synthesis*, (2006) 4017-4031; A.A. Grachev, A.G. Gerbst, N.E. Ustuzhanina, V.B. Krylov, A.S. Shashkov, A.I. Usov, and N.E. Nifantiev, «Modeling of polysaccharides with oligosaccharides: how large should the model be?» (Focus Article), *Mendeleev Commun.* 17 (2007) 57-62; A. Cumashi, N.A. Ushakova, M.E. Preobrazhenskaya, A.D'Incecco, A. Piccoli, L. Totani, N. Tinari, G.E. Morozevich, A.E. Berman, M.I. Bilan, A.I. Usov, N.E. Ustuzhanina, A.A. Grachev, C.J. Sanderson, M. Kelly, G.A. Rabinovich, S. Iacobelli, and N.E. Nifantiev, "A comparative study of the antiinflammatory, anticoagulant, antiangiogenic, and antiadhesive activities of nine different fucoidans from brown seaweeds", *Glycobiology*, 17 (2007) 541-552; V.B. Krylov, N.E. Ustyuzhanina, A.A. Grachev, and N.E. Nifantiev "Efficient acid-promoted per-O-sulfation of organic polyols", *Tetrahedron Lett.* 49 (2008) 5877-5879; N.E. Ustyuzhanina, V.B. Krylov, A.I. Usov, N.E. Nifantiev "Synthesis of fucoidan fragments" In: "Progress in the synthesis of complex carbohydrate chains of plant and microbial polysaccharides", N.E. Nifantiev Ed., ISBN 978-81-7895-424-0; 2009, 131-154; V. B. Krylov, Z.M. Kaskova, D. Z. Vinnitskiy, N.E. Ustyuzhanina, A.A. Grachev, A.O. Chizhov, N.E. Nifantiev "Acid-promoted synthesis of per-O-sulfated fucooligosaccharides related to fucoidan fragments", *Carbohydr. Res.* 346 (2011) 540-550; D.O. Croci, A. Cumashi, N.A. Ushakova, M.E. Preobrazhenskaya, A. Piccoli, L. Totani, N.E. Ustyuzhanina, M.I. Bilan, A.I. Usov, A.A. Grachev, G.E. Morozevich, A.E. Berman, C.J. Sanderson, M. Kelly, P. Di Gregorio, C. Rossi, N. Tinari, S. Iacobelli, G.A. Rabinovich, N.E. Nifantiev "Fucans, but not fucomannoglucuronans, determine the biological activities of sulfated polysaccharides from *Laminaria saccharina* brown seaweed" *PLoS ONE* 6(2): e17283. doi:10.1371/journal.pone.0017283.

**PHOSPHORYLATION OF DIENONE
PHARMACOPHORE FOR TARGETED DESIGN OF
HIGHLY EFFECTIVE AND FLUORECENT
CYTOSTATICS**

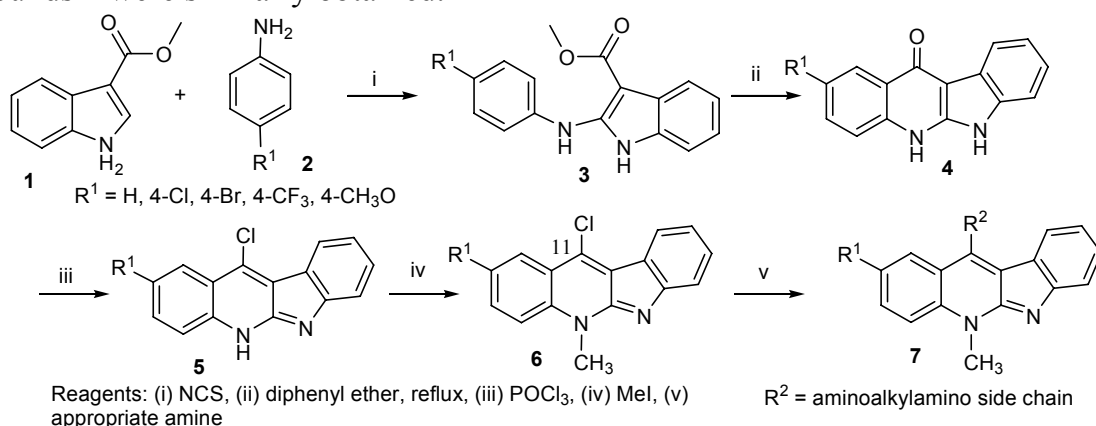
T. Inokuchi¹
I. El Sayed²
Z.-W. Mei¹
L. Wang¹
W. Peng¹
W.-J. Lu¹

1 - Graduate School of Natural Science and Technology, Okayama University, Japan
 2 - El Menoufeia University, Chemistry Department, Faculty of Science, Egypt
 inokuchi@cc.okayama-u.ac.jp

Malaria is a major cause of morbidity and mortality worldwide, especially in developing countries where it has serious economic and social costs. In search for novel anti-infective compounds, we focused on minor alkaloids of *C. sanguinolenta* such as neocryptolepine (5-methyl-5*H*-indolo[2,3-*b*]quinoline, cryptotackieine) (**C**), which also showed antiparasmodial activity against chloroquine-resistant *P. falciparum*.



Neocryptolepines with a substitution in position 11 were prepared from indole-3-carboxylate **1** and anilines **2**. The intermediate methyl 2-(phenylamino)-1*H*-indole-3-carboxylates **3**, obtained via chlorination with NCS followed by addition of the aniline as trichloroacetate, were cyclised in boiling diphenyl ether to 5,6-dihydro-11*H*-indolo[2,3-*b*]quinolin-11-ones **4** which were dehydroxychlorinated with POCl₃, giving **5**. Methylation afforded 11-chloroneocryptolepine **6**, which was aminated via an S_NAr reaction in neat *N*¹,*N*¹-diethylpentane-1,4-diamine at high temperature, yielding the target compound **7**. Using 3- and 4-chloroanilines **2** as starting materials, 2- and 3-chloro-substituted compounds **7** were similarly obtained.



Aminoalkylamino-substituted compounds and their chloro-substituted precursors were evaluated for *in vitro* antiparasmodial activity against a chloroquine-sensitive *P. falciparum* strain. In addition, we would describe the improved synthetic strategy for neocryptolepine analogues and extent of their diversity, and application to the anticancer agents.

6-BENZYLPIRIMIDIN-4(3H)-ONES. NON-NUCLEOSIDE HIV REVERSE TRANSCRIPTASE INHIBITORS: CHEMICAL SYNTHESIS AND STRUCTURE-ACTIVITY RELATIONSHIPS

I.A. Novakov¹
B.S. Orlinson¹
L.L. Brunilina²
M.B. Nawrozkij¹

1 - Volgograd State Technical University, Analytical, Physical Chemistry and Chemistry of Polymers Department, Volgograd, Russia
2 - Volgograd State Technical University, Organic Chemistry Department, Volgograd, Russia
alfentanyl@rambler.ru

6-Benzylpyrimidin-4(3H)-ones, bearing different substituents at the second position of the pyrimidine nucleus, together with the presence of small alkyl groups in the fifth position of the heterocyclic moiety and benzyl radical alpha position represent the family of potent and selective anti-HIV agents, targeting the viral reverse transcriptase. This class of compounds was first described by the group of professor Marino Artico in 1993. The above mentioned prototypes, so called DABOs (3,4-dihydro-2-alkoxy-6-benzyl-4-oxopyrimidines) have been prepared during the search of new antibacterials, structurally related to trimethoprim - a well-known dehydrofolatereductase inhibitor. For today, a great number of DABO analogues are described and tested for their biological activity: DABOs, S-DABOs (2-(alkylsulfanyl)-6-benzylpyrimidin-4(3H)-ones), F₂-S-DABOs (2-(alkylsulfanyl)-6-(2,6-difluorobenzyl)pyrimidin-4(3H)-ones), DATNOs (2-(alkylsulfanyl)-6-(naphthylmethyl)pyrimidin-4(3H)-ones), NH- and N,N-DABOs (2-(alkylamino)- and 2-(dialkylamino)-6-benzylpyrimidin-4(3H)-ones) and C-DABOs or *carbo*-DABOs (2-alkyl-6-benzylpyrimidin-4(3H)-ones) are among them.

Classical DABO-synthesis utilizes 2-arylacetic (or 2-arylpropionic) acids and their nitriles as the starting materials. Successful conversion of the latter into the corresponding alkyl esters of 4-aryl-3-oxobutanoic acids and subsequent condensation with different carbamide derivatives leads to the construction of 6-(arylmethyl)pyrimidin-4(3H)-one scaffold. An additional pyrimidine C² modification results in a variety of DABO-analogues, differing in profile and potency of antiviral activity. Systematic SAR investigations of the DABO class, led to the identification of their chemical structure elements, being essential for the antiviral activity. They are: the presence of the benzylic moiety at the pyrimidine C⁶; an alkyl or cycloalkyl side chain at S, O² (for uracils and 2-thiouracils) or N² (for isocytosines). An appearance of the lower alkyl fragment (normal or ramified) at the C⁵ position of the pyrimidine nucleus is also an important structural feature of DABOs. The substitution of the benzylic portion is a moderator of the antiviral activity, as well.

The present work was supported in part by the grant of the President of Russian Federation for support of the young Russian scientists - the candidates of sciences MK-1351.2011.3 and federal programme "Investigation and development of the priority areas of progress of the scientific and technical complex of Russia in 2007-2012", lot number 2011-1.2-512-055 "Creation of the low-molecular non-nucleoside compounds, inhibiting the HIV-1 replication enzymes" on the topic "Directed construction of the novel non-nucleoside HIV-1 reverse transcriptase inhibitors: the derivatives of pyrimidin-4(3H)-one and their bioisosteric analogues" number 2011-1.2-512-055-011.

**SUPRAMOLECULAR STRUCTURE OF PLANT
CELL WALL POLYSACCHARIDES: NOVEL
PLAYERS**

T. Gorshkova
P. Mikshina
A. Petrova
S. Chemikosova

Kazan Institute of Biochemistry and Biophysics, Kazan Scientific
Center, Russian Academy of Sciences
gorshkova@mail.knc.ru

Plant cell wall is an example of a widespread natural supramolecular structure: its components are considered to be the most abundant organic compounds renewable by living organisms. Plant cell wall includes numerous components, mainly polysaccharidic; its formation is largely based on carbohydrate-carbohydrate interactions. Existing approaches to the study of interactions between polysaccharides during plant cell wall formation include: (i) characterization of the structure of natural polysaccharide complexes obtained during cell wall fractionation; (ii) analysis of the interactions between polysaccharides "at mixing in a tube"; (iii) study of the interactions between isolated individual plant cell wall matrix polysaccharides and microfibrils formed by cellulose-synthesizing microorganisms; and (iv) investigation of cell wall formation and modification directly in plant objects.

We applied several approaches including diffusion-ordered NMR spectroscopy for characterization of complex polysaccharide macromolecular packing in vitro and in vivo. Novel type of associates formed by pectic polymers grouped as rhamnogalacturonans I due to the presence in the backbone of repeating dimers $[\rightarrow 4)\text{-}\alpha\text{-D-GalAp-(1}\rightarrow 2)\text{-}\alpha\text{-L-Rhap(1}\rightarrow]$ was revealed. Polymer structural parameters necessary to make such associations were established. The relevance of the ability to form specific associates to functional role and potential application will be discussed in presentation.

**NEW ANTICANCER COMPOUNDS
ENCAPSULATED WITH SUPRAMOLECULAR
THIXOTROPIC HYDRO GEL SHOWING FRACTAL
STRUCTURE BASED ON CYSTEINE, AND SILVER
IONS AND NANOPARTICLES**

**B.S. Fedorov¹
P.M. Pakhomov²
M.A. Fadeev¹
N.P. Konovalova¹
L.V. Tatjanenko¹
B.P. Kulagin¹
S.D. Khizhnyak²
M.M. Ovchinnikov³**

1 - Institute of Problems of Chemical Physics, Chernogolovka,
Russian Federation

2 - Tver State University

3 - Tver State Academy of Medicine
boris-45@inbox.ru

The laboratory of biologically active compounds of IPCP RAS has been developing synthesis of new antimetastatic and anticancer drugs based on biogenic compounds including those comprising groups able to generate nitrogen monoxide at biotransformation [1]. The experiments with laboratory animals in the laboratory of experimental chemotherapy of tumors of IPCP RAS were performed to test antimetastatic activity of the number of NO donor compounds. Those were nitro- and dinitrocompounds, alcohol nitrates and oxamides of dicarboxylic acids. When used in cytostatic therapy in combination with low doses of cytostatics (cisplatin or cyclophosphan) when neither of them shows a therapeutic effect, these compounds allow full inhibition of metastatic disease in experimental Lewis carcinoma of lung and melanoma B-16 and provide 100% survival of laboratory animals at leukaemia P-388.

Throughout these investigations, a hybrid compound based on glycine was synthesized [2], which allows carcinoma 755 and Lewis carcinoma of lung to be reduced by 54-68%. The analysis of the experimental data allows an assumption on that an insufficiently high inhibition of tumor growth in Lewis carcinoma of lung and carcinoma 755 is possibly because of that the biologically active compound (substituted glycine) is not lipophilic enough to be delivered to mitochondrion and, hence, does not show its full effect. We suppose that the solution of this task is directly associated with the development of nanotechnology of encapsulation and delivery of substituted glycines to target cells. To design such an encapsulated compound we used a supramolecular gel with fractal structure developed at Tver State University [3,4] based on cysteine, and silver ions and nanoparticles [3,4]. Concentration of substances dissolved in water is from 0.1 to 0.01 %. The use of such hydro gel as a matrix for introducing a hybrid compound based on glycine allowed us to successfully solve this task and use this encapsulated compound to treat epidermoid cancer of auricle. In combination with radiotherapy, the use of this encapsulated compound provided full recovery from epidermoid cancer of auricle. This approach allows this development to be used in nonhazardous treating of cancer of neck, larynx, and human and animal cutaneous covering at melanomas. Such treatment mode allows one to observe dynamics of treatment.

References:

1. B.S.Fedorov, M.A.Fadeev, N.P.Konovalova, T.E.Sashenkova, S.M.Aldoshin, M.V.Laryukova. Russian patent N2295517. Application for the grant of the Russian patent N2009148636 with priority of December 29, 2009.
2. B.S.Fedorov, M.A.Fadeev. Application for the grant of the Russian patent N2009148636 with priority of December 29, 2009.
3. M.M.Ovchinnikov, P.M.Pakhomov, S.D.Khizhnyak. Russian patent N2310663.
4. M.M.Ovchinnikov, P.M.Pakhomov, S.D.Khizhnyak. Russian patent N2317305.

The work was supported by ADTP, project №2.1.1./10767.

PHOSPHORUS AS ENABLING VEHICLE – NEW DEVELOPMENTS AND APPLICATIONS

K. Lammertsma

VU University Amsterdam, the Netherlands
k.lammertsma@vu.nl

Phosphorus, an essential element in the life cycle, is going to become scarce within 75-150 years when the world's reserves in phosphate rock will have been exhausted at the expected rate of consumption. The impact will be monumental, far exceeding 'peak oil' or climate change. Our chemical community needs to embed this realization and offer society solutions to turn the table. This is a daunting task, because our society should also take advantage of the beneficial and enabling properties that the element phosphorus offers.



In this presentation topics will be identified where contributions can be made to curb the current waste in phosphorus. Also new developments will be presented, highlighting selected examples of organophosphorus functionalities for new chemical, material, and catalytic applications.

The examples will focus on rapidly accessing new reagents for the efficient synthesis of valuable products. These include phosphinidenes, phosphalkenes, phosphalkynes, but also new classes of phosphines such as in Frustrated Lewis Pairs that are capable of binding CO₂, transition metal cages that can form polymers dynamically, iron complexes containing novel ligands, and new P,N-ligands for homogenous catalysts. Contributing to highlight Butlerov's eminent place in chemistry, the structural relationship between organophosphorus compounds and hydrocarbons will be demonstrated including the similarity for complex rearrangements using theoretical analyses.

A.E. Nikolaev
V.E. Semenov
R.Kh. Giniyatullin
A.S. Mikhailov
A.D. Voloshina
N.V. Kulik
V.V. Zobov
V.S. Reznik

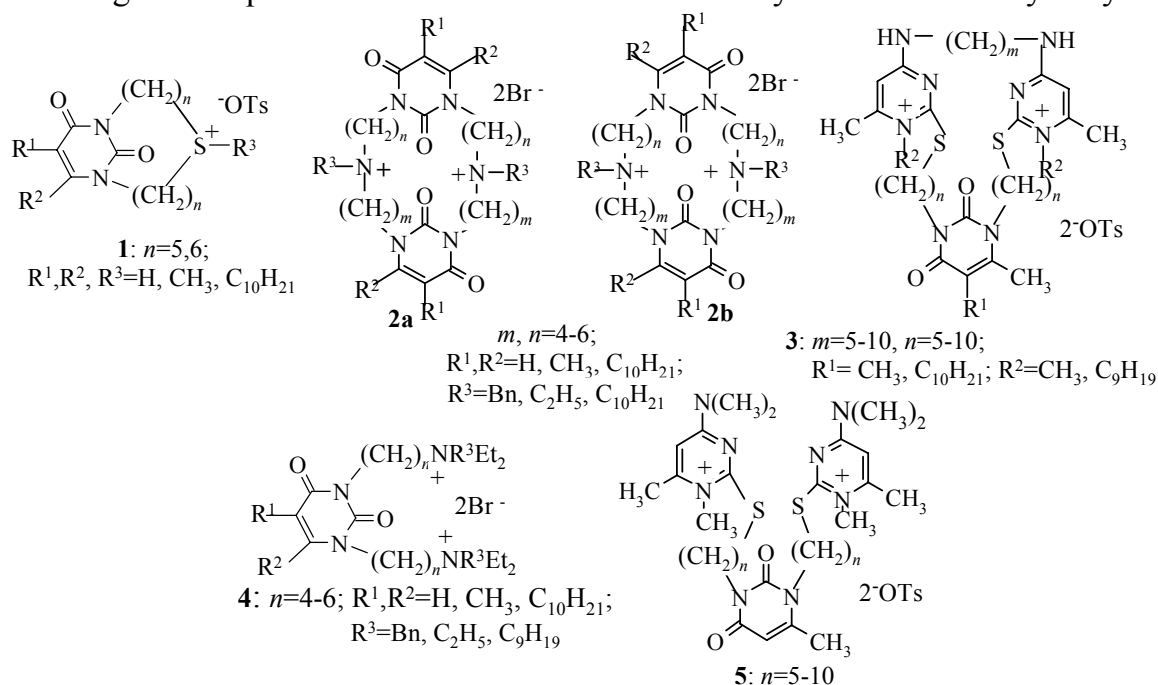
SYNTHESIS AND ANTIMICROBIAL ACTIVITY OF AMPHIPHILIC MACROCYCLES AND THEIR ACYCLIC COUNTERPARTS

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia

aenikolaev@iopc.ru

Herein the research on amphiphilic pyrimidinophanes with uracil moieties 1-3 and their acyclic counterparts 4 and 5 is presented. Pyrimidinophanes 1-3 represent a new class of biologically active macrocycles.

Strategy of their preparation is described. The idea is that the macrocyclic and acyclic compounds with different structure can be synthesized from N(1),N(3)-bis(ω -bromoalkyl)uracils by substituting the terminal atoms of Br with appropriate fragments [1]. The next stage is the quartenization of heteroatoms with alkyl bromides or alkyl tosylates.



The macrocyclic and acyclic compounds **1-5** were screened for antibacterial and antifungal activity. There is a general trend for pyrimidinophanes and their acyclic counterparts: increase of the polymethylene chain length leads to the decrease of MICs. For pyrimidinophanes **1-3** the remarkable selectivity against *S. aureus* was found. Some recent results on the synthesis and antibacterial activity of nanosized oligomeric pyrimidinophanes will be also presented.

References:

[1] V.E. Semenov, A.D. Voloshina, E.M. Toroptzova, N.V. Kulik, V.V. Zobov, R.Kh. Giniyatullin, A.S. Mikhailov, A.E. Nikolaev, V.D. Akamsin, V.S. Reznik. *Eur. J. Med. Chem.* **2006**, 41, 1093-1101.

This work was supported by the Research Programs of the RAS and grants (RFBR 10-03-00365 and MK-64480.2010.3).

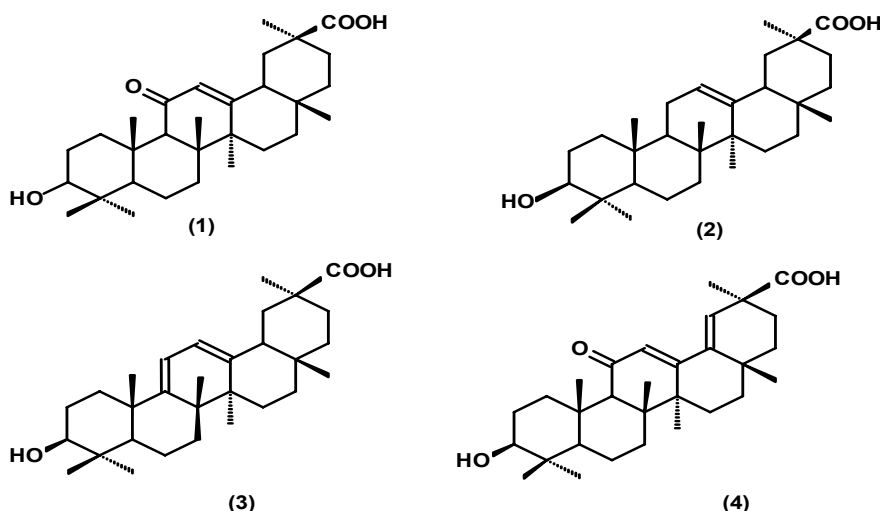
NEW SKELETAL AND OXIDATIVE TRANSFORMATIONS OF LICORICE ROOT TRITERPENIC ACIDS

L.A. Baltina
L.R. Mikhailova

Institute of Organic Chemistry Ufa Scientific Centre of RAS
baltina@anrb.ru

Synthesis of novel biologically active compounds of medicinal use based on the low molecular plant's metabolites is one of the important trends in the modern organic and medicinal chemistry. Development of triterpenoids chemistry last twenty years led to the opening of some unique biologically active substances to be perspective for medicine as medicinal preparations for the treatment of viral and cancer diseases.

The major triterpenic acids of licorice root (*Glycyrrhiza glabra* L., *Gl. uralensis* Fisher) Glycyrrhizic acid (GA) and its metabolite Glycyrrhetic acid (GLA) (**1**), which are known as anti-inflammatory, anti-ulcerogenic, anti-allergic, antioxidant, antitumor and antiviral agents¹. The present work is devoted to the development of new skeletal and oxidative transformations of GLA, 11-desoxo-GLA (**2**), 18,19-dehydro-GLA (**3**) and olean-9(11),12(13)-dien-30-oic acid (**4**) to obtain novel derivatives and analogs with modified rings A and C for the structure-activity relationships studies.



Novel derivatives of triterpenoids containing additional oxo- and hydroxyl functional groups were synthesized by using ozone, meta-chloroperbenzoic acid, dimethyldioxirane and air's oxygen as the oxidants. The changes in ring A of the given group of triterpenoids were made with the transformation into 1,2-en, 2-hydroxy, -carboxy, and halogen-3-oxo-derivatives. The schemes of synthesis of 30-carboxy analogs of 2-cyano-3,12-dioxo-1,9-dien-28-oic acid (CDDO) to be the derivative of oleanolic acid in the clinical trials as an anticancer agent were proposed.

Novel derivatives of licorice roots triterpenic acids are testing *in vitro* as an antiviral, antitumor, antiinflammator and antidiabetic agents.

References:

1) Tolstikov, G.A., Baltina L.A., Grankina V.P., Kondratenko R.M., Tolstikova T.G. Licorice: biodiversity, chemistry, and application in medicine. Novosibirsk: Academic Publishing House "Geo", 2007. 311 pp.

This work was supported by the RFBR (projects 08-03-00366, 11-03-00452), SC-3756.2010 and SK 14.740.11.0367.

**MECHANISMS OF ANTIBODY-MEDIATED
CLEAVAGE OF PHOSPHOORGANIC PESTICIDES**

A.G. Gabibov

Shemyakin–Ovchinnikov Institute of Bioorganic Chemistry RAS,
Moscow, Russia
gabibov@mx.ibch.ru

Immunoglobulins offer a versatile template for combinatorial and rational design approaches to the de novo creation of catalytically active proteins. We have used a covalent capture selection strategy to identify biocatalysts from within a human semi-synthetic antibody variable fragment library that use a nucleophilic mechanism. Specific phosphorylation at a single tyrosine within the variable light chain framework was confirmed in a recombinant IgG construct. High resolution crystallographic structures of unmodified and phosphorylated Fabs display a novel, 15 Å-deep, two-chamber cavity at the interface of VH and VL having a nucleophilic tyrosine at the base of the site. The depth and structure of the pocket are atypical of antibodies in general but can be compared qualitatively to the catalytic site of cholinesterases. A structurally disordered HCDR3-loop, constituting a wall of the cleft, is stabilized following covalent modification by hydrogen bonding to the phosphonate tropinol moiety. These features and pre-steady state kinetics analysis indicate that an induced fit mechanism operates in this reaction. Mutations of residues located in this stabilized loop do not interfere with direct contacts to the OP-ligand but can interrogate second shell interactions because the H3 loop has a conformation adjusted for binding. Kinetic and thermodynamic parameters along with computational docking support the active site model including plasticity and simple catalytic components. Though relatively uncomplicated, this catalytic machinery displays both stereo- and chemical selectivity. The organophosphate pesticide paraoxon is hydrolyzed by covalent catalysis with rate-limiting dephosphorylation. This reactibody is therefore a kinetically-selected protein template that has enzyme-like catalytic attributes.

**NEW MULTIFUNCTIONAL DERIVATIVES OF
BETULIN**

S.P. Yurchenko
O.A. Aimakov

Sh. Yalikhonov Kokshetau State University MES RK, Kokshetau,
Republic of Kazakhstan
aimakov@rambler.ru

Betulin is a pentacyclic triterpenoid from the series of loopan, one of the main components of various kinds of birch bark. Betulin possesses anti-inflammatory, antioxidant, antiseptic, antitumor, antiviral, hepatoprotective, choleretic characteristics. Betulin has the antiviral effect against human immunodeficiency virus (HIV), herpes simplex virus and Epstein-Barr virus.

It is known that betulinic acid derived from betulin has the antimelanoma activity, i.e. inhibits the growth of melanoma and other cancer cells of neuroectodermative origin.

Due to the research of triterpenoids with alleged physiological activity we carry out experiments to obtain new heteroatom derivatives of betulin.

The reaction mechanisms of condensation of betulin with paraform and secondary aliphatic amines as well as the substitution reactions caused by the acidating agent in relation to chloride of nicotinic acid are being researched.

The presence of alcohol group (at C₃, C₂₈) and the double bond (at C₂₀₋₂₉) in the betulin molecule makes it interesting to make the chemical modification with oxo compounds, secondary amines, aliphatic, aromatic and halide nicotinic acid. The obtained new compounds may have a broad spectrum of biological activity.

A.A. Albantova¹
O.M. Alekseeva¹
A.V. Kremetsova¹
L.S. Shibryaeva¹
E.M. Mill¹
V.I. Binyukov¹
A.N. Goloshapov¹
E.B. Burlakova¹
E.A. Yagolnik²
Yu.A. Kim³

THE ACTION OF MELAFEN AQUEOUS SOLUTIONS UNDER WIDE CONCENTRATIONS INTERVAL TO BIOLOGICAL STRUCTURES

1 - Institute of Biochemical Physics. NM Emanuel Academy of
Sciences, Russia

2 - Tulskey State University

3 - Institute of Cell Biophysics, Pushchino

olgavek@yandex.ru

Study of actions of aqueous solutions of Melafen to the models and components of animal cells was carried out with the methods: spectral, potentiometric, DSK (adiabatic differential scanning calorimetric) and AFM (atomic forced microscopy). We revealed noticeable structural changes of artificial phospholipids membranes at concentrations of Melafen (10^{-13} - 10^{-10} M), when tested with DSK under the different velocity of heating. At melafen concentration 10^{-13} , 10^{-12} M the enthalpy changes were deterred. Similar data were obtained for maximum of temperature of thermoinducted transition and cooperativity. In the erythrocytes ghost, a model of protein-lipid membrane, melafen does not cause any significant changes in the organization of protein-lipid microdomains even under the high concentrations 10^{-8} - 10^{-2} M. But the structure of soluble protein BSA was loosed under the Melafen actions. The native cells erythrocytes showed the shape changes of AFM erythrocytes images, under the concentrations of melafen aqueous solutions (10^{-11} - 10^{-6} M). The perimeter of AFM images, altitude and volume of AFM images erythrocytes, which correlated to shape's change, were decreased in dose dependence manner that indicates the influence on cells life activity. Based on obtained results we concluded about existence of action of aqueous solutions of melafen at wide range of concentrations on components of animal cells. Melafen in aqueous solutions forms the supramolecular structures involving of water molecules. The obtained data next time suggested that the supramolecular aqua-melafen structures may be interact with biological objects. The basic targets of aqua-melafen there are attractable and labile objects: instable structure and cell functioning.

SYNTHESIS, STRUCTURE AND BIOLOGICAL ACTIVITY OF QUATERNARY PHOSPHONIUM SALTS ON THE BASIS OF STERIC SUBSTITUTED PHENOLS

V.V. Andriyashin
Yu.V. Bakhtiyarova
I.V. Galkina
V.I. Galkin

Kazan Federal University, A.M. Butlerov Chemical Institute, Kazan, Russia
anvi87@ya.ru

It's known that 2,6-dialkylphenols are widely used in various fields of medicine.

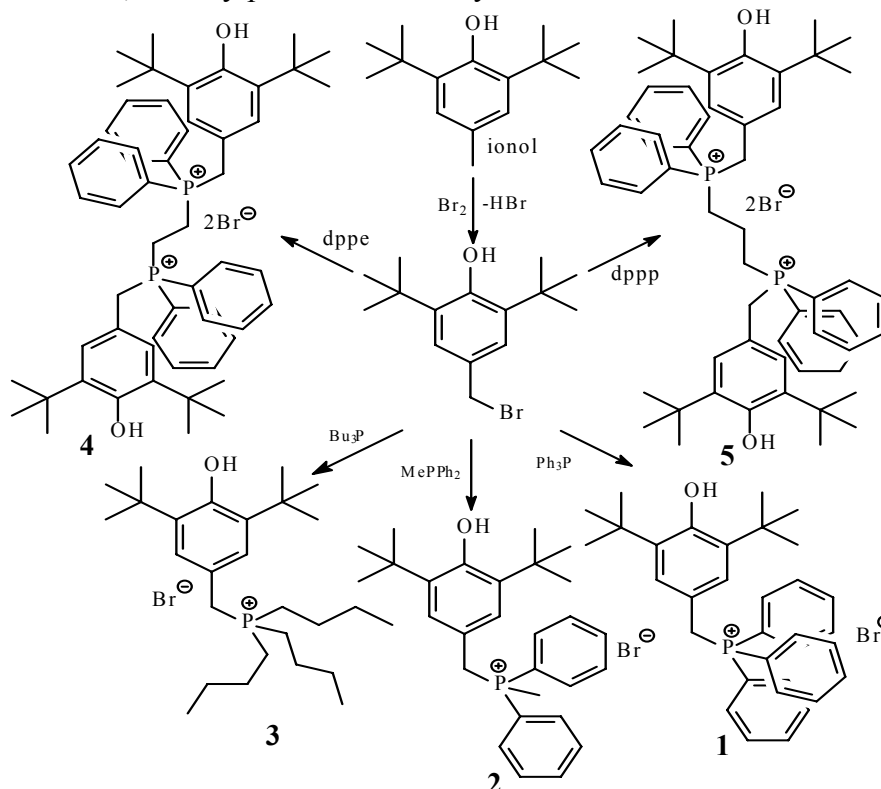


Table 1. Antibacterial and antifungal activities of synthesized compounds

In the presented work we synthesized a series of quaternary phosphonium salts (**1-5**) on the basis of 3,5-di-*t*-butyl-4-hydroxybenzyl bromide and tertiary phosphines. Their antibacterial and antifungal activities have been studied (Table 1). The structure of compounds obtained has been confirmed by complex of modern physical methods, including X-ray analysis for three key structures.

Compounds (concentration)	Zones of inhibition, d (mm)				
	<i>E. coli</i>	<i>Salmonella p.B</i>	<i>Ps. aeruginosa</i>	<i>S. aureus</i>	<i>Candida albicans</i>
1. (1%)	18	16	16	43	46
2. (1%)	15	-	8	45	48
3. (1%)	9	-	-	45	35
4. (1%)	17	-	7	32	25
5. (1%)	19	-	11	25	25
Control drugs		Zones of inhibition, d (mm)			
Ampicillin (1%)		16	16	15	-
Penicillin (1%)		-	-	-	29
Chlorohexydin (1%)		19	18	15	22

STUDY OF ANTITUMOR ACTIVITY OF 6-ARYLAZO DERIVATIVES 5,7-DIMETHYL-3H-THIAZOLO[4,5-b] PYRIDINE-2-ONE

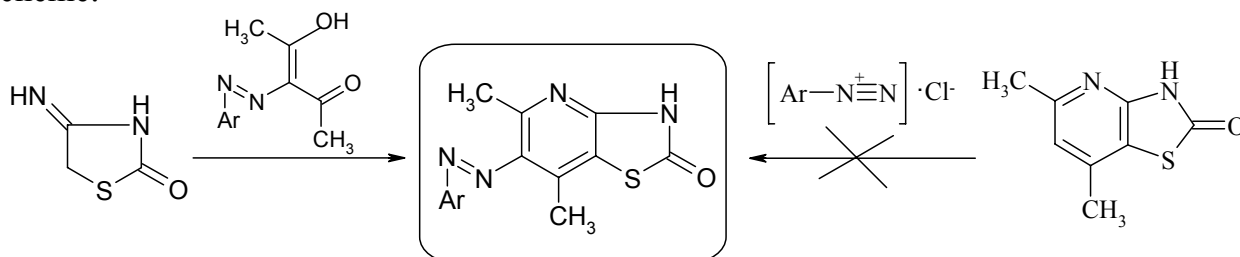
T.I. Chaban
V.V. Ogurtsov
I.H. Chaban

Danylo Halytsky Lviv National Medical University, Ukraine
chabantaras@ukr.net

The intensive researches have been focused on the novel five-membered heterocyclic systems synthesis in nowadays organic, pharmaceutical and medical chemistry as the promising drug candidates whose quotient among the existing drugs is significant. Thiazolepyridines have the wide range of biological action on account of their iso-steric to pyrine and pyrimidine bases structure.

In this work we are reporting the convenient 3H-thiazolo[4,5-b]pyridine-2-one derivatives synthetic route development. The aim of the present report is the novel 5,7-dimethyl-6-arylazo-3H-thiazole[4,5-b]pyridine-2-one synthesis and its antitumor action studying.

The azo-affiliation reaction of 5,7-dimethyl-3H-thiazole[4,5-b]pyridine-2-one being treated with aryldiazonium salts was studied in order to obtain 5,7-dimethyl-6-arylazo-3H-thiazole[4,5-b]pyridine-2-on. The synthesis of the compound is depicted in the following Scheme:



It was defined the 5,7-dimethyl-3H-thiazole[4,5-b]pyridine-2-one does not undergo the azo-affiliation reaction at normal conditions what makes evident the low 5,7-dimethyl-3H-thiazole[4,5-b]pyridine-2-one molecule nucleophilic properties in its 6th position. However the required 5,7-dimethyl-6-phenylazo-3H-tiazole[4,5-b]pyridine-2-one could be synthesized by the employment of acetylacetone arylazoderivative treating with 4-iminothiazolidone-2 in their equivalent moles moieties. The best results were observed when the reactants mixture was hold up in methanol in the presence of sodium methylate during 5 days.

The synthesized compound structure was proved with the elemental analysis and PMR spectroscopy method.

The antitumor activity evaluation of the substances was performed by the National Cancer Institute, USA the screening had been carried out on 60 human cancer cell lines. The preliminary antitumor activity screening showed the considerable selective cytostatic effect of the substances on some non-small cell lung cancer, CNS cancer, melanoma and brest cancer lines what reasoning the further advanced antitumor activity evaluation according to NCI requirements.

SYNTHESIS, GENOTOXICITY AND UV-PROTECTIVE ACTIVITY OF NEW DERIVATES OF AMINE-CONTAINING BENZOFUROXANS

E.A. Chugunova¹
E.M. Gibadullina¹
A.R. Burilov¹
L.M. Yusupova²
M.A. Sazykina³
V.A. Chistyakov³
I.S. Sazykin³

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan Scientific Center of Russian Academy of Sciences, the Laboratory of Organoelemental Synthesis, Kazan, Russia

2 - The Kazan National Research Technological University, Institute of Chemical Engineering and Technology, Faculty Energy Intensive Materials, Department of Chemistry and Technology of Organic Nitrogen Compounds, Kazan, Russia

3 - The Research Institute of Biology, Southern Federal University (SFedU), Genome Variability Department, the Laboratory of Industrial Microorganisms, Rostov-on-Don, Russia

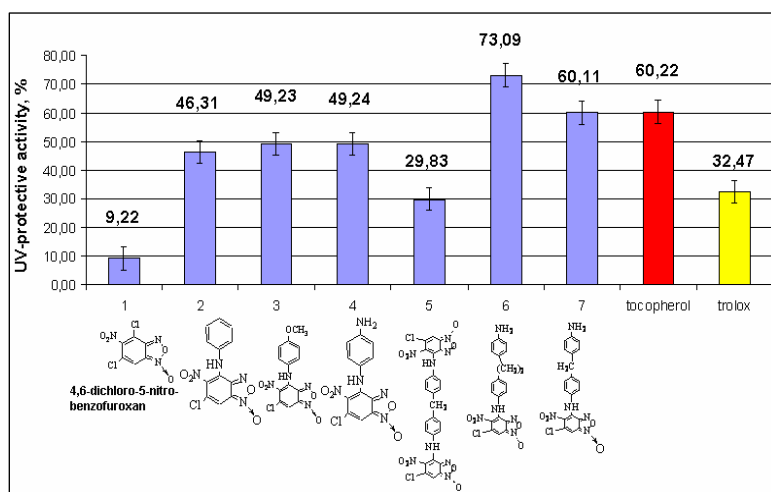
elena-chugunova@list.ru

Synthesis of new organic compounds with practically useful properties is a current trend in synthetic science. From the point of view of medical and combinatory chemistry benzofuroxans are of great interest, as, being effective biologically active compounds, they are relatively available, are easily functionalized and allow creating databases in which a researcher can find information to create a preparation with necessary selective effect.

In the compounds synthesized by us on the basis of the reactions of 4,6-dichloro-5-nitrobenzofuroxan with aromatic amines and diamines the ability to suppress genotoxic effects of UV-radiation with 300-400 nanometer wavelength has been studied. It was shown that compounds based on 4,6-dichloro-5-nitrobenzofuroxan and aromatic amines and diamines protect bacterial cells from destructive effects of UV-radiation with 300-400 nanometer wavelength. The initial compound – 4,6-dichloro-5-nitrobenzofuroxan doesn't possess the protective effect, and replacement of chlorine atom by nitrogen-containing fragments increases the protective potential. By comparison of the results received for various benzofuroxans, the natural antioxidant α -tocopherol (vitamin E) and for the synthetic antioxidant trolox it is clear that benzofuroxans show

quantitatively similar protective effect, and the compound based on 4,6-dichloro-5-nitrobenzofuroxan and ethylenedianilin possesses higher protective potential.

Thus, benzofuroxans protect bacterial cells from destructive effects of UV-radiation with 300-400 nanometer wavelength, that is, are substances, promising for creation of highly effective UV-protective preparations.



This work is completed with the financial support of the Ministry of Education and Science of the Russian Federation (the project under the analytical departmental target program «Development of scientific potential of the higher school (2009-2011)», the grant № 2.1.1/5028) and of the Russian Fundamental Research Fund (grants 11-03-00416a).

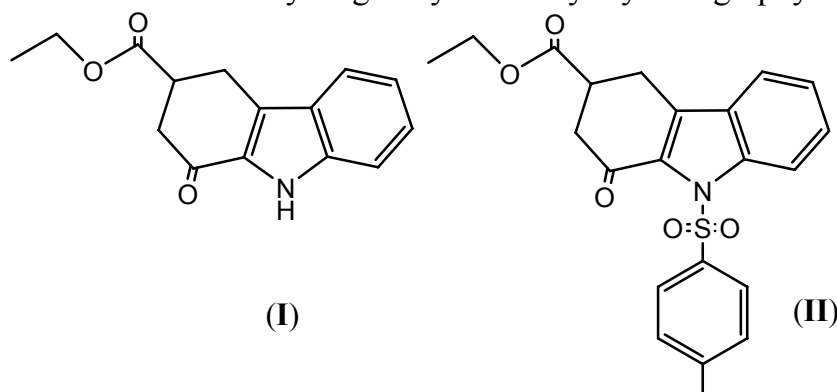
THE STRUCTURES OF ETHYL 1-OXO-1,2,3,4-TETRAHYDRO-9H-CARBAZOLE-3-CARBOXYLATE AND ETHYL 4-HYDROXY-9-TOSYL-9H-CARBAZOLE-3-CARBOXYLATE

H. Dal¹
T. Hokelek²
B. Tercan³
M. Göçmentürk⁴
S. Güle⁴
Y. Ergün⁴

1 - Department of Chemistry, Anadolu University, Eskisehir, Turkey
2 - Department of Physics, Hacettepe University, Ankara, Turkey
3 - Department of Physics, Karabuk University, Karabuk, Turkey
4 - Department of Chemistry, Dokuz Eylül University, Izmir, Turkey
hakandal@anadolu.edu.tr

Tetrahydrocarbazole derivatives can be considered to be synthetic precursors of cyclic indole-type alkaloids of biological interest [1]. The compound (I) was used in the synthesis of the precursor compound for the synthesis of anti-tumor drug ellipticine [2]. *Murraya L.* (Rutaceae) is a genus of shrubs or small trees from Southern Asia [3]. The main constituent of this genus include carbazole alkaloids. Several biological properties have been reported for carbazole alkaloids including antibiotic, cytotoxic and antiviral activities. Compound (I) may also be used as a precursor in the synthesis of *Murraya* alkaloids. On the other hand, the tetrahydrocarbazolone derivatives were used in the synthesis of Ondansetron, which is an excellent antiemetic drug inhibiting 5-HT₃ receptor [4]. Tetrahydrocarbazolone ester derivatives can also be considered to be synthetic precursors of tetracyclic aspidosperma alkaloids [5]. Compound (II) may be considered as a synthetic precursor of tetracyclic indole alkaloids of biological interest.

In this study, we synthesized the title compounds (I) [6] and (II) [7] and their structures have been characterized by single crystal X-ray crystallography.



References:

1. Saxton, J. E. (1983). Editor. *Heterocyclic Compounds*, Vol. 25, *The Monoterpenoid Indole Alkaloids*, chs. 8 and 11. New York: Wiley
2. Ergün, Y., Patir, S. & Okay, G. (2004). *Synth. Commun.* **34**, 435-442
3. Chang, C. E. (1977). *Flora of Taiwan*, Vol. 3, pp. 520-523. Taipei, Taiwan: Poch Publishing Co. Ltd
4. Molnar, S., Szabo, C., Sos, E. M., Salyi, S. & Tamas, T. (2006). US Patent. US 7 098 345 B2
5. Ergün, Y. (2007). *J. Heterocycl. Chem.* **44**, 539-541
6. Hökelek, T., Dal, H., Tercan, B., Göçmentürk, M. & Ergün, Y. (2009). *Acta Cryst.* **E65**, o1702–o1703
7. Hökelek, T., Dal, H., Tercan, B., Güle, S. & Ergün, Y. (2009). *Acta Cryst.* **E65**, o1515–o1516

**HYPOGLYCEMIC ACTIVITY OF AMPELODESMA
MAURITANICA SAPONINS**

A.D. Djilani

Annaba University
jilaniouaheb@yahoo.fr

The aim of this study is to evaluate hypoglycemic effect of saponin fractions of *Ampelodesma mauritanica*. The saponins are obtained from the aerial part of *A. mauritanica* plant by conventional method are tested on normal glucose-fed hyperglycemic mice to evaluate its efficacy as a hypoglycemic compound. The extract administered intraperitoneally to mice significantly reduced blood glucose level. This acute effect presents a comparable glucose lowering effect with the oral hypoglycemic drug, glibenclamide.

I.V. Galkina¹
 E.V. Tudriy¹
 M.P. Spiridonova¹
 G.L. Tahautdinova¹
 L.M. Yusupova²
 M.P. Shulaeva³
 O.K. Pozdeev³
 S.N. Egorova³
 V.I. Galkin¹

IN VITRO ANTIBACTERIAL AND ANTIFUNGAL STUDIES OF PHOSPHORYLATED AND AMINATED 4,6-DINITROBENZOFUROXANS

1 - Kazan Federal University, A.M. Butlerov Chemical Institute, Kazan, Russia

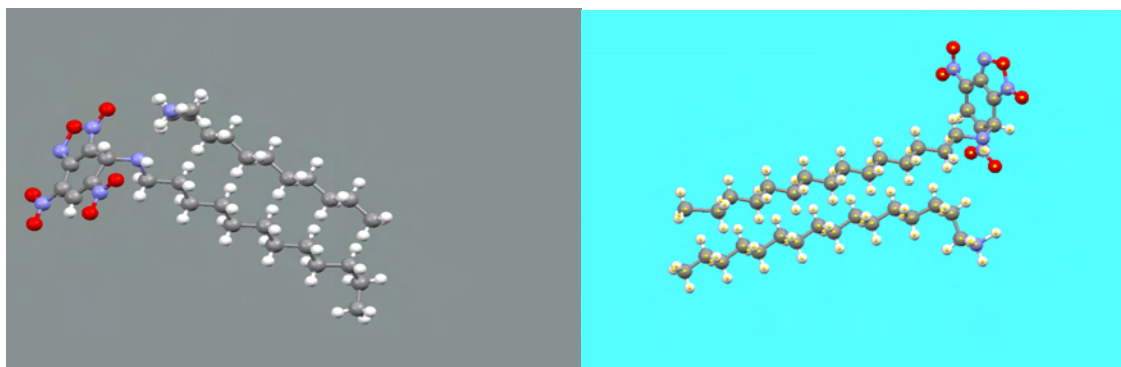
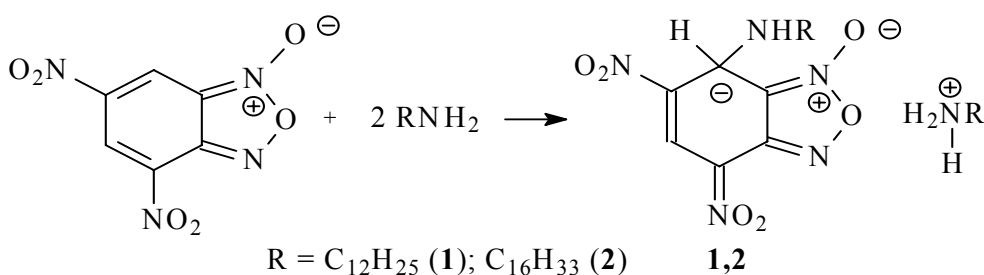
2 - Kazan State Technological University, Kazan, Russia

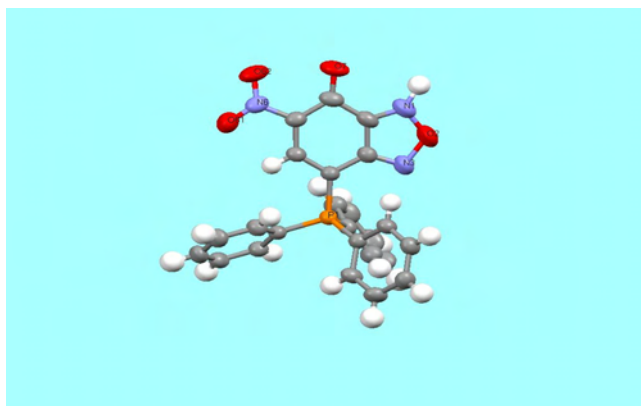
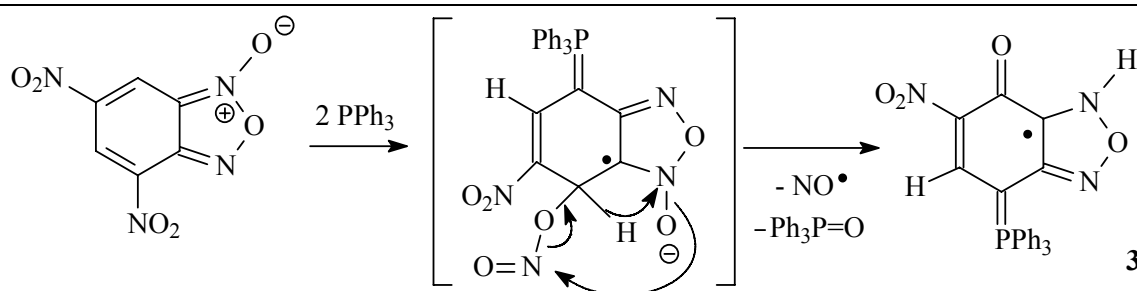
3 - Kazan State Medical University, Kazan, Russia

vig54@mail.ru

Phosphorylated and aminated dinitrobenzofuroxans (**1-3**) are efficiently synthesized by reaction of 4,6-dinitrobenzofuroxan with triphenylphosphine, dodecyl- and hexadecylamines. Products as monocrystals were have been isolated and characterized by elemental and X-ray analyses, spectral (IR, ESR, NMR) and thermal studies. The compounds were also tested for their *in vitro* antibacterial and antifungal activities.

4,6-Dinitrobenzofuroxan ring is a simple system with an enigmatic and intriguing chemistry. The benzofuroxan derivatives have showed a wide spectrum of biological activities and the interest to them in medicinal chemistry has grown over the last 20 years. Recently we began a systematic study of *in vitro* antibacterial and antifungal activity of three the most active substituted benzofuroxans synthesized in our laboratory. Nucleophilic reactions S_NAr take place in the homocyclic ring, when they are activated by electron-withdrawing substituents. Nitro-containing benzofuroxans are represented a class of neutral 10- π -electron-deficient system, which exhibits an extremely high electrophilic character in many covalent nucleophilic and substitution processes. 4,6-Dinitrobenzofuroxan has been defined as superelectrophile and used as convenient probe to estimate the N- and P-basicity of nitrogen and phosphorus nucleophiles, resulting in the formation of anionic σ -adducts. Stable Meisenheimer complexes **1** and **2** have been obtained in the case of amination, and product **3** – stable radical – has been obtained in the case of phosphorylation of 4,6-dinitrobenzofuroxan.





Biological activities of compounds **1-3** have been studied by agar and potato dextrose agar diffusion methods. Standard antibacterial and antifungal drugs (Ampicillin and Fluconazole) have been used for comparison under similar conditions.

Compound	<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>E. coli</i>	<i>P. mirabilis</i>	<i>C. albicans</i>
1.	25.0±0.3	12.0±0.2	18.0±0.7	10.6±0.5	38.0±0.6
2.	17.7±0.5	11.3±0.3	9.7±0.3	10.3±0.2	11.0±0.4
3.	33.1±0.4	7.6±0.5	21.1±0.5	9.7±0.7	36.4±0.3
Ampicillin	12.7±0.5	11.5±0.6	11.7±0.3	10.9±0.7	-
Fluconazole	-	-	-	-	20.0±0.5

Positive control ampicillin and fluconazole measured by the Halo Zone Test (Unit, mm).

Acknowledgment. We are grateful to Dr. D.B. Krivolapov and Prof. I.A. Litvinov (A.E. Arbuzov Institute of Organic and Physical chemistry of the Russian Academy of Sciences) for X-ray investigation.

**DEVELOPMENT OF METHODS FOR THE
SYNTHESIS OF UNSATURATED FATTY ACIDS
HIGHER PLANTS ORIGIN**

**A. Golovanov
N. Groza
G. Miagkova**

Moscow Lomonosov State Academy of Fine Chemical Technology,
Moscow, Russia
a.golovanov@chemist.com

Lipids are important structural components of biological membranes. It is now known that certain types of lipids act as signaling molecules that regulate many cellular processes, including growth and cell death and inflammatory responses.

Lipids are not only structural components of membranes or substrates consumed in physiological reactions, they represent a central cohesive platform to regulate the accuracy and speed of signaling intracellular and intercellular reactions, and have a significant effect on inflammatory processes.

To study the mechanisms of plant response to environmental factors has been developed synthetic scheme for producing short-analogue of linoleic acid: (5Z,8Z)-tetradecadienoic acid. This analogue of the natural polyenoic fatty acids was obtained by stereoselective reduction of triple bonds in polyacetylenic precursors using a palladium catalyst. Polyacetylenic acid methyl ester (5,8-tetradecadiynoate) was synthesized using organocuprate reagents in cross-coupling reaction of propargylic type tosylate with terminal acetylenic acid methyl ester. The strategy of synthesis is based on the formation of methyl tetradeca-5,8-diynoate, which is obtained using the cross-coupling reaction of oct-2-yn-1-yl 4-methylbenzene-1-sulfonate with 5-hexynoic acid methyl ester. Methyl ester of 2-octynoic acid was prepared using diazomethane by the standard procedure from commercially available 2-octynoic acid. Methyl ester of 2-octynoic acid was reduced to 2-octynol with LiAlH_4 followed by tosylation under basic conditions.

References:

1. S.Kh. Nurtdinov, R.S. Khairullin, V.S. Tsivunin, T.V. Zykova. G.Kh. Kamai. *Zh. Obshch. Khim.* 1970, **40**, (11), 2377.
2. K.I. Novitskii, N.A. Razumov, A.A. Petrov. *Khimiya organicheskikh soedinenii phosphora* (Chemistry of Organic Phosphorus Compounds), Leningrad: Nauka, 1967, p. 248.
3. B.A. Arbuzov, V.E. Bel'skii, A.O. Vizel', K.M. Ivanovskaya, G.Z. Motygullin. *Dokl. Akad. Nauk SSSR*. 1967, **176** (2), 323.

The work is supported by the Russian Foundation for Basic Research – Academy of Sciences of Tatarstan (grant 09-03-97007_p).

NEWLY SYNTHESIZED UNSYMMETRIC BF₂ COMPLEX OF AZADIPYRROMETHENE (AZA BODIPY)

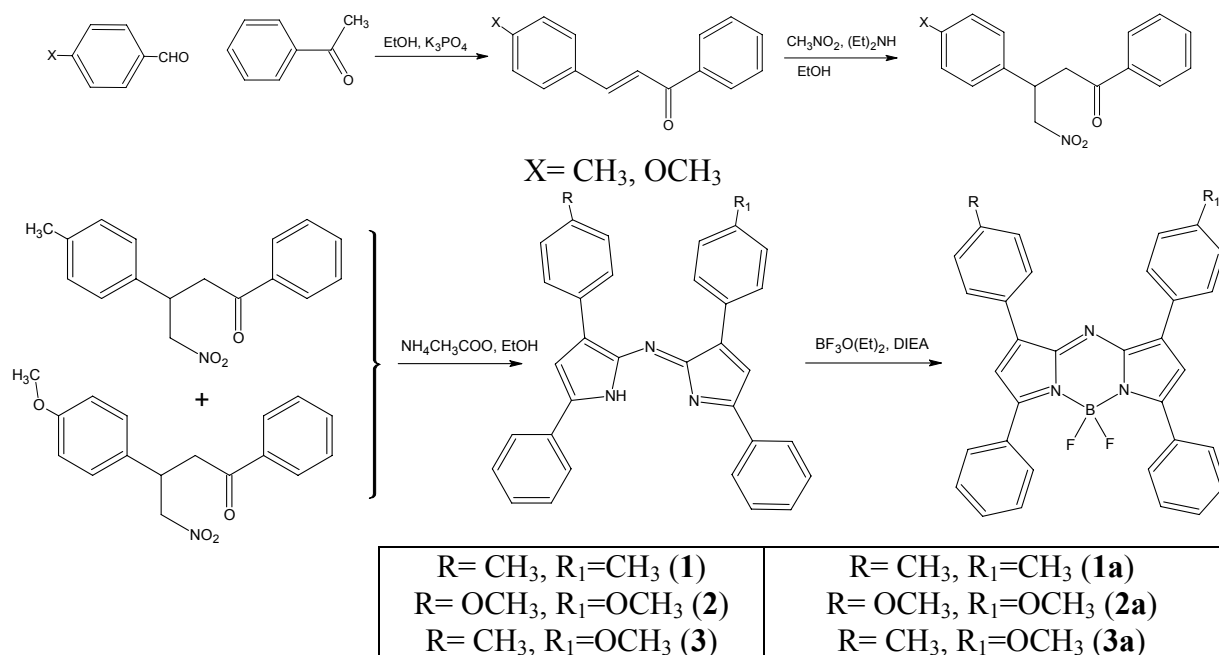
M. Hayvali¹
A. Elmali²
G. Yaglioglu²
H. Yilmaz¹

1 - Ankara University, Faculty of Science, Department of Chemistry,
 Tandogan, 06100 Ankara, Turkey

2 - Ankara University, Faculty of Engineering, Department of Physics,
 Tandogan, 06100 Ankara, Turkey
hayvali@science.ankara.edu.tr

Azadipyrromethenes are the bridged nitrogen analogues of dipyrromethenes and have longer wavelengths of maximum visible absorption. Some of azadipyrromethene BF₂ complexes have shown potential applications in photodynamic therapy as biological probes. BF₂ complexes of azadipyrromethene have excellent thermal, chemical, and photochemical stability, high molar absorptivity, fluorescence quantum yields, relatively long excited-state lifetimes, a large two-photon absorption cross-section for multiphoton excitation, good solubility. Recently, special attention has been given this type of dyes with long-wavelength absorption due to the practical applications in near infrared (NIR)[1].

We describe here the design and synthesis of the azadipyrromethene and their BF₂ complexes (Scheme).



The synthesis and spectral characteristics of a novel BF₂ complexes of arylazadipyrromethene as new azabodipies. The variation of the phenyl ring substituents and their effect on maximum absorption as well as their photophysical properties are in reported. The structures of the free-ligands and their complexes determined by elemental analyses, mass spectrometry (MS), Fourier transform infrared spectroscopy (FTIR), ¹H and ¹³C NMR, and UV-visible data.

References:

[1]. *J. Am. Chem. Soc.* **2004**, 126, 10619-10631.

**A NEW LOOK AT METAL FLUORIDE COMPLEXES
OF KINASES USING ^{19}F NMR**

Y. Jin
G.M. Blackburn
J.P. Waltho

University of Sheffield, Dept. Molecular Biology and Biotechnology,
Sheffield, UK
mbp08yj@sheffield.ac.uk

Tetrafluoroaluminate, AlF_4^- , forms octahedral complexes for many enzymes that catalyse phosphoryl transfer. Several trigonal bipyramidal complexes, tpbs, have been assigned as AlF_3^0 species by inference, based on electron densities of protein complexes. A tbp complex for $\text{RhoA} \cdot \text{GDP} \cdot \text{MF}_3 \cdot \text{RhoGAP}$ was identified as a trifluoromagnesate (MgF_3^-) transition state analogue and now ^{19}F NMR has provided positive fluorine analyses for octahedral and tbp complexes establishing MgF_3^- in tbps for β -phosphoglucose mutase, phosphoserine phosphatase, and phosphoglycerate kinase. pH Titrations from low to high pH for $\text{RhoA} \cdot \text{RhoGAP}$ complexed with GDP and for UMP/CMP kinase, show collapse of AlF_4^- NMR signals above pH 8 and their replacement by three ^{19}F signals associated with MgF_3^- . Critically, the anionic character of such complexes supports a CBH, “charge balance hypothesis” for enzymatic phosphoryl transfer.

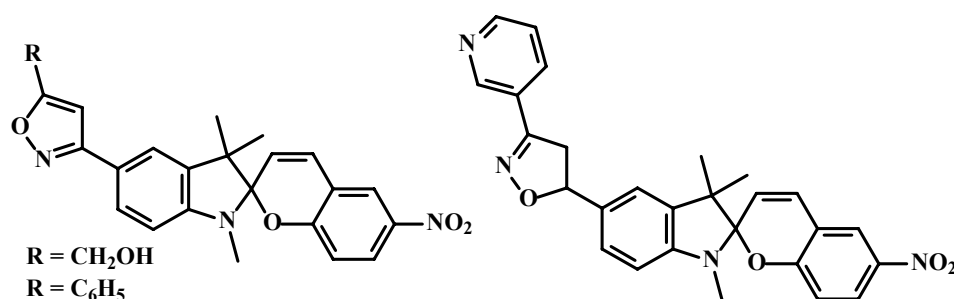
SYNTHESIS AND STUDY OF SPECTRAL PROPERTIES OF ISOXAZOLE DERIVATIVES WITH PHOTOCHROMIC LABEL

A.V. Laptev¹
O.V. Demina²
A.A. Khodonov¹
N.E. Belikov¹
A.Yu. Lukin¹
M.A. Fomin¹
V.I. Shvets¹
S.D. Varfolomeev²

1 - M.V. Lomonosov State Academy of Fine Chemical Technology,
Department of Biotechnology and Bionanotechnology, Moscow,
Russia
2 - N.M. Emanuel Institute of Biochemical Physics RAS, Moscow,
Russia
biolapa@inbox.ru

The investigation of the regulation of ligand – receptor or ligand - enzyme interactions by the usage of organic compounds with photochromic labels on the subcellular or molecular levels is one of the significant tasks of bionanophotonics. The search of new effective variants of the direct regulation of the human hemostasis system definite stages is the important medicine problem, because the mortality from cardio-vascular diseases takes first place in the world.

It was shown by us that a number of 3,5-substituted isoxazoles were potent anti-aggregatory compounds. A few 3,5-substituted isoxazole analogs contained photochromic label - spiropyran moiety at 3- or 5-position of isoxazole ring were synthesized by us for the determination of molecule pharmacophoric fragment detail structure and the investigation of the action mechanism of this class compounds. Photochromic properties of synthesized compounds were investigated by spectral – kinetic methods.



This work was partly supported by RFBR grants (projects № 09-04-01003). State contract № 16.740.11.0177 of FCP «Scientific and scientific-pedagogical staff of innovational Russia» 2009-2013.

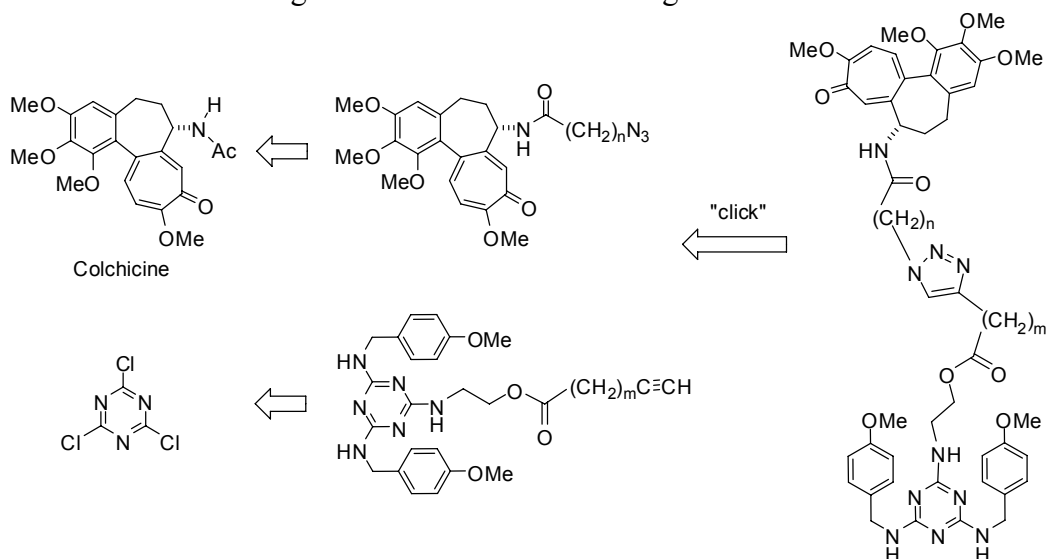
SYNTHESIS OF A NEW GENERATION OF HYBRID ANTICANCER AGENTS

Yu.B. Malysheva¹
S. Combes²
A.E. Gavryushin³
P. Knochel³
A.Yu. Fedorov¹

1 - N.I. Lobachevsky Nizhny Novgorod State University, Department of Organic Chemistry, Nizhny Novgorod, Russia
 2 - Universite d'Aix Marseille 1 et 2, UMR 6264, Faculte des Sciences Saint-Jerome, France
 3 - Ludwig Maximilians – Universitat Munchen, Department Chemie und Biochemie, Munchen, Germany
 maljb@rambler.ru

Search for substances able to block the cell cycle has always been regarded as a major challenge in cancer therapy. Antimitotic compounds inhibit the formation or the disaggregation of microtubules formed by the tubulin protein. Various strategies are being developed to increase the therapeutic index of different drugs. The concept of multivalent interactions is now accepted as an effective strategy for designing ligands, inhibitors and drugs.¹ Polyvalent interactions are normally much stronger than the corresponding monovalent contacts.

Several new antimitotic bivalent ligands were synthesized by linking of azide-containing deacetylcolchicine and acetylene-substituted tubulizine entities, known to bind with colchicine and tubulizine sites of tubulin protein, using “click”-chemistry. Our approach allows a simple generation of tubulin bivalent ligands with various linker lengths.



The cytotoxic activity of the modified tubuline ligands as well as the target heterodimers was investigated using human mammalian cancer cell line HBL100. All of the tested heterodimers presented relatively good cytotoxic activity, $IC_{50} = 0.599 - 2.93 \mu M$. The proposed methodology makes it easy to expand the bivalent hybrid library with a variety of new members.

References:

[1] M. Mammen, S.-K. Choi, G.M. Whitesides, *Angew. Chem. Int. Ed.*, **1998**, 37, 2754-2794.

This work was supported by Russian Foundation for Basic Research (09-03-00647-a and 09-03-97038-r_povolzh'e_a), German Academic Research Service (A/08/81119) and Council for grants under the President of Russia (MD-5606.2010.3).

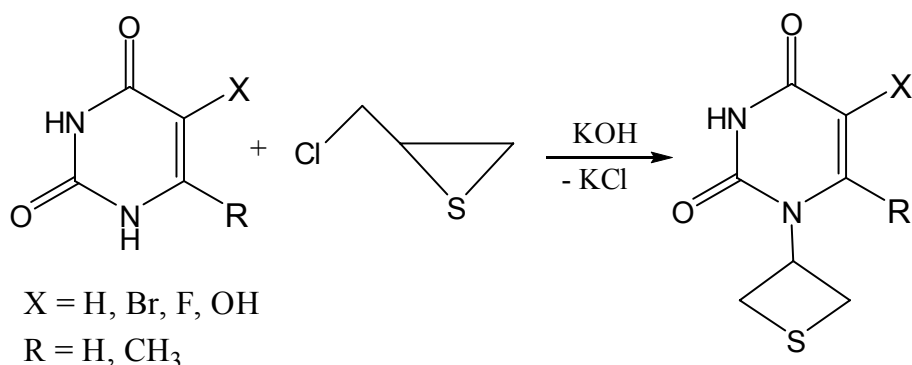
STUDIES ON REACTION OF 5,6-SUBSTITUTED PYRIMIDINE-2,4-DIONE AND 2-CHLOROMETHYLTHIIRANE

S.A. Meshcheryakova
D.A. Munasipova
T.G. Safiullin
T.A. Ivanova
V.A. Katayev

Bashkirian State Medical University, Ministry of Health and Social
Development, Ufa, Russia
SvetlanaMA@mail.ru

According to the literature data, there is interaction between heterocyclic azoles (xanthines, imidazoles, benzimidazoles, triazoles) and mono- and multifactoral thiiranes. Studies need to be done on reactions of pyrimidine-2,4-dione derivatives with thiiranes. In this paper, we report on the results of the study of reactions of pyrimidine-2,4-dione derivatives with 2-chloromethylthiirane. Of interest are reaction products presenting as analytical reagents and organic synthons for synthesis of diverse heterocyclic compounds.

It has been demonstrated that with interaction between equimolar amount of pyrimidine-2,4-dione derivatives and 2-chloromethylthiirane in the presence of potassium hydroxide at 50-60°C in the water or water-alcohol mixtures, N(1)-thietanyl derivatives of 5-halogeno(hydroxy)pyrimidine-2,4-dione are being formed as a result of thiirane-thietane rearrangement.



Under similar conditions, reactions of 6-aminopyrimidine-2,4-dione derivatives result in polymers formation. A two-fold increase in 2-chloromethylthiirane failed to lead to N(1)-thietanyl derivatives.

The identity and structure of the synthesized compounds are confirmed by thin-layer chromatography, elemental assay and IR, NMR-spectroscopy.

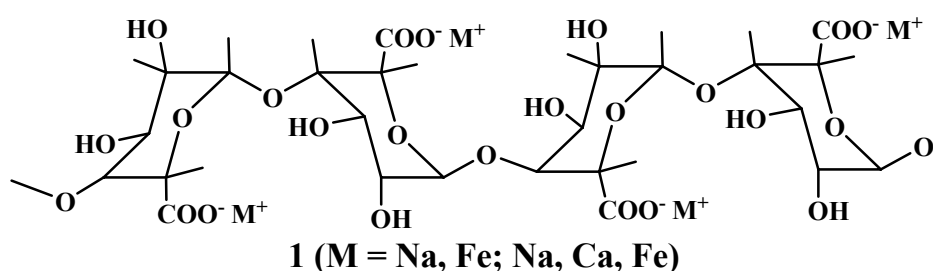
A.B. Vyshtakaliuk
S.T. Minzanova
L.G. Mironova
V.V. Zobov
V.F. Mironov

ANTIANEMIC FERROPOLYGALACTURONATES

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
eugene@kndvor.ru, minzanova@iopc.ru

The solution of microelementosis problems is an important for health of people as well as animals. One of the most spread form of microelementosis is anemia.

The water soluble metal complexes of pectin polysaccharides with Na, Fe and Na, Ca, Fe (**1**) possessing obvious antianemic activity were obtained. Synthesized compounds combine both biological properties of pectin biopolymers and ones of metal ions responsible for important functions in living organisms.



Ferropolygalacturonates are stable in the acid conditions at pH 3-7, minimizes the influence of free metal ions on the gastric wall.

The ferropolygalacturonates polymer matrix provides a gradual separation of metal ions passing through the gastrointestinal tract without causing their local high concentrations of metal ions that lead to negative effects on gastric and intestinal wall.

Complex formation of metal ions with pectin biopolymers ensures the high bio accessibility of macro and microelements and leads to decrease of their toxicity.

The antianemic activity of obtained complexes is higher than the activity of Ferroplex, Tot'hema, Sorbifer, Actiferrin, Ferroglobin B₁₂ preparations. Na-, Fe- and Na-, Ca-, Fe-polygalacturonates (**1**) are not toxic at the dose of 15-25 g/kg. They don't irritate the gastric well, have no irritation and skin-resorbtion effect, don't have teratogenic and embriotoxic effects on the posterity.

MICRONIZATION OF IBUPROFEN BY SPRAY FREEZE-DRYING

A.G. Ogienko¹
E.V. Boldyreva²
A.Yu. Manakov³
V.V. Boldyrev²
A.A. Ogienko⁴
S.A. Myz²
A.S. Yunoshev⁵
N.V. Kutaev¹
A.A. Krasnikov⁶
A.V. Ildyakov³

1 - Novosibirsk State University, REC-008 "Molecular Design and Ecologically Safe Technologies", Novosibirsk, Russia
 2 - Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia
 3 - Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia
 4 - Institute of Cytology and Genetics SB RAS, Novosibirsk, Russia
 5 - Lavrentiev Institute of Hydrodynamics SB RAS, Novosibirsk, Russia
 6 - Central Siberian Botanical Garden SB RAS, Novosibirsk, Russia
 andreyogienko@gmail.com

Ibuprofen - a very common analgetic and antiinflammatory drug - is an example of an active pharmaceutical ingredient exhibiting bad compaction behavior and has to be granulated in most cases before tableting. Beside these disadvantageous properties ibuprofen shows bad dissolution behavior because of its hydrophobic structure. However, a rapid drug release is preferable, especially for analgesic drugs.

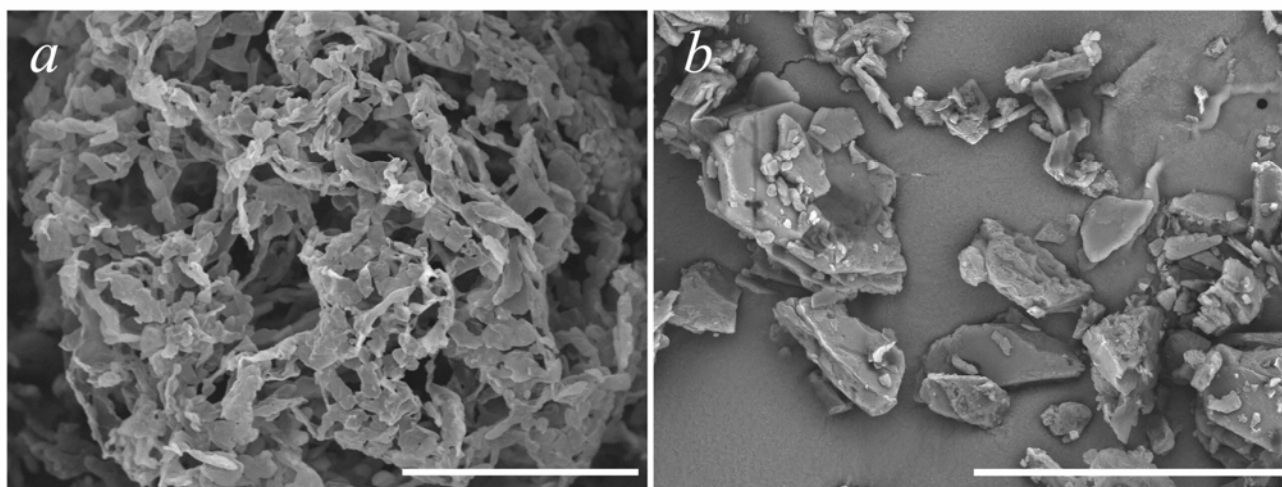


Fig. 1. SEM images of the ibuprofen samples, obtained by freeze-drying (a), and raw material (b). a - bar equal to 50 μm ; b - bar equal to 100 μm .

In the presentation we plan to discuss the preparation method of the ultrafine ibuprofen powder, consisting of planar micron-sized particles, by ultra rapid freezing of solutions followed by removal of the solvent by sublimation under conditions excluding the formation of liquid phases and examination of the properties of the prepared samples by scanning electron microscopy, X-ray powder diffraction, dissolution dynamics experiments, as well as compression properties and specific area measurements.

The authors wish to thank "Tatchempharmpreparaty" for kindly providing the ibuprofen sample. This work was supported by the Integration project No 109 SB RAS, Projects 21.44 and 5.6.4 of Presidium of RAS and Russian Ministry of Education and Science (State Contract of RF № 14.740.11.1023).

PREPARATION AND INVESTIGATION OF PHYSICAL AND CHEMICAL PROPERTIES OF ULTRAFINE FORMS OF MELOXICAM

A.G. Ogienko¹S.A. Myz²N.A. Tumanov²A.S. Yunoshev³A.S. Stoporev¹A.Yu. Manakov⁴T.P. Shakhtshneider²E.V. Boldyreva²V.V. Boldyrev²

1 - Novosibirsk State University, REC-008 "Molecular Design and Ecologically Safe Technologies", Novosibirsk, Russia

2 - Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia

3 - Lavrentiev Institute of Hydrodynamics SB RAS, Novosibirsk, Russia

4 - Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia

andreyogienko@gmail.com

Meloxicam belongs to nonsteroidal anti-inflammatory drugs, therapeutic efficacy of which can be enhanced by improving bioavailability. We used freeze-drying technique to prepare samples of ultrafine meloxicam with particle sizes ~ 100 nm. The concentration of the obtained samples during the first minutes of dissolution being 4 times larger than that of the raw material at the same time (Fig. 1). Afterwards, the concentration goes down to the equilibrium value characteristic of the original substance. Such dissolution dynamics is often observed for amorphous samples, and it is very advantageous for improving therapeutic efficacy, as fast dissolution, avoiding the risks of side effects, such as ulceration. Also, we have developed a method of preparation of co-crystals of meloxicam with carboxylic acids. Co-crystals of meloxicam with succinic and malonic acids were obtained, which have been previously prepared by solid-phase synthesis. The advantage of our technique is that it gives ultrafine forms of the co-crystals of meloxicam.

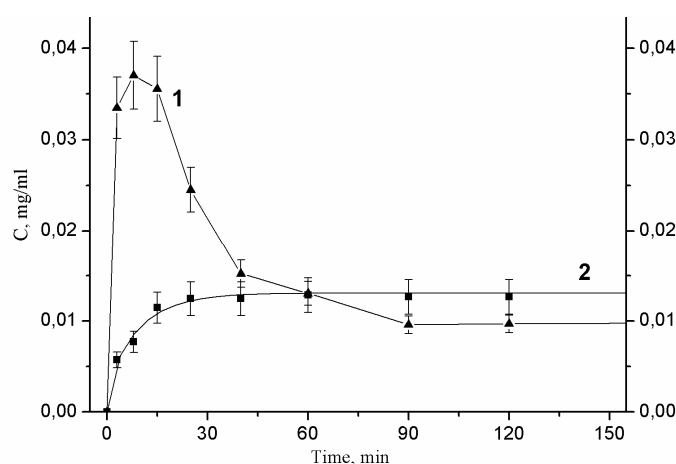


Fig. 1. Dissolution of meloxicam: 1 - nano-porous sample obtained by a freeze-drying technique; 2 – raw material.

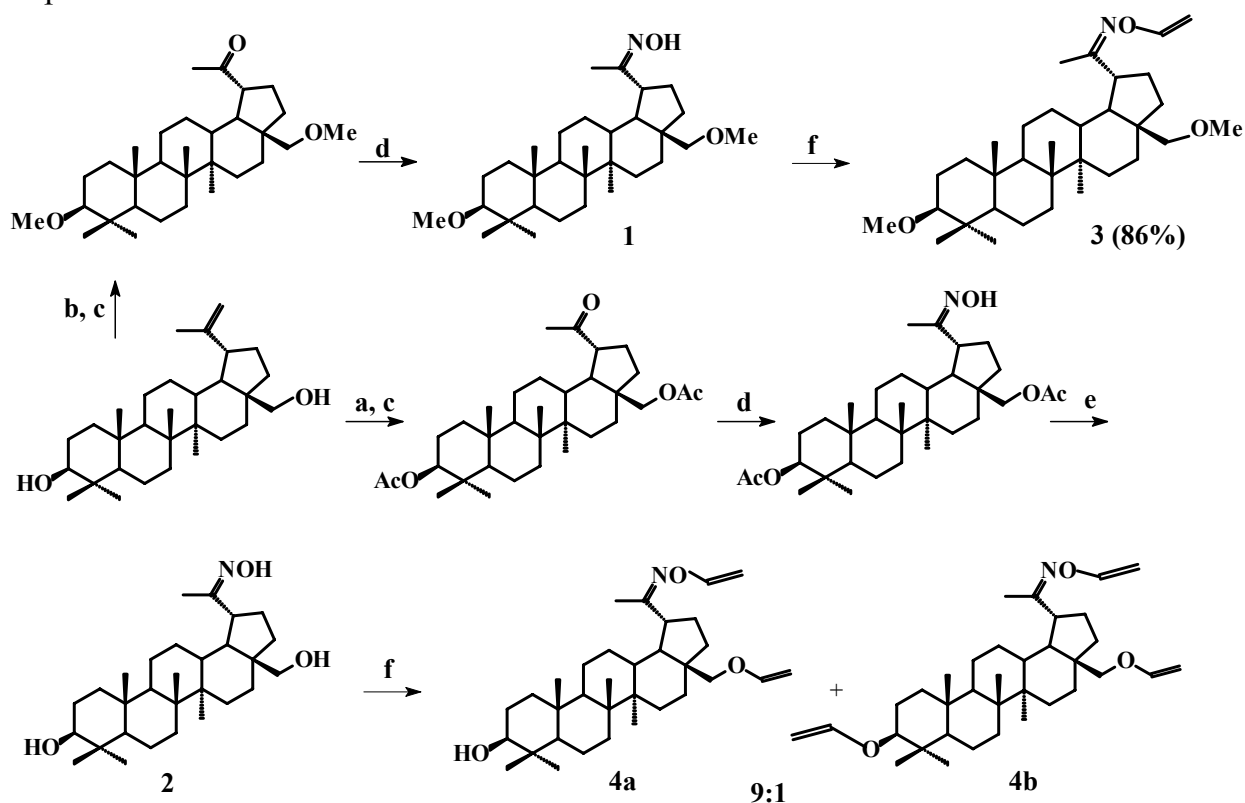
The authors are indebted to "Altaivitaminy" for kindly granting us the meloxicam substance. This work was supported by the Integration project No 109 SB RAS, Projects 21.44 and 5.6.4 of Presidium of RAS and Russian Ministry of Education and Science (State Contract of RF № 14.740.11.1023).

THE FIRST SYNTHESIS OF O-VINYLKETOXIMES IN THE PENTACYCLIC TRITERPENOID SERIES

A.V. Orlov
G.R. Khazipova
N.G. Komissarova
M.S. Yunusov

Institute of Organic Chemistry, Ufa Research Centre, RAS, Ufa,
Russia
adler_orel@mail.ru

Lupan series pentacyclic triterpenoids are perspective class of natural products with a wide spectrum of biological activities. The first representatives of pentacyclic triterpene O-vinylketoximes (3), (4a) and (4b) are synthesized by vinylation of 29-nor-lupan-20-ketoximes (1), (2) with acetylene in a superbase system of KOH-DMSO [1]. Obtained compounds are the new group of stable O-vinylketoximes, a key intermediate of the Trofimov reaction, which may be used in polymer chemistry, and also as biologically active compounds.



a: Ac₂O, Py, 8h; b: NaH, MeI, THF, DMF, 6h; c: O₃, CH₂Cl₂, -60°C, Me₂S; d: NH₂OH·HCl, Py, MeOH, ref., 6h; e: Ca(OH)₂, 70h, 50°C; f: acetylene, KOH/DMSO, 80°C, 15min. (for 1). 50min. (for 2)

References:

1. Trofimov B.A., Gusarova N.K. Acetylene: new prospects of classical reactions. // *Rus. Chem. Rev.* – 2007. V. 76. N. 6. – P. 507–527.

This work was supported by the Presidium of the Academy of Sciences (Basic Research Program number 7), and a grant from the President of Russia for leading scientific schools (NSH-3756.2010.3).

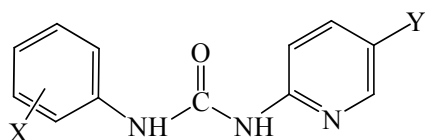
THEORETICAL SCORE OF ENZYME-LIGAND INTERACTION OF SOME DERIVATIVES OF 2-PYRIDINYLUREA WITH GLUCOKINASE

P.S. Petrov
A.V. Semenov
I.V. Tarasova

Mordovian State University named after N.P. Ogarev, Saransk, Russia
petrovps@rambler.ru

Glucokinase is a key enzyme in glucose homeostasis. Glucokinase activators (GKAs) can be used to treat patients with type II diabetes. It is known that activation of the enzyme can be achieved through the interaction of a number of heteroaromatic compounds with its allosteric binding site.

Virtual screening of a series of heteroaromatic structures containing carbamate fragment was carried out by molecular docking in order to search for potential GKAs. The structure of glucokinase was taken from RCSB PDB (PDB ID: 3IMX). It was found that the allosteric site is a T-shaped cavity formed by 33 amino acid residues. Evaluation of ligand-enzyme interaction was carried out by the anchor and grow docking using a software package DOCK 6.4. The scoring function based on the AMBER force field was used for the ranking of ligands. The number of 2-pyridinylureas was selected as lead compounds collected in table.



X	E _{bind} , kcal/mol			
	Y = H	Y = NO ₂	Y = COOH	Y = CONH ₂
H	- 28.41	- 34.23	- 35.36	- 33.63
<i>m</i> -NO ₂	- 33.49	- 39.13	- 35.73	- 38.10
<i>p</i> -NO ₂	- 29.95	- 29.74	- 37.97	- 36.92
<i>m</i> -OH	- 32.98	- 37.17	- 38.05	- 36.33
<i>p</i> -OH	- 33.21	- 34.39	- 37.24	- 36.67
<i>m</i> -NH ₂	- 29.54	- 32.13	- 33.97	- 36.49
<i>p</i> -NH ₂	- 29.82	- 30.38	- 38.87	- 37.70

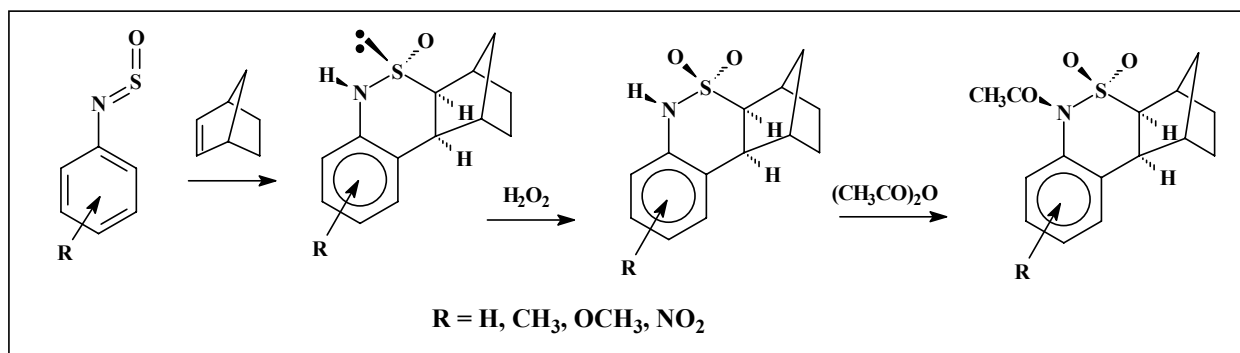
It was found that all ligands forms the hydrogen bonds with key amino acid residues of the allosteric site, or interacts with the enzyme through the van der Waals interaction. The obtained binding energies indicate the formation of stable ligand-enzyme complexes of 2-pyridinylureas with glucokinase. Thus, this compounds may be used as potential GKAs.

CYCLIC SULFONAMIDES AS NEW TYPE OF PHARMACOPHORES. SYNTHESIS, STRUCTURE, ACTIVITY

Ya.V. Veremeychik¹
V.V. Plemenkov¹
O.V. Kazimirchenko²
V.V. Spirihin³
A.N. Lobov³

1 - Immanuel Kant Baltic Federal University, Kaliningrad, Russia
2 - Kaliningrad State Technical University, Kaliningrad, Russia
3 - Institute of Organic Chemistry, Ufa Scientific Center of RAS, Ufa, Russia
plem-kant@yandex.ru

Recently synthesis of compounds containing sulfonamide functional group as potential pharmacophores acquired new significance due to development of new synthetic methods which lead to new structures. We have developed a protocol of synthesis of sulfonamides with benzo-thiazine structure. It has a hybrid composition combining sulfonamide functional group with 1,2-thiazine heterocycle (two in one). Sulfonamides were obtained by Diels-Alder reaction of thionilanilines and norbornene with further acylation of this adducts. Their structure was determined using methods of X-ray diffraction, IR and NMR spectroscopy.



Considered sulfonamides and sulfinamides are showing significant bactericide activity in relation to *Escherichia coli*, *Staphylococcus sp.*, *Pseudomonas sp.*

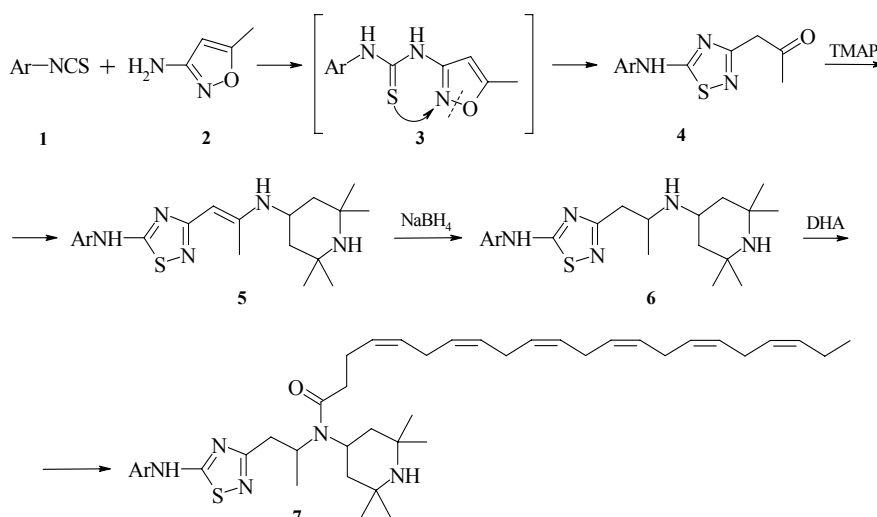
AMIDES OF THE DOCOSAHEXAENOIC ACID WITH THE NOVEL DERIVATIVES OF 1,2,4-THIADIAZOLE AND THEIR INFLUENCE ON NMDA-RECEPTORS

A.N. Proshin¹
I.V. Serkov¹
L.N. Petrova¹
V.V. Bezuglov²
N.M. Gretskeya²
S.O. Bachurin¹

1 - Institute of Physiologically Active Compounds RAS,
Chernogolovka, Russia

2 - Institute of Bioorganic Chemistry RAS, Moscow, Russia
proshin@ipac.ac.ru

Docosahexaenoic acid (DHA, C22:6 ω-3), the most abundant n-3 polyunsaturated fatty acid in the brain, is essential for brain growth and development. Recent evidence has indicated the potential health benefits of DHA for managing Alzheimer's disease. Combination of DHA with other neuroactive substances provide a promising approach to novel pharmaceuticals. We synthesized several new derivatives of DHA functionalized with complex thiadiazoles. The synthesis **7** was performed *via* mixed anhydride strategy yielding products with moderate to good outcome.



The first stage is the reaction of arylisothiocyanates **1** with 3-amino-5-methylizoxazole **2** at which the rearrangement of the intermediate thiourea **3** in the 1,2,4-thiadiazole ring **4** have been occurred due to of the nucleophylic attack of Se-atom on the NO bond of izoxazole cycle. The reaction of ketons **4** with 4-amino-2,2,6,6-tetramethylpyridine (TMAP) gives vinylamine **5** which hydrogenated to amines **6**. Last used for functionalization of DHA and amides **7a** and **7b** have been prepared.

Neuroprotective action on glutamate receptors of the [1-methyl-2-(5-aryl-amino-[1,2,4]thiadiazol-3-yl)-ethyl]-(2,2,6,6-tetramethylpyridin-4-yl)-amines **6** and their derivatives with DHA was estimated in the test on inhibition of glutamate-induced $^{45}\text{Ca}^{2+}$ uptake into synaptosomes of cortex of rat brain. 2,2,6,6-Tetramethylpyridinamines **6** (more than 20 compounds) glutamate-induced $^{45}\text{Ca}^{2+}$ uptake into synaptosomes showing the properties of "NMDA-kines". The spect-rum of action amides **7a** and **7b** on NMDA-receptors cardinally differs from initial **6a** and **6b**.

Table 1. Influence of the synthesized compounds glutamate-induced $^{45}\text{Ca}^{2+}$ uptake into synaptosomes of cortex of rat brain.

	K, %*	IC ₅₀ (mM)		K, %	IC ₅₀ (mM) **
6a	304.6±17.7	-	7a	26.1±6.3	58.9
6b	213.7±12.4	-	7b	38.9±4.8	67.6

**INTERACTION OF IBUPROFEN, S-IBUPROFEN
AND NAPROXEN WITH β -CYCLODEXTRIN AND ITS
DERIVATIVES/POLYMER : EXPERIMENTAL AND
MOLECULAR MODELING STUDIES**

**M.D. Saikia
A. Banik**

Arya Vidyapeeth College, Department of Chemistry, Guwahati, India
monalisaikia@hotmail.com

The interaction of non-steroidal anti-inflammatory drugs such as ibuprofen, S-ibuprofen and naproxen (guests) with β -cyclodextrin (β -CD) and its derivatives (hosts) as well as polymer has been studied using UV visible, Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) spectroscopy and Scanning electron microscopy. In this paper, the solid inclusion complexes were prepared by freeze drying method. The formation constants of the complexes were determined by UV visible method. The adsorption properties of the guests with β -Cyclodextrin-bonded silica particles (CDS) were studied for an in-depth understanding of the host-guest interaction. Infrared (IR) studies indicated the formation of hydrogen bonds between the guests and CDS. The inclusion process involving guests and hosts was investigated by using the PM3 quantum-mechanical semiempirical method. The stabilization energy values obtained from the semiempirical calculation showed the same relation with the formation constant values determined by UV-Vis spectroscopy. In the inclusion process intermolecular hydrogen bonding and Van der Waals interactions were found to be the most prominent interactions. From comparative assessment of inclusion properties, we got that among the systems studied two chemically modified varieties i.e. 2-hydroxypropyl- β -CD (HP- β -CD) and β -CD-sulphated sodium salt (S- β -CD) were more preferable for inclusion compared to native β -CD and of which S- β -CD system was the most, which might possibly give further hopeful applications like chiral separations etc. The β -CD polymer functionalized on silica gel also represented a very interesting choice for inclusion with the guest molecule.

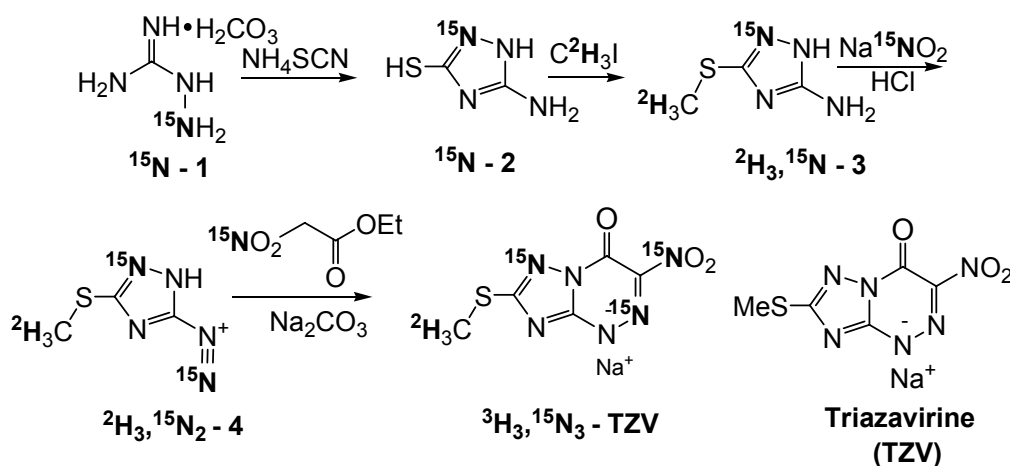
THE SYNTHESIS OF $^2\text{H}_3$, $^{15}\text{N}_3$ -LABELED TRIAZAVIRINE

T.S. Shestakova¹
 S.L. Deev¹
 I.A. Khalymbadza¹
 V.L. Rusinov¹
 O.N. Chupakhin²

1 - Ural Federal University, Ekaterinburg, Russia
 2 - I.Ya. Postovsky Institute of Organic Synthesis, Russian Academy of Sciences, Ekaterinburg, Russia
 tanyash@mail.ustu.ru

The incorporation of stable isotopes into molecules of biological active compounds can be used on early phase development of the drugs. For example, application of ^2H -, ^{15}N -, ^{13}C -labeled compounds allows to study of metabolism and pharmacokinetics [1,2].

Herein we report the synthesis of ^2H , ^{15}N - labeled *Triazavirine* which is new effective inhibitor of human influenza A and B viruses [3,4]. Incorporation of ^2H and ^{15}N isotopes in molecule of *Triazavirine* (TZV) was achieved according to the Scheme 1.



The compound $^2\text{H}_3$, $^{15}\text{N}_3$ -TZV will be used for studies of pharmacokinetics and metabolism of the *Triazavirine* by the mass spectroscopy.

References:

1. T.R Browne, *J. Clin. Pharmacol.*, **1998**, 38, 213.
2. T.R. Browne, G.K. Szabo, A. Ajame, D.G. Browne, *J. Clin. Pharmacol.*, **1998**, 54, 2017.
3. I. Karpenko, S. Deev, O. Kiselev, V. Charushin, V. Rusinov, E. Ulomsky, E. Deeva, D. Yanvarev, A. Ivanov, O. Smirnova, S. Kochetkov, O. Chupakhin, M. Kukhanova, *Antimicrob. Agent. Chemother.*, **2010**, 24, 646.
4. O.N. Chupakhin, V.L. Rusinov, E.N. Ulomsky, V.N. Charushin, A. Yu. Petrov, O.I. Kiselev, Patent RU 2294936, 2007.

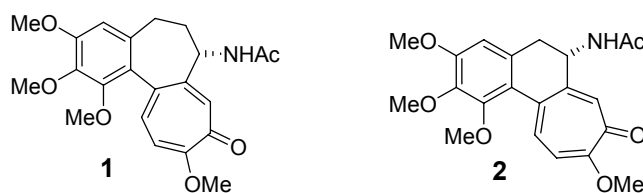
This work was financially supported by the Ministry of Science and Education of the Russian Federation (State contract № 02.740.11.0260 and grant for Leading Scientific Schools, project Nsh-65261.2010.3) and RFBR (project № 10-03-01007-a).

SYNTHESIS OF B-RING-MODIFIED COLCHICINE-ANALOGS AND DERIVATISATION OF B NOR COLCHICINE THROUGH CLICK-CHEMISTRY

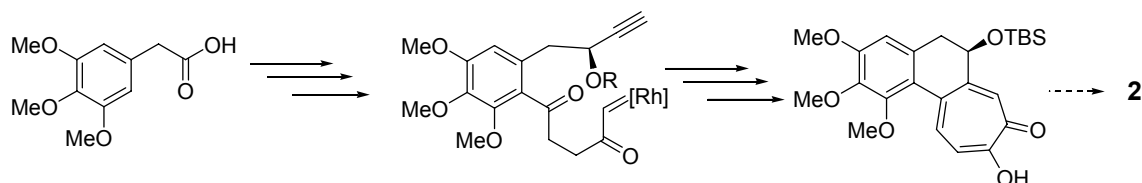
A. Termath
S. Ritter
H.-G. Schmalz

Institute of Organic Chemistry, University of Cologne, Cologne, Germany
termatha@uni-koeln.de

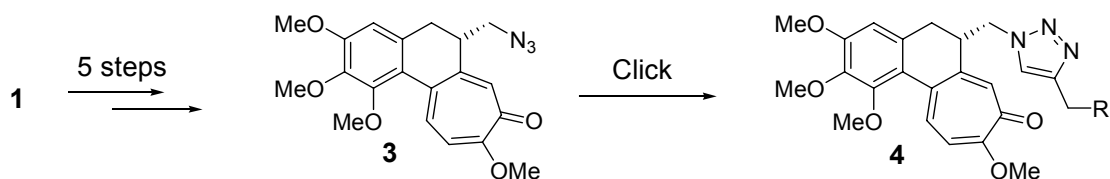
Colchicine (**1**), the main alkaloid of the meadow saffron (*Colchicum autumnale*), is well known for its remarkable antimitotic activity and therefore represents an important lead structure for anti-cancer drug development.^[1]



Interestingly, little is known about the biological activity of B-nor-colchicine derivatives such as **2**. Therefore we applied our strategy, developed in the total synthesis of **1**, also to the preparation of B-nor-analogs.^[2]



In addition, we succeeded to convert natural Colchicin (**1**) into the azide **3**, which was then diversified through Huisgen-1,3-dipolar cycloaddition to give triazols, such as **4**.^[3] First derivatives were synthesized, the biological activity is under investigation.



References:

- [1] T. Graening; H.-G. Schmalz, *Angew. Chem.* **2004**, *116*, 3292.
- [2] Total synthesis: a) T. Graening, W. Friedrichsen, J. Lex, H.-G. Schmalz, *Angew. Chem. Int. Ed.* **2002**, *41*, 1524, b) T. Graening, V. Bette, J. Neudörfl, J. Lex, H.-G. Schmalz, *Org. Lett.* **2005**, *7*, 4317.
- [3] N. Nicolaus; J. Zapke, P. Riesterer, J.-M. Neudörfl, A. Prokop, H. Oschkinat and H.-G. Schmalz, *ChemMedChem* **2010**, *5*, 661.

THE INVESTIGATION OF ACUTE TOXICITY AND PHYSICAL-CHEMICAL PROPERTIES OF ORGANIC SUBSTANCES ON THE BASE OF 2D SIMPLEX REPRESENTATION OF MOLECULAR STRUCTURE

O.V. Tinkov¹
A.G. Artemenko²
P.G. Polishchuk²
L.N. Ognichenko²
V.E. Kuzmin²

1 - T.G. Shevchenko Transdnistria State University, Tiraspol, Moldova, Transdnistria

2 - A.V. Bogatsky Physical-Chemical Institute NAS of Ukraine, Odessa, Ukraine
tinkov84@mail.ru

Nowadays the pollution of the environment is a global problem. The main factor of pollution is different chemical compounds [1].

The data base «Toxic v.1.1.5.» for acute toxicity and physical-chemical properties of organic substances has been prepared. It's contain the information about 2030 chemical compounds. The samples for different conditions have been generated.

The investigation of influence of the molecular structure of different organic compounds on acute toxicity has been carried out by 2D simplex representation of molecular structure [2] with help of approaches Partial Least Squares (PLS) [3] and Random Forest (RF) [4]. The quite satisfactory QSAR models has been obtained. The accuracy of prediction of acute toxicity and physical-chemical properties estimated with help of test correlation coefficient (R^2_{test}) for external test set (ts).

Table 1. The statistic characteristics of QSAR models on the base of approach RF.

№	Test Type	Organism	Route	Quantity compounds in set (ws/ts)	R^2_{test}
1	Ld ₅₀	rat	oral	940(752/188)	0,560
2	Ld ₅₀	mouse	intravenous	302(241/61)	0,603
3	Lc ₅₀	mouse	inhalation	210(168/42)	0,591

Table 2. The statistic characteristics of QSAR model on the base of approach PLS.

№	Test Type	Organism	Route	Quantity compounds in set (ws/ts)	R^2_{test}
1	Ld ₅₀	rat	intravenous	127(101/26)	0,697

Table 3. The statistic characteristics of QSAR models on the base of approach RF.

№	Physico-chemical property	Quantity compounds in set (ws/ts)	R^2_{test}
1	log P (octanol-water)	792(633/159)	0,877
2	Water Solubility	821(656/165)	0,790

In addition relative influence of some physical-chemical factors on variation of acute toxicity estimated on the base of QSAR models.

The statistic characteristics of the 2D-QSAR models for the prediction of physical-chemical properties on the base of approach RF are quite satisfactory.

«Toxic v.1.1.5.» database and developed models are realized as Expert Systems for Ecological Risk Prediction. The authors express sincere gratitude to A.E. Shustikov for fruitful cooperation that made possible the development of this task.

References:

1. Kurlyandsky B.A., Filov V.A.. General Toxicology. – M.: Medicine, 2002, P.10-11
2. Kuz'min, V. E.; Artemenko, A. G.; Muratov, E. N. Hierarchical QSAR technology on the base of simplex representation of molecular structure. J. Comp. Aid. Mol Des. 2008, 22, P.403-421.
3. Rannar S., Lindgren F., Geladi P., Wold S., J. Chemom., 1994, 8, P 111-125.
4. Polishchuk P.G., Muratov E. N., Artemenko A. G., Kolumbin O. G., Muratov N. N., Kuz'min V. E., Application of Random Forest Approach to QSAR Prediction of Aquatic Toxicity, J. Chem. Inf. Model. 2009, 49, P. 2481-2488

MOLECULAR STRUCTURE AND SUPRAMOLECULAR ARCHITECTURE OF THE CLATHROCHELATE IRON AND COBALT(II) COMPLEXES WITH DISK-LIKE FULLY FLUORINATED EXTERNAL SHELL

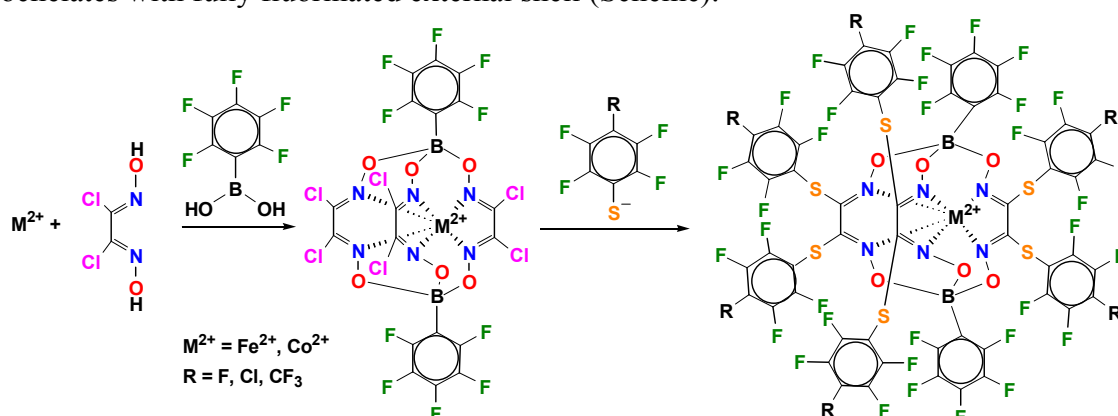
Y.Z. Voloshin¹
A.S. Belov¹
A.V. Vologzhanina¹
O.A. Varzatskii²
I.G. Makarenko¹
A.I. Isachenko¹
G.E. Zelinsky¹

1 - Nesmeyanov Institute of Organoelement Compounds RAS,
Moscow, Russia

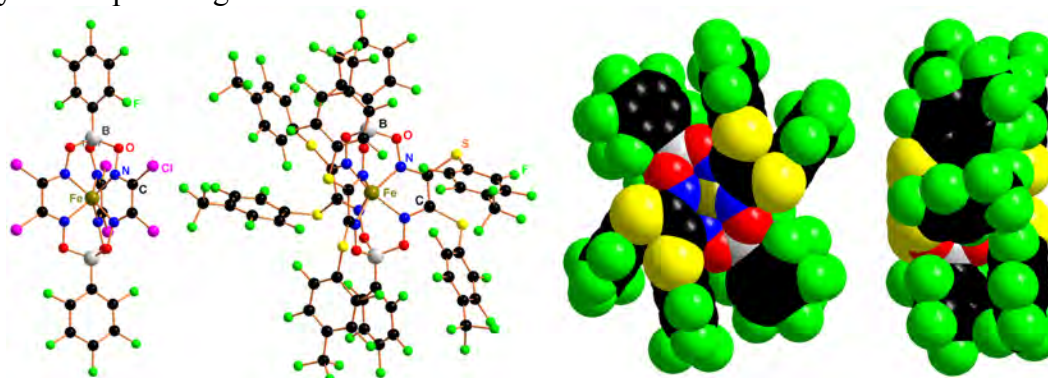
2 - Vernadskii Institute of General and Inorganic Chemistry NANU,
Kiev, Ukraine
voloshin@ineos.ac.ru

The clathrochelate transition metal complexes have recently been proposed as the components of the efficient initiating catalytic systems of olefin polymerization, the electrocatalysts for the production of the molecular hydrogen and the inhibitors of RNA polymerase (and, therefore, the potent antiviral and anticancer drugs). The physical and physicochemical properties of the functionalized macrobicyclic complexes as well as their supramolecular interactions are determined, to a great extent, by the nature of the functionalizing apical and ribbed substituents.

The direct template condensation of dichloroglyoxime with pentafluorophenylboronic acid on the iron and cobalt(II) ions as a matrix afforded the hexachlorine-containing iron and cobalt(II) clathrochelates. The nucleophilic substitution of the reactive chlorine atoms of these macrobicyclic precursors with generated *in situ* fluoroarylsulfate ions gave the ribbed-functionalized clathrochelates with fully fluorinated external shell (Scheme).



According to X-ray diffraction data, their fully fluorinated molecules possess the unusual disk-like shape (Figure). Two apical pentafluorophenyl and six ribbed fluoroarylsulfide substituents form the second superhydrophobic shell around an encapsulated metal ion and determine their solubility in non-polar organic media.



The authors gratefully acknowledge support of the RFBR (grants 09-03-00540, 09-03-00688 and 11-03-00986) and RAS (programmes 6,7 and P7).

NEW FUNCTIONALIZED CHLOROCYCLOPENTENONES FROM 6,8,9-TRICHLORO- AND 8,9-DICHLORO-1,4- DIOXASPIRO[4.4]NON-8-EN-7-ONES

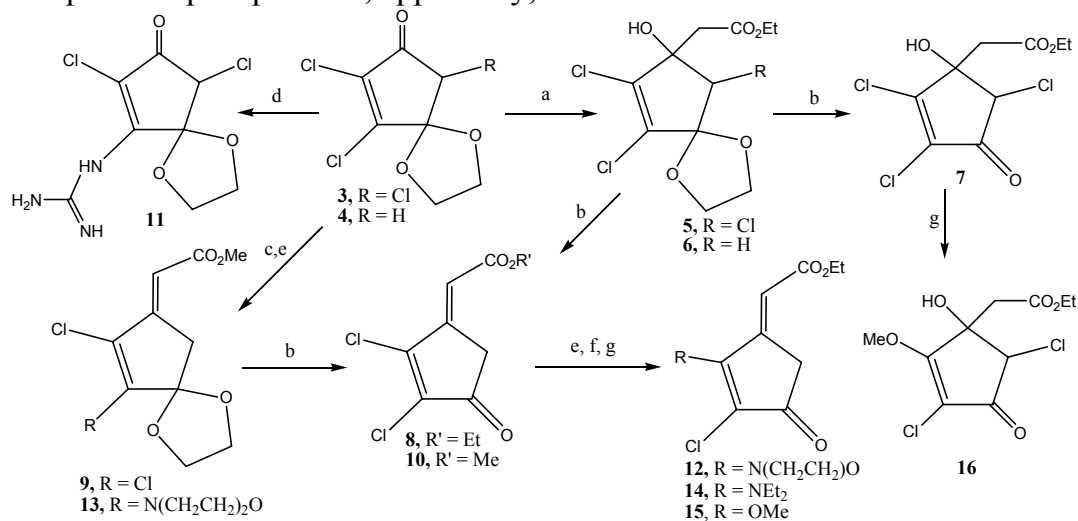
V.A. Yegorov¹
F.A. Gimalova¹
M.S. Miftakhov¹
G.M. Khalikova²

1 - Institute of Organic Chemistry, Ufa Scientific Centre of the Russian Academy of Sciences, Ufa, Russia

2 - Bashkir State University, Ufa, Russia
fangim@anrb.ru

In connection with growth of virus diseases in the world search of the new compounds possessing anti-virus activity, remains an actual problem for chemists. Among representatives of anti-virus compounds of new generation we shall note widely put into practice carbocyclic inhibitor of Neuraminidase Tamiflu and its cyclopentene analogue Peramavir which passes last stage of clinical tests [1,2].

In the given work with the purpose of synthesis the isosteric to **2** compounds by us are investigated some transformations of chlorocyclopentenones **3** and **4** [3]. For introduction of carboxy-functions in structures **3** and **4** we used reactions with a Li-derivative of EtOAc, thus with a good yield received hydroxyethers **5** and **6**, hydrolysis of dioxalane protective group by action of 98% H₂SO₄ at 0°C resulted to hydroxyketone **7** and dienone **8** correspondingly. The methyl ether **9** is received by interaction chlorocyclopentenone **4** with Ph₃P=CHCO₂Me in benzene. In similar conditions ketone **3** no react with specified phosphorane, apparently, because of steric factors.



a) THF, LDA, CH₃COOEt; b) 98% H₂SO₄; c) MeO₂CCH=PPh₃, PhH; d) H₂NC(NH)NH₂·HCl, KOH, MeOH; e) morfoline, PhH; f) metionine, MeOH; g) Et₂NH, PhH or MeOH.

Introduction of N-function we carried out in standard conditions N-ketovinilation [3]. By interaction of compounds **8-10** with secondary amines (morfoline, diethylamine) and chlorocyclopentenone **3** with a guanidine hydrochloride in benzene are synthesized new vinyllogues amides **11-14**. Similar reactions **7** and **8** with methionine and diethylamine in MeOH instead of expected N-derivatives has led to enoethers **15** and **16**.

References:

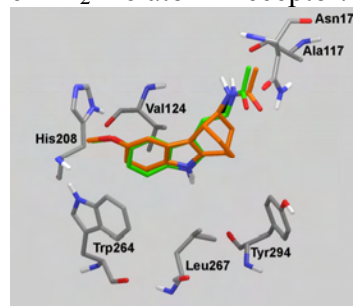
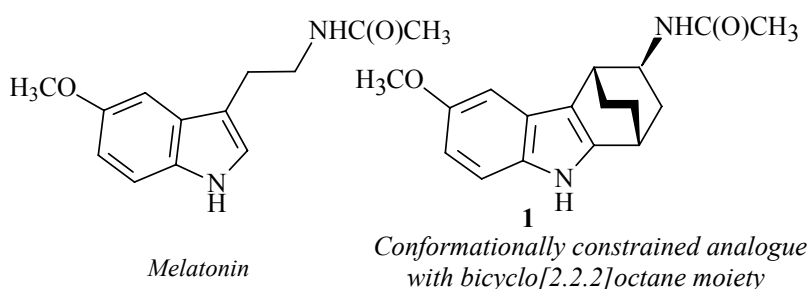
- 1) Shibasaki M., Kanai M. *Eur. J. Org. Chem.* **2008**, 1839.
- 2) Babu Y.S., Chand P., Bantia S., Kotian P., Dehghani A., e.a. *J. Med. Chem.* **2000**, 43, 3482.
- 3) Akhmetvaleev R.R., Akbutina F.A., Ivanova N.A., Miftakhov M.C. *Russ. Chem. Bull.* **2001**, 1417.

BRIDGEHEAD MELATONIN ANALOGUE: MOLECULAR DESIGN, SYNTHESIS AND BIOTESTING

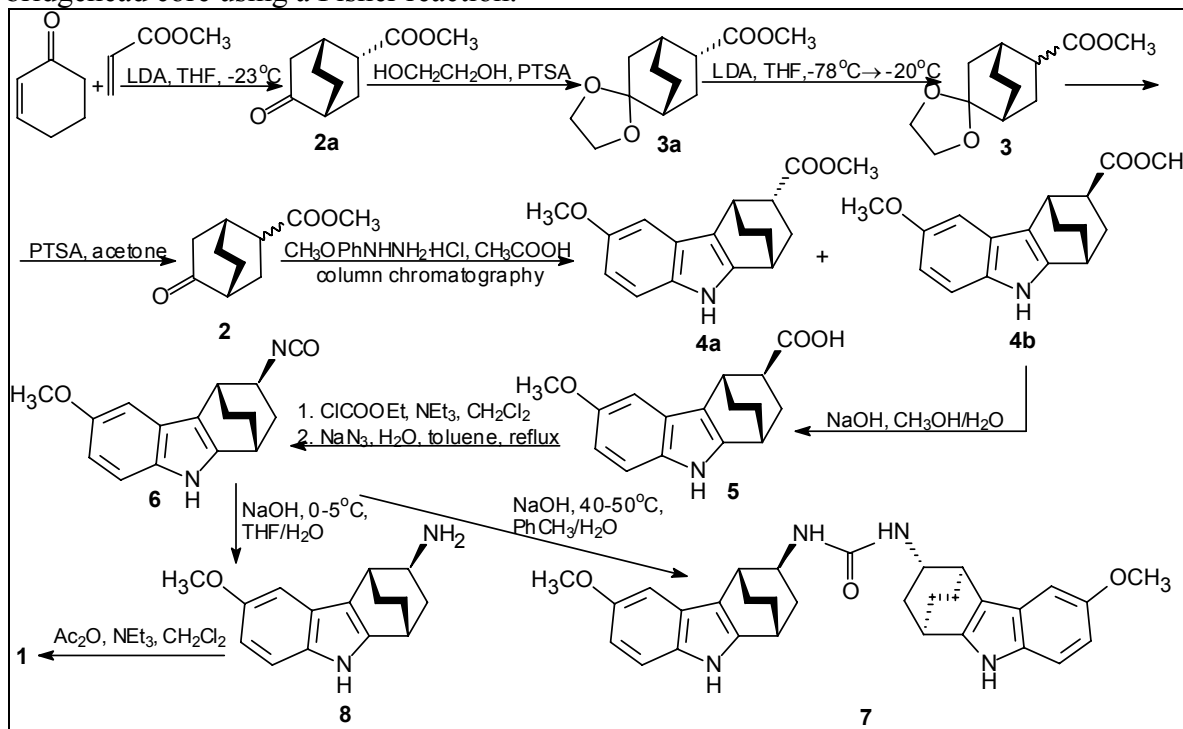
O.N. Zefirova¹
T.Yu. Baranova¹
A.A. Ivanova¹
A.A. Ivanov²
N.S. Zefirov¹

1 - M.V. Lomonosov Moscow State University, Department of Chemistry, Moscow, Russia
2 - Emory University School of Medicine, Department of Biochemistry, Atlanta, GA, USA
olgaz@org.chem.msu.ru

Conformationally constrained analogue of the hormone melatonin with a side chain incorporated into the bicyclo[2.2.2]octane core (structure **1**) was synthesized based on the homology modeling and molecular docking studies performed for the MT₂ melatonin receptor.



Synthesis of the purpose compound **1** was performed by the indole fragment formation on the bridgehead core using a Fisher reaction.



The compound **1** (as racemic mixture) was found to possess 2.75 nM affinity to human MT₂ receptor.

References:

1. O.N. Zefirova, T.Yu. Baranova, A.A. Ivanova, A.A. Ivanov, N.S. Zefirov. Bioorg. Chem. 2011, 39, 67–72.

The work was supported by the Russian Fund for Basic Research (project 09-03-879).

REACTIVITY OF NATURAL POLYPHENOLS TOWARDS ELECTROGENERATED OXIDANTS

G.K. Ziyatdinova
A.M. Nizamova
H.C. Budnikov

Department of Analytical Chemistry, Kazan (Volga Region) Federal
University, Russia
Ziyatdinovag@mail.ru

Polyphenols are important antioxidants having ability to scavenge free radicals. They participate in prevention of lipids peroxidation in biological tissues and subcellular structures (mitochondria, microsomes, liposomes and erythrocyte membranes). Therefore investigation of natural polyphenols reactivity reflecting their antioxidant properties is of interest.

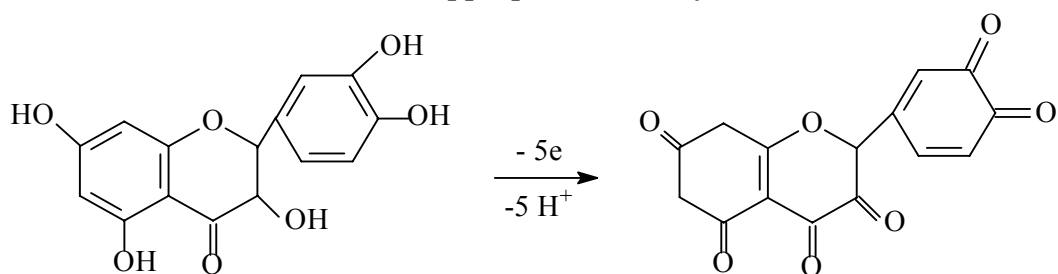
Constant-current coulometry is suitable method for the evaluation of polyphenols antioxidant properties as far as allows to get useful information about reactions with electrogenerated oxidants that can be applied for the modeling of processes taking place in living systems.

Reactions of natural polyphenols (rutin, quercetin, dihydroquercetin, gallic acid, catechin, tannin, curcumin and luteolin) with electrogenerated halogens and hexacyanoferrate(III) ions have been investigated. The corresponding stoichiometric coefficients have been found. The schemes of the reaction with electrogenerated hexacyanoferrate(III) ions for polyphenols under investigation have been proposed.

Number of electrons participating in reactions of polyphenols with electrogenerated halogens is big enough that is caused by oxidation of hydroxyl groups as well as reactions of electrophilic substitution.

Hexacyanoferrate(III) ions act as one-electron oxidant. Titration of the standard solutions of natural polyphenols showed their reactions with titrant were fast and quantitative. The number of electrons involved in the oxidation stage corresponds to the number of OH-groups present in the molecules of polyphenols excluding of catechin and curcumin. Curcumin is destroyed partially in basic media with formation of ferulic acid and feruloylmethane but these processes are time dependent.

Oxidation leads to formation of appropriate carbonyl derivatives.



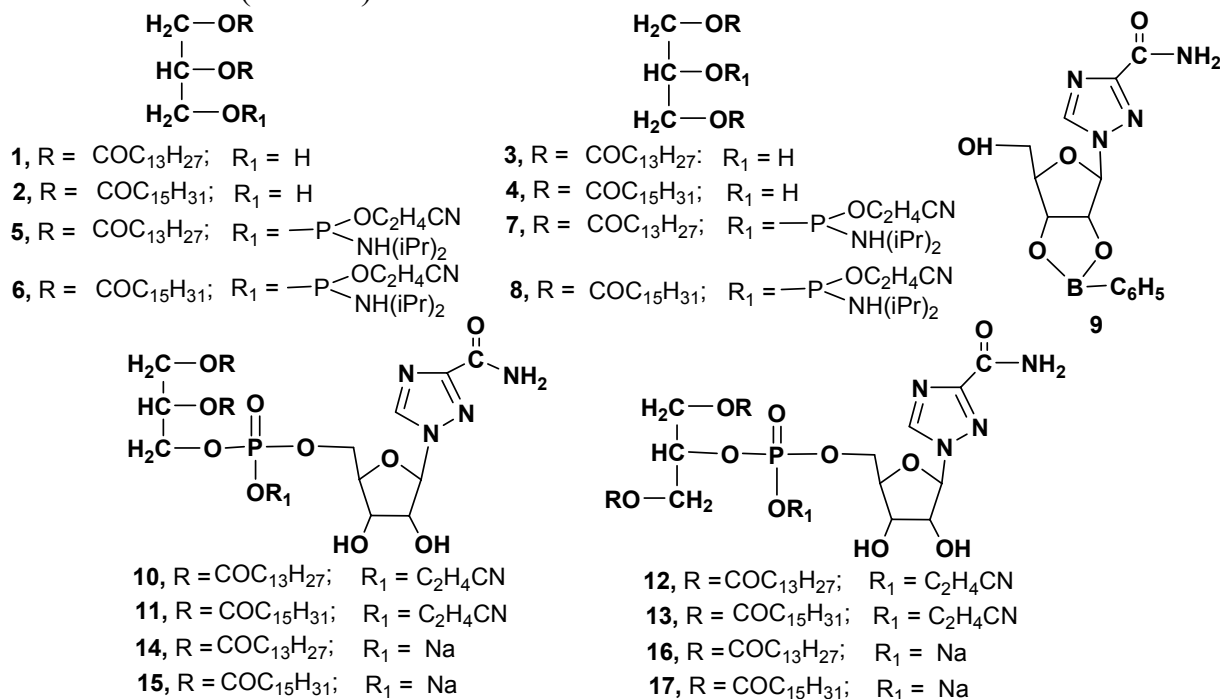
For rutin, only aromatic hydroxyl groups are oxidized. Saccharide residue is not involved in the reaction with electrogenerated hexacyanoferrate(III) ions. This was confirmed by titration of glucose and rhamnose performed in the same experimental conditions.

The investigations carried out have shown high reactivity of natural polyphenols toward electrogenerated oxidants of different nature.

SYNTHESIS AND PROPERTIES OF NEW
RIBAVIRIN-LIPID CONJUGATESI.A. Oleynikova
T.I. Kulak
E.N. KalinichenkoInstitute of Bioorganic Chemistry, the National Academy of Sciences
of Belarus, Minsk, Belarus
ilona.olenikova@mail.ru

The conjugation of bioactive nucleosides with lipids often leads to prodrugs possessing improved pharmacokinetics and reduced cytotoxicity as compared with original nucleosides.

In this work a set of new conjugates of antiviral nucleoside ribavirin [1-(β-D-ribofuranosyl)-1,2,4-triazole-3-carboxamide] with 1,2- or 1,3-diacylglycerophosphates has been prepared. The interaction of 1,2- (1,3-) diacylglycerols (**1-4**) with 2-cyanoethyl N,N-diisopropylchlorophosphoramidite in acetonitrile in the presence of N-ethyldiisopropylamine led to obtaining 3- or 2-phosphoramidites **5-8** (81-87%), which were conjugated with 2',3'-di-O-phenylboronate **9** synthesized by the treatment of ribavirin with phenylboric acid in pyridine (84%). After iodine oxidation, the phosphotriesters **10-13** have been obtained (56-79%).



The removal of cyanoethyl group from the compounds **10-13** has been performed by the interaction with NEt_3/Py (1:1) to give triethylammonium salts of conjugates **14-17** (56-76%), which have been transformed to the stable sodium salts by the treatment with NaI in acetone.

The substrate properties of ribavirin-diacylglycerophosphate conjugates **14-17** toward the action of pancreatic phospholipase A_2 have been investigated.

This work has been done with financial support from the National Academy of Sciences of Belarus within the research project number 4.19 of ChemPharmSynthesis Program.

SYNTHESIS OF ACYCLIC NUCLEOSIDES ANALOGUES BASED ON 6-PHENYL-1,2,4- TRIAZOLO[1,5-a]PYRIMIDIN-7-ONES

I.A. Khalymbadza¹T.S. Shestakova¹S.L. Deev¹V.L. Rusinov¹O.N. Chupakhin²

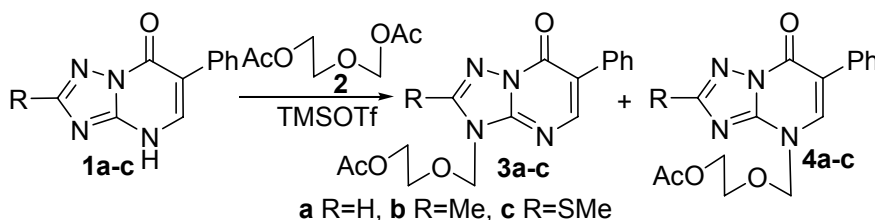
1 - Ural Federal University, Ekaterinburg, Russia

2 - I.Ya. Postovsky Institute of Organic Synthesis Russian Academy of Sciences, Ekaterinburg, Russia

XAJIbIM@MAIL.RU

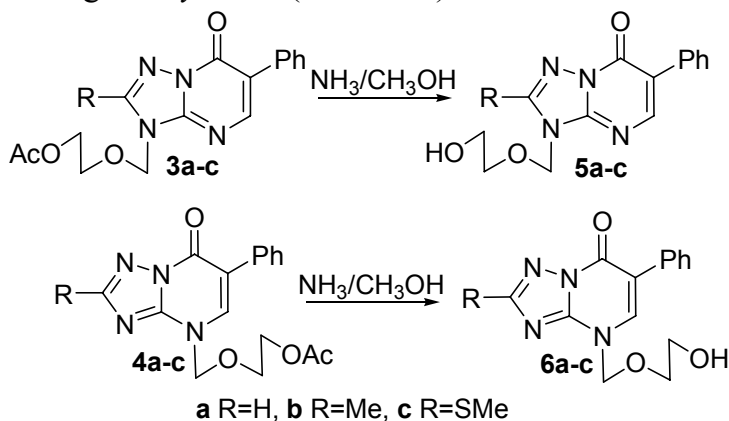
Analogues of nucleosides are widely presented in the antiviral medicine [1,2]. Acyclic derivatives of this class of compounds (*Acyclovir*, *Gancyclovir*) have demonstrated activity against *herpes simplex viruses*, *varicella-zoster virus* and *cytomegalovirus*.

We synthesized analogues of *Acyclovir* based on 1,2,4-triazolo[1,5-a]pyrimidin-7-ones **1a-c** according to the Vorbrüggen-type glycosylation procedure [3]. The alkylation of **1a-c** with **2** gave the mixture of compounds **3a-c** and **4a-c** (Scheme 1). The study of this reaction showed that compounds **4** are thermodynamically more favored in comparison with **3**.



Scheme 1

Ammonolysis of compounds **3a-c** and **4a-c** gave nucleosides **5a-c** and **6a-c** that are analogues of antiviral drug of *Acyclovir* (Scheme 2).



Scheme 2

The structures of compounds **3a-c** and **4a-c** were confirmed by ¹H and ¹³C NMR spectra. The study of antiviral action of these compounds showed a moderate activity against *herpes simplex virus*.

References:

1. E. De Clercq, *J. Pharmacology and Experimental Therapeutics*, **2001**, 297, 1.
2. E. De Clercq, *Clinical Microbiology Reviews*, **2001**, 14, 382.
3. H. Vorbrüggen, *Acc. Chem. Res.*, **1995**, 28, 509.

This work was financially supported by the Ministry of Science and Education of the Russian Federation (State contract № 02.740.11.0260 and grant for Leading Scientific Schools, project Nsh-65261.2010.3) and RFBR (project № 10-03-01007-a).

Section 7.

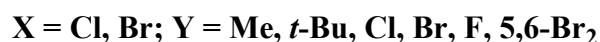
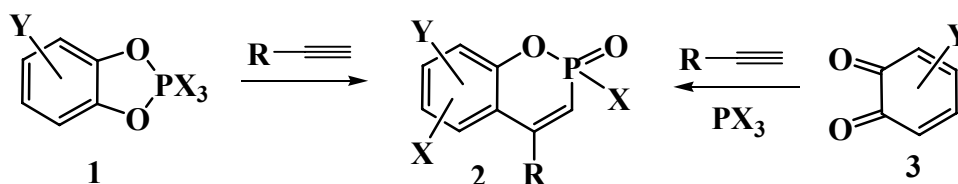
Organometallics in Organic Synthesis

REACTION OF 2,2,2-TRIHALOGENBENZO-1,3,2-DIOXAPHOSPHOLES WITH TERMINAL ACETYLENES: EASY *ipso*-SUBSTITUTION OF OXYGEN BY CARBON AND P-C BOND FORMATION

V.F. Mironov
A.V. Nemtarev

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
mironov@iopc.ru

The results of investigation of the new reaction in phosphorus chemistry, namely, the interaction 2,2,2-trihalogenobenzo-1,3-dioxaphospholes (**1**) substituted in aromatic moiety and monosubstituted alkyl-, arylacetylenes are summarized in the report. The experimental data for the three-component system of *ortho*-quinone – arylacetylene – phosphorus halogenide are also analyzed. The reaction leads to formation of six-membered fused P-heterocycles – 2-oxo-4-R-areno[*e*]-1,2-oxaphosphinines or “phosphacoumarins.” The easy formation of a P–C bond and phosphoryl group, the *ipso*-substitution of the oxygen atom by the carbon one, and selective chlorination *para* to endocyclic oxygen are realized under mild conditions in this reaction [1,2]. The *ipso*-substitution of a tertiary butyl group and a bromine atom also takes place in some cases. The regiochemistry of *ipso*-substitution of oxygen and halogenation of the arylene moiety depends on the substituents nature in the P(V) derivative and acetylene. The regioselectivity of chlorination and bromination of the aromatic moiety is lower for propargylchloride than for the arylacetylenes. The classic addition to multiple bond of acetylene took place in reaction of ethoxyacetylene along with the formation of benzophosphinines. The by-side substitution reaction of bromine by chlorine in the forming benzophosphinine was found for reaction of propargylbromide with phosphorane (**1**).



The possibility of the utilization of the hexacoordinated phosphorus derivatives such as the neutral and anionic phosphorates was also shown. The scheme of the reaction was proposed on the basis of the obtained experimental data. It includes the stage of the formation of the intermediate hexacoordinated phosphorus derivatives, 2,2,2-trihalogeno- λ^5 -1,2-oxaphospholenes and dichlorovinylphosphonates containing a quinoid fragment. The structures of benzo[*e*]-1,2-oxaphosphinines were confirmed by NMR and XRD.

References:

1. V.F. Mironov, A.V. Nemtarev, E.N. Varaksina. In book: Phenolic Compounds: Fundamental and Applied Aspects (in Russian). Moscow, Scientific World, 2010. P. 6-37.
2. V.F. Mironov, A.V. Nemtarev, *Rev. J. Chem.* 2011, Vol. 1 (1), 27-55.

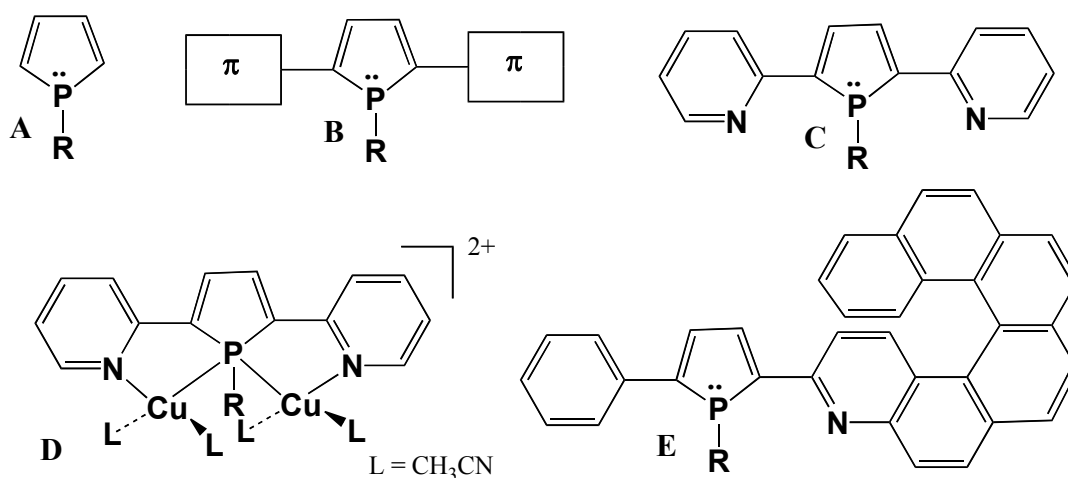
The work was supported by the Russian Foundation for Basic Research (grant 10-03-00525).

ORGANOPHOSPHORUS AND ORGANOMETALLIC CHEMISTRY FOR THE DESIGN OF ORGANIC CONJUGATED SYSTEMS

M. Hissler
R. Reau

Universite de Rennes1, CNRS, Sciences Chimiques de Rennes,
Rennes cedex, France
regis.reau@cnrs-dir.fr

π -Conjugated oligomers and polymers based on aromatic heterocyclopentadienes have attracted strong interest in recent years owing to their potential applications for electronic devices (light emitting diodes, thin film transistors, photovoltaic cells...). The tailoring of these semi-conducting organic materials for improving their electrochemical and optical properties towards plastic electronic applications necessitates extensive experimental molecular engineering. We have showed that the phosphole unit is an appealing building block for this molecular engineering due to its low aromatic character and the versatile reactivity of its P-centre that allow a structural diversity to be easily generated. The synthesis of π -conjugated systems based on phosphole synthons and their use as materials for OLEDs, including white-emitting devices, will be presented. Their coordination chemistry was also exploited towards the design of new helicenes derivatives with tuneable, large chiroptical properties.



For recent references see:

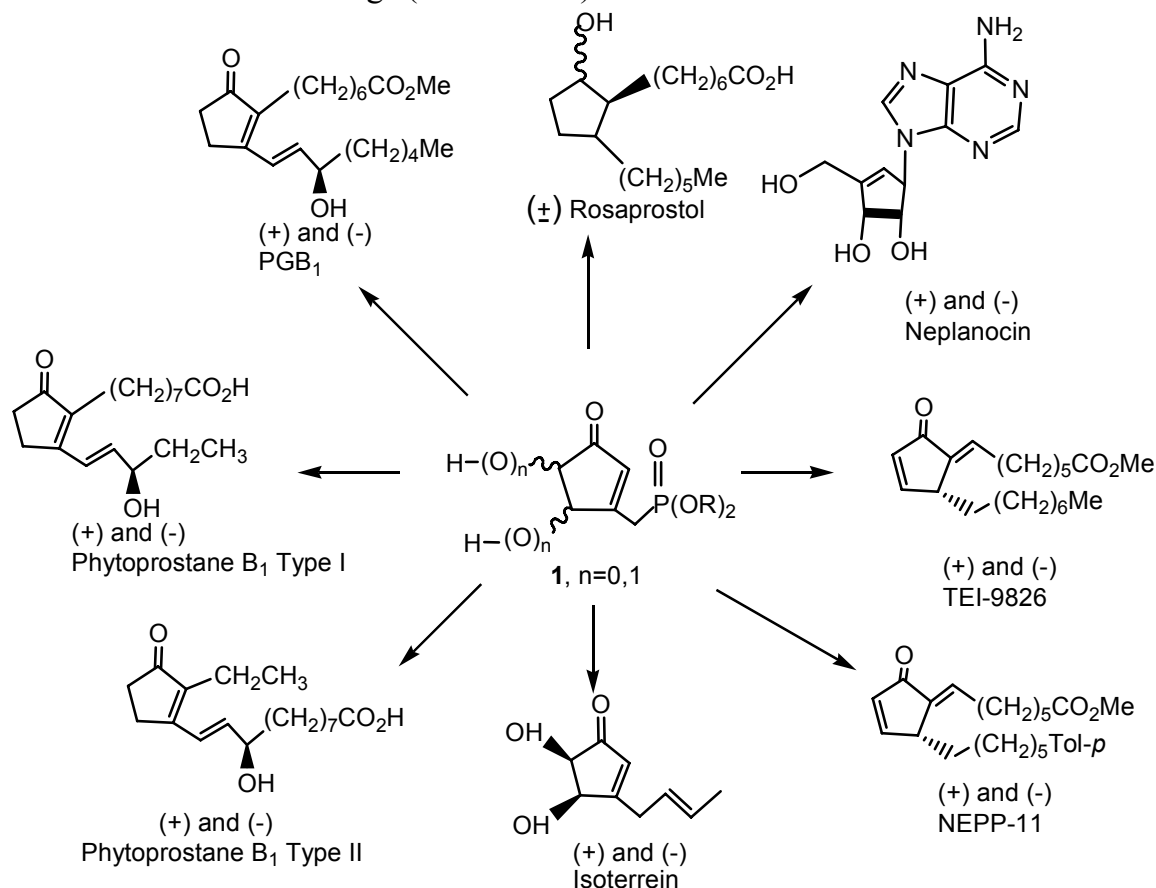
Adv. Mat., **2009**, 21, 1261 ; *J. Am. Chem. Soc.*, **2009**, 131, 3183 ; *Chem. Eur. J.*, **2010**, 16, 11340, **2010**, 16, 5976 and **2010**, 16, 7143; *Angew. Chem. Int. Ed.*, **2010**, 49, 99; *J. Am. Chem. Soc.*, **2011**, 133, 3800 ; *Chem. Eur. J.*, **2011**, 4, 1357 ; *Chem. Eur. J.*, **2011**, in press.

PHOSPHONATE-BASED STRATEGY FOR SYNTHESIS OF CYCLOPENTENONE AND CYCLOPENTANONE NATURAL AND BIOACTIVE PRODUCTS

M. Mikołajczyk

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-363 Lodz, Sienkiewicza 112 str., Poland
marmikol@bilbo.cbmm.lodz.pl

The lecture will highlight one area of our current research dealing with the use of achiral and chiral 3-(phosphorylmethyl)cyclopent-2-enones **1** in the synthesis of bioactive compounds¹. In the first part of the lecture the synthetic approaches to and reactivity of **1** will be briefly discussed as a platform for developing new strategy for functionalization of the cyclopentenone ring. The major part of the lecture will be devoted to demonstration of the utility of **1** in the total syntheses of selected representatives of cyclopentanoid antibiotics, carbocyclic nucleosides, prostaglandins and analogues, phytoprostanes as well as antiulcer and anticancer drugs (see Scheme).



References:

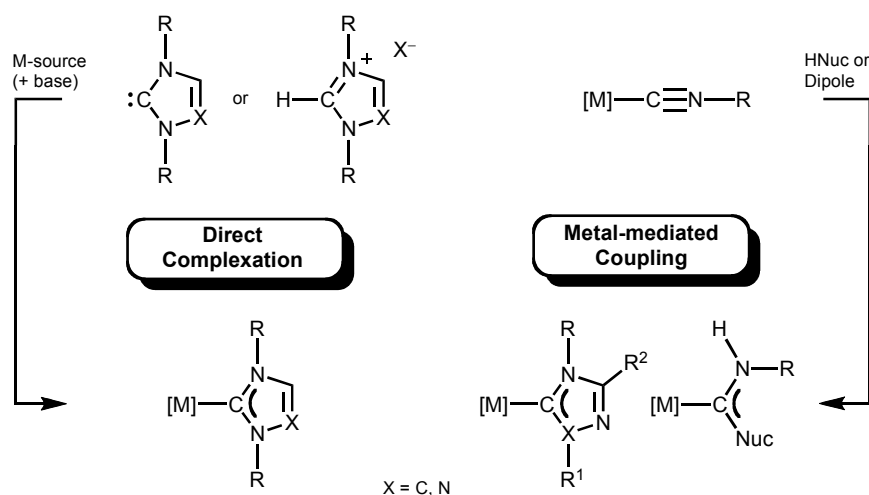
1. For our recent paper on this topic see: Zurawiński, R. ; Mikina, M.; Mikołajczyk, M. *Tetrahedron: Asymmetry* **2010**, *21*, 2794-2799 and references therein.

AMINOCARBENES: "X.O" OF ORGANOMETALLIC CHEMISTRY

V.Yu. Kukushkin

Department of Chemistry, Saint-Petersburg State University, Stary
 Petergof, Russia
 kukushkin@vk2100.spb.edu

Heteroatom-stabilized carbene complexes (e.g., *N*-heterocyclic carbenes or NHC's) have acquired a high importance in modern organic and organometallic chemistry. In particular, these species are prominent in organometallic catalysis for, for instance, hydrosylation of alkenes and diversity of cross-coupling reactions (e.g., Heck, Suzuki–Miyaura, Sonogashira, Kosugi–Migita, and Stille). Two general main approaches for the preparation of such carbene complexes include (i) a direct complexation of pre-prepared free carbenes (or typically generated *in situ* from their precursors and a base) to a metal center, and (ii) a metal-mediated nucleophilic addition, or a 1,3-dipolar cycloaddition to isonitriles.



This report provides a synthetic, structural, and mechanistic overview of the recent advances in the field of metal-mediated transformations of isonitriles with a particular emphasis addressed to the activation of the C≡N moiety toward the addition of protic nucleophiles and dipoles. We also report that the aminocarbene complexes generated in the reaction exhibit (i) a very high, the so-called homoeopathic catalytic activity in the Suzuki–Miyaura cross-coupling; (ii) catalytic activity in the Sonogashira reaction; (iii) important substituent-dependent luminescent properties.

References:

Chem. Rev., **102** (2002) 1771; *Chem. Eur. J.*, **15** (2009) 5969; *J. Org. Chem.*, **75** (2010) 1474; *Organometallics*, **27** (2008) 5379; **28** (2009) 1406; **28** (2009) 6559; **30** (2011) in press; doi: 10.1021/om101041g.

Acknowledgements: A large part of this project was carried out jointly with Dr. K.V. Luzyanin (IST, Lisbon). The author thanks him for his efforts and enthusiasm that made the collaboration enjoyable. The author also expresses his gratitude to Federal Grant-in-Aid Program "Human Capital for Science and Education in Innovative Russia" (Governmental Contract No P676 from 20/05/2010), Russian Fund of Basic Research (grant 09-03-00065), Saint-Petersburg State University (research grant 2011–2013), RAS Presidium Subprogram coordinated by acad. N.T. Kuznetsov, and Fundação para a Ciência e a Tecnologia, Portugal (Project PTDC/QUI-QUI/098760/2008), for support of these studies.

**PROGRESS IN SYNTHETIC APPLICATIONS OF
ALKOXYTITANACYCLOPROPANE REAGENTS**

O.G. Kulinkovich

Tallinn Technical University, Department of Chemistry, Tallinn,
Estonia
o.kulinkovich@gmail.com

The use of organometallic reagents in organic synthesis has a sesquicentennial history, in the beginning of which Alexander Butlerov synthesised pinacolone by the reaction of trimethylacetyl chloride with dimethylzinc.¹ In that way the correctness of the proposed structure of the skeletal rearrangement product was proved. In large part due to the results obtained by his students Zaitsev and Reformatskii, organozinc compounds have continued to be used for creation of carbon-carbon bonds till nowadays.

Recent advances in the synthetic applications of non-transition organometallics are mainly associated with the reactions catalyzed by transition metal salts. As a result, transfer of alkyl group from reagent to substrate in a structurally changed form is, in some cases, observed. The reaction of ethylmagnesium bromide and its higher homologues with carboxylic esters in the presence of titanium alkoxides proceeds in such manner that affords tertiary cyclopropanols. In this case, the catalyst ensures the action of Grignard reagents as the equivalents of the corresponding alkenyl 1,2-dianions owing to the formation of key alkoxytitanacyclopropane intermediates. Progress in the development of the synthetic applications of these highly reactive compounds will be summarized in this presentation.

References:

1. A. Butlerov, *Justus Liebigs Ann. Chem.* **1874**, 174, 125.

IMITATION AND MODIFICATION OF BIOACTIVE LEAD STRUCTURES VIA INTEGRATION OF BORON CLUSTERS

E. Hey-Hawkins¹R. Frank¹S. Boehnke¹M. Scholz¹V. Ahrens²A.G. Beck-Sickinger²1 - Universitaet Leipzig, Institute of Inorganic Chemistry,
Johannisallee 29, D-04103 Leipzig, Germany2 - Universitaet Leipzig, Institute of Biochemistry, Bruederstrasse 34,
D-04103 Leipzig, Germany
hey@rz.uni-leipzig.de

Carbaboranes are highly hydrophobic and extremely stable icosahedral carbon-containing boron clusters. The cage framework of these clusters can easily be modified with a variety of substituents both at the carbon and at the boron atoms. We are interested in substituted carbaboranes which can be used in medicine as suitable boron neutron capture therapy (BNCT) agents or as pharmacophores in which the carbaborane replaces the phenyl rings in drug candidates.

High and selective accumulation in tumour cells is an important requirement for a BNCT agent. Up to now, only BPA (L-*para*-boronophenyl-alanine), its fructose complex and BSH (sodium mercapto-*closo*-dodecaborate) made it into clinical trials. In the past few years promising approaches in the area of tumour targeting have been established, in which selectively acting hormones or antibodies are employed for the localisation and destruction of tumours. The combination of the pharmacologically active scaffolds of cancer pharmaceuticals with a tumour-specific ligand is envisioned to be used for selective accumulation of the pharmaceutical in diseased cells and their elimination without harming the healthy tissue. Increasing the tumour selectivity of BNCT agents may be possible by incorporating carbaboranes into breast-tumour-selective modified neuropeptide Y^[1] (Figure 1).

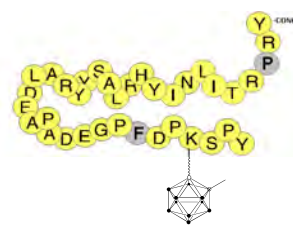


Fig. 1. Carbaborane-moc neuropeptide Y ([Phe⁷, Pro³⁴] NPY)

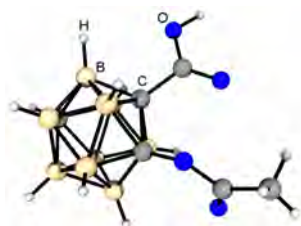


Fig. 2. Asborin

Up to now, the use of carbaboranes as pharmacophores is limited to just a few examples; only carbaborane analogues of tamoxifen, trimethoprim, transthyretin amyloidosis inhibitors derived from flufenamic acid and diflunisal, and two nonsteroidal anti-inflammatory drugs (NSAID) have been reported. We are focussing on drug mimetics of cyclooxygenase inhibitors, e.g., aspirin or indomethacin, in which the phenyl ring is replaced by a carbaborane cage (Fig. 2).^[2]

References:

- [1] S. Stadlbauer, E. Hey-Hawkins, in: *Boron Science, New Technologies and Applications*, chapter 1.2., ed. N. S. Hosmane, ISBN 978-1-4398266-3-8, CRC Press, **2011** (in press); D. Zwanziger, A.G. Beck-Sickinger, *Curr. Pharm. Des.* **2008**, *14*, 2385; V.M. Ahrens, R. Frank, S. Stadlbauer, A.G. Beck-Sickinger, E. Hey-Hawkins, *J. Med. Chem.* **2011**, *54*, 2368.
- [2] M. Scholz, M. Steinhagen, J.T. Heiker, A.G. Beck-Sickinger, E. Hey-Hawkins, *ChemMedChem* **2011**, *5*, 89-93; M. Scholz, G.N. Kaluderović, H. Kommera, R. Paschke, J. Will, W.S. Sheldrick, E. Hey-Hawkins, *Eur. J. Med. Chem.* **2011**, *46*, 1131; M. Scholz, A.L. Blobaum, L.J. Marnett, E. Hey-Hawkins, *Bioorg. Med. Chem.* **2011** (in press).

Financial support from the European Union and the Free State of Saxony, the Studienstiftung (PhD grant M.S.) and Fonds der Chemischen Industrie (VCI, PhD grant R.F.) is gratefully acknowledged.



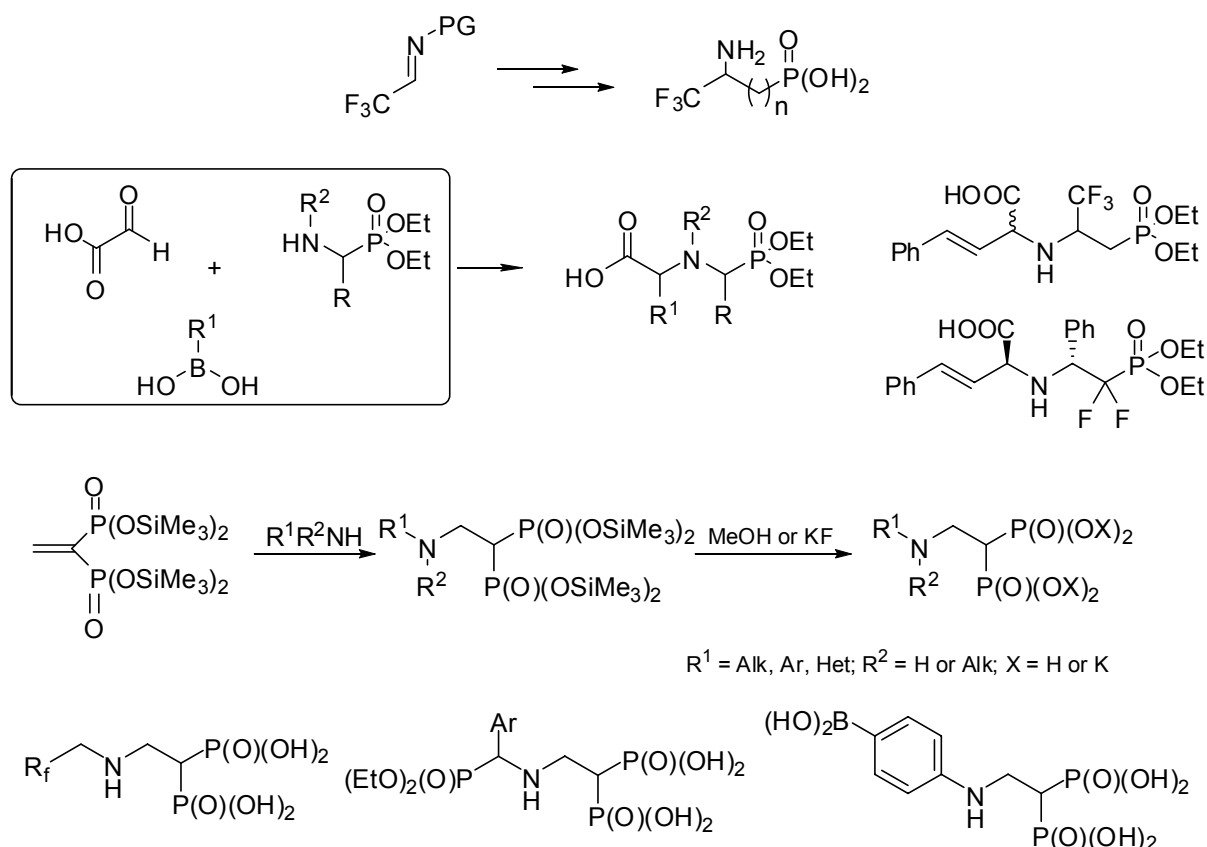
AMINO-PHOSPHONATES AND BIS-PHOSPHONATES - NEW SYNTHETIC ADVANCES

V.P. Kukhar
M.V. Shevchuk
V.D. Romanenko
A.E. Sorochinsky

Institute of Bioorganic Chemistry and Petrochemistry, Nat. Acad. Sci.
of Ukraine, Kyiv, Ukraine
kukhar@bpci.kiev.ua

Aminophosphonic acids occupy a prominent position in the understanding of bioprocesses and in construction of new bioregulators – pharmaceuticals and agrochemicals. Introduction of fluoroalkyl residue in amino phosphonic and bisphosphonic acids are the subject of considerable attention in organic and bioorganic chemistry as a tool to modify their activity as inhibitors of some enzymes and bioactive agents. To synthesize these compounds we applied the nucleophilic addition of phosphites or phosphonate α -carbanions to fluoroalkyl aldimines as a convenient synthetic route leading to fluoroalkyl α - and β -aminophosphonates in racemic and chiral forms.

Aminophosphonic acid derivatives were used as substrates in the Petasis boronic acid reaction to prepare highly functionalized *N*-phosphonomethylglycines and their analogues. The method is shorter and more convenient than traditional routes in preparation of pseudo-peptides with phosphonate residues. Various *N*-substituted β -amino-bis-phosphonic acids have been easily synthesized via the Michael addition of amines to easily available tetrakis(trimethylsilyl) ethenylidene-1,1-bisphosphonate, $\text{H}_2\text{C}=\text{C}[\text{P}(\text{O})(\text{OSiMe}_3)_2]_2$. The potassium salts of the title compounds were also easily achieved in high yield by reacting the Michael adducts with potassium fluoride.



D.G. Yakhvarov
R.M. Kagiroy
S.V. Kvashennikova
E.A. Trofimova
O.S. Fomina
O.G. Sinyashin

**SYNTHETIC ELECTROCHEMISTRY - RECENT
DISCOVERIES AND PERSPECTIVES**

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
yakhvar@iopc.ru

The search for new valuable synthetic tools in organic and organoelement chemistry is one of the key strategic directions in the development of science and technology. In this respect, the application of electrochemical methods allows creating of new effective synthetic processes of the chemical bond formation and cleavage.

Currently, the electrochemical methods were successfully applied for generation of organonickel sigma-bonded complexes,¹ high reactive precatalysts for the ethylene oligomerization processes,² selective preparation of organophosphorus compounds from white phosphorus (P₄),³ activation of inert oligophosphorus moieties formed in coordination sphere of transition metal complexes from P₄ tetrahedron,⁴ selective cleavage of the tungsten-phosphorus bond resulting in valuable metal-free phosphorus heterocycles obtained via phosphinidene intermediates.⁵

Herein, we present the description of the recently discovered methods and new perspectives of electrochemical techniques application for discovering of new compounds⁶ and application in material chemistry.⁷

References:

- ¹ D.G.Yakhvarov, Yu.S.Ganushevich, E.A.Trofimova, O.G.Sinyashin. Russ.Pat. 2396375, reg. 10.08.2010, priority 09.04.2009.
- ² D.G.Yakhvarov, Yu.S.Ganushevich, O.G.Sinyashin. Russ.Pat. 2400488, reg. 27.09.2010, priority 09.04.2009.
- ³ D.G.Yakhvarov, Yu.G.Budnikova, O.G.Sinyashin *Russ. J. Electrochem.* 2003, 39, 1261
- ⁴ D.Yakhvarov, P.Barbaro, L.Gonsalvi, S.Mañas, S.Midollini, A.Orlandini, M.Peruzzini, O.Sinyashin, F.Zanobini. *Angew. Chem. Int. Ed.* 2006, 45, 4182.
- ⁵ D.G.Yakhvarov, Yu.H.Budnikova, N.H.Tran Huy, L.Ricard, F.Mathey. *Organometallics*, 2004, 23, 1961.
- ⁶ D.Yakhvarov, M.Caporali, L.Gonsalvi, Sh.Latypov, V.Mirabello, I.Rizvanov, O.Sinyashin, P.Stoppioni, M.Peruzzini. *Angew. Chem.* 2011, 50, 5370
- ⁷ D.Yakhvarov, E.Trofimova, O.Sinyashin, O.Kataeva, P.Lönnecke, E.Hey-Hawkins, A.Petr, Yu.Krupskaya, V.Kataev, R.Klingeler, B.Büchner. *Inorg. Chem.* 2011, 50, 4553.

Financial support from the Russian Foundation for Basic Research (RFBR 09-03-00933-a) is gratefully acknowledged.

**ORGANIC CHEMISTRY ON AN INORGANIC
PLATFORM: APPROACHES TO ORGANIC-
INORGANIC HYBRID POLYMERIC MATERIALS**

C. Allen

University of Vermont, Burlington, USA
Christopher.Allen@uvm.edu

We have explored three classes of phosphazene base polymers: carbon backbone polymers with cyclophosphazene substituents (class A), cyclomatrix cyclophosphazenes (class B) and linear polyphosphazenes (class C). We have optimized two monomers for class A polymers, (methacryloylbutenedioxy)pentachloro cyclotriphosphazene, $\text{N}_3\text{P}_3\text{Cl}_5[\text{O}(\text{CH}_2)_4\text{OC}(\text{O})\text{CMe}=\text{CH}_2$ (**1**) and styryloxy pentachlorocyclotriphosphazene, $\text{N}_3\text{P}_3\text{Cl}_5\text{OC}_6\text{H}_4\text{CH}=\text{CH}_2$ (**2**). Radical initiated olefin addition polymerization leads to a broad range of polymers and copolymers which can undergo additional chemical modification. The hexa substituted analogs of **1** and **2** have been used as cross linking agents in olefin polymerization leading to densely cross linked polymers and hyperbranched polymers which are an attractive alternative to dendrimers. Our approach to class B materials is also based on the hexa substituted analog of **2** which is prepared by reductive debenzoylation route involving mono the monoprotected butane diol phosphazene derivative. Photo-polymerization of thin films of this monomer provides hard materials which can be plasma etched to give a resist material. The chemistry of the class C polymers is extended by using organofunctional polyphosphazene derivatives. The styryloxy derivatives undergo hydrosilylation reactions with long chain hydride terminated poly(dimethylsiloxanes), $\text{H}(\text{SiMe}_2\text{O})_n\text{SiMe}_2\text{H}$, to give polyphosphazene/polysiloxane graft polymers. Palladium coupling reactions of p-iodophenoxy polyphosphazenes allows for the preparation of the p-ethynylphenoxy derivatives which undergo thermal cross linking at elevated temperatures. Addition of dicobalt octacarbonyl to the alkyne center gives the cobalt carbonyl cluster as a substituent. This material eliminates CO at modest temperatures to give nanometallic particles distributed in a polymeric matrix. Other organometallic derivatives include ferrocenyl species which exhibit electron transfer mediator properties in electrochemical systems.

DESULFURIZING PALLADIUM-CATALYZED CROSS-COUPLING REACTION: A USEFUL TOOL IN HETEROCYCLIC CHEMISTRY

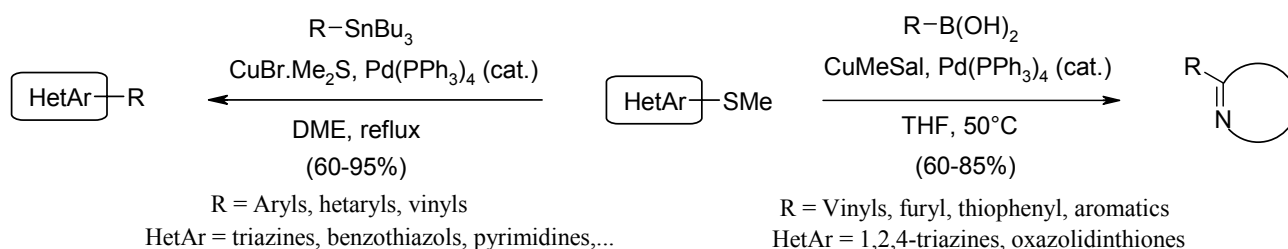
F. Suzenet

Institut de Chimie Organique et Analytique, UMR-CNRS 6005, FR
CNRS 2708, rue de Chartres, 45067 Orleans Cedex 2, University of
Orleans, France
franck.suzenet@univ-orleans.fr

Although several highly selective and reliable methods for the construction of C-C bonds are available to organic chemists, there is growing interest in the development of new ligands, new protocols and new substrates that offer different or orthogonal reactivity to that of existing methods.

Finding new electrophiles to replace the generally used halide or triflate substituents in cross-coupling reactions remains very attractive to provide alternative pathways for C-C bond formation. Our group has been interested to evaluate the electrophilic potential of the alkylsulfanyl function in the henceforth well known Liebeskind-Srögl palladium-catalyzed cross-coupling reaction.¹

In this context, we disclosed that boronic acids can be efficiently cross-coupled with alkylsulfanyls on π -electron deficient heterocycles and that organostannanes readily cross-couple in the presence of copper bromide. The scope of this reaction was extended to heterocyclic systems which cannot be used in the Stille or Suzuki cross-coupling reactions.² A unique and efficient copper bromide-mediated pallado-catalyzed coupling of protecting group free 2-thiouracil derivatives with organostannanes was also investigated^{2c} as well as the first copper-catalyzed desulfurizing Sonogashira cross-coupling reaction.³



References:

- 1) (a) H. Prokopcová, C. O. Kappe, *Angew. Chem. Int. Ed.* **2008**, 47, 2. (b) C. Savarin, J. Srögl, L. S. Liebeskind, *Org. Lett.* **2001**, 3, 91. (c) F.-A. Alphonse, F. Suzenet, A. Keromnes, B. Lebre, G. Guillaumet, *Synlett.* **2002**, 447. (d) L. S. Liebeskind, J. Srögl, *Org. Lett.* **2002**, 4, 979. (e) M. Egi, L. S. Liebeskind, *Org. Lett.* **2003**, 5, 801. (f) F.-A. Alphonse, F. Suzenet, A. Keromnes, B. Lebre, G. Guillaumet, *Org. Lett.* **2003**, 5, 803.
- 2) (a) N. Leconte, A. Keromnes-Wuillaume, F. Suzenet, G. Guillaumet, *Synlett.* **2007**, 204. (b) N. Leconte, L. Pellegatti, A. Tatibouët, F. Suzenet, P. Rollin, G. Guillaumet, *Synthesis*, **2007**, 857. (c) Qi Sun, Franck Suzenet, Gérald Guillaumet, *J. Org. Chem.* **2010**, 75, 3473-3476.
- 3) S. Silva, B. Sylla, F. Suzenet, A. Tatibouët, A. P. Rauter, P. Rollin, *Org. Lett.* **2008**, 10, 853.

I.L. Fedushkin
A.S. Nikipelov
A.G. Morozov
A.A. Skatova
G.A. Abakumov

**ADDITION OF ALKYNES TO GALLIUM BIS-AMIDO
COMPLEX: IMITATION OF TRANSITION METAL-
BASED CATALYTIC SYSTEMS**

G.A. Razuvaev Institute of Organometallic Chemistry, Russian
Academy of Sciences, Nizhny Novgorod, Russia
igorfed@iomc.ras.ru

Acetylene, phenylacetylene, methyl- and ethylbutynoates add reversibly to a gallium complex (dpp-bian)Ga–Ga(dpp-bian) (**1**) (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)-imino]acenaphthene) affording the corresponding addition products (dpp-bian- $R^1C=CR^2$)Ga–Ga($R^2C=CR^1$ -dpp-bian) ($R^1 = R^2 = H$, **2**; $R^1 = Ph$, $R^2 = H$, **3**; $R^1 = CH_3$, $R^2 = COOCH_3$, **4**; $R^1 = CH_3$, $R^2 = COOCH_2CH_3$, **5**). In each case the alkyne adds across the Ga–N–C fragment resulting in new carbon–carbon and carbon–gallium bonds. Complexes **2–5** have been characterized by electron absorption, IR-, and ^1H NMR spectroscopy, their molecular structures have been determined by X-ray crystallography. According to the X-ray data changing of the coordination number of gallium from three in **1** to four in **2–5** results elongation of the metal–metal bond by 0.13 Å. Compounds **2–5** undergo an elimination of alkyne at elevated temperatures. An equilibrium between **3** and [**1** + $PhC\equiv CH$] in toluene have been studied by ^1H NMR spectroscopy. The equilibrium constants in the temperature range 298–323 K have been determined from which thermodynamic parameters for elimination of $PhC\equiv CH$ were calculated: $\Delta G^\circ = 25$ kJ/mol, $\Delta H^\circ = 94.8$ kJ/mol and $\Delta S^\circ = 234$ J/mol·K. Reactivity of **1** towards alkynes allows using it as catalyst for C–N and C–C bond formation reactions. Complex **1** is highly effective catalyst for hydroamination of phenylacetylene with different anilines with Markovnikov's selectivity. For instance, with 2 mol % of **1** in benzene 99 % conversion of $PhNH_2$ and $PhC\equiv CH$ into $PhN=C(Ph)CH_3$ was achieved in 16 h at 90 °C. In similar conditions the reaction of 1-aminoanthracene with $PhC\equiv CH$ catalyzed by compound **1** gave a carbon–carbon bond formation product, 1-amino-2-(1-phenylvinyl)anthracene, with 99 % yield.

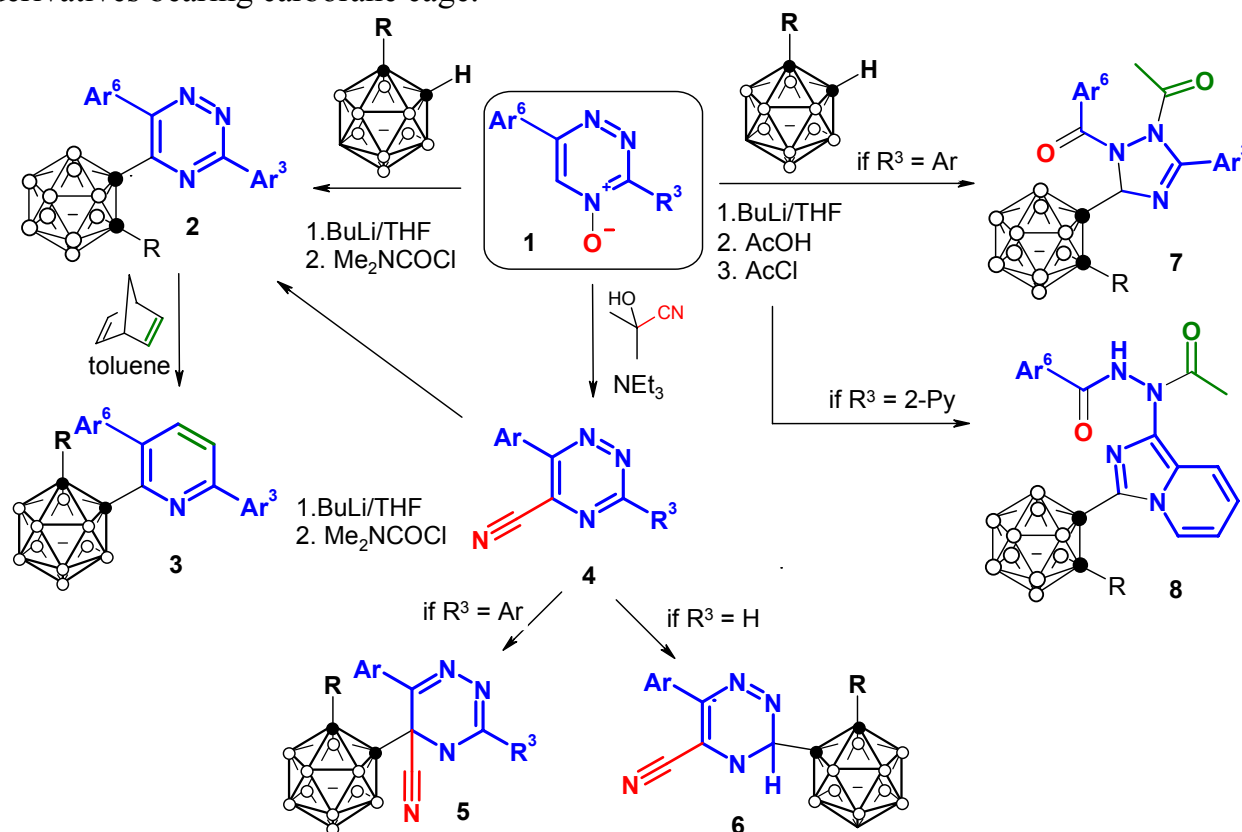
This work was supported by the Russian foundation for basic research (grant No. 11-03-01184).

HETEROAROMATIC DERIVATIVES OF CARBORANE BY C-H BOND FUNCTIONALISATION IN AZINES

A.M. Prokhorov

 Ural Federal University, Organic Chemistry, Ekaterinburg, Russia
 aprohor@yandex.ru

The nucleophilic addition of lithium carboranes to highly electrophilic 1,2,4-triazine-4-oxides **1** at the unsubstituted carbon atom can lead to a different *N*-heterocyclic derivatives bearing carborane cage.



Depending on substituents in the starting 1,2,4-triazine ring and the reaction conditions it is possible to obtain 5-carboranyl 1,2,4-triazines **2** and then 6-carboranyl pyridines **3**. The triazines **2** can be synthesised *via* alternative way, by *ipso*-substitution of cyano group, as well non-aromatic products of nucleophilic addition **5** and **6**.

Another possible route is a transformation of the 1,2,4-triazine ring with formation of different heterocyclic systems: carboranyl 1,2,4-triazolines **7** or imidazopyridines **8**. In this case, the nucleophilic addition of lithium carboranes is followed by unprecedented sigmatropic shift of hydroxyl to C⁶-atom with C⁵-C⁶ bond cleavage and following recyclisation. These transformation are of particular interest, as the carborane cage plays a primordial role as carrier of OH due to coordination by the electronegative hydrogens bonded to boron atoms.

The work is supported by Ural Federal University and German Academic Exchange Service (DAAD).

USING FUNCTIONALIZED ALUMINUM COMPLEXES AS A NEW APPROACH TO RING- OPENING POLYMERIZATION

K.V. Zaitsev¹
Y.F. Oprunenko¹
S.S. Karlov¹
G.S. Zaitseva¹
S.V. Kostjuk²
I.V. Vasilenko²
A.V. Churakov³

1 - Moscow State University, Chemistry Department, Moscow, Russia

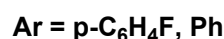
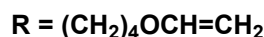
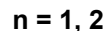
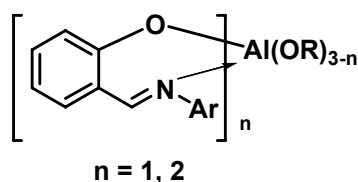
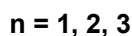
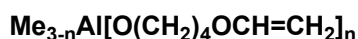
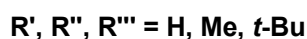
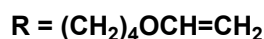
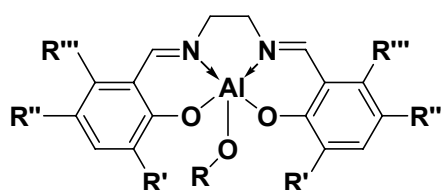
2 - Belarusian State University, Phys. Chem. Problems Res. Inst., Minsk, Belarus

3 - Russian Acad. Sci, N.S. Kurnakov General and Inorganic Chem. Inst., Moscow, Russia

zaitsev@org.chem.msu.ru

Materials based on aliphatic polyesters attract much attention due to their biodegradation and biocompatibility. The ring opening polymerization using metal complexes as catalysts is the most usable method for synthesis of such materials due to reproducibility and reaction control. Development of new catalysts for the process discussed is the actual problem for modern organometallic chemistry.

In our work we synthesized new aluminum complexes containing functionalized unsaturated alcoholates and/or iminophenolates as ligands. The structures of the compounds obtained were confirmed by NMR spectroscopy and mass-spectrometry and in several cases by X-ray analysis.



These compounds were used as catalysts in ring opening polymerization of cyclic lactones. In the course of polymerization the unsaturated group is transferred to the end of polymer chain. This synthetic strategy allows us to obtain macromonomers based on biodegradable materials with high degree of functionalization.

ORGANOALUMINUMS IN CYCLOPROPANE SYNTHESIS

U.M. Dzhemilev¹
 I.R. Ramazanov¹
 L.O. Khafizova¹
 L.K. Dil'mukhametova¹
 A.V. Yaroslavova¹
 R.R. Gubaidullin¹
 O.M. Nefedov²

1 - Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, Ufa, Russia
 2 - N.D. Zelinskii Institute of Organic Chemistry of Russian Academy of Sciences, Moscow, Russia
 iramazan@inbox.ru

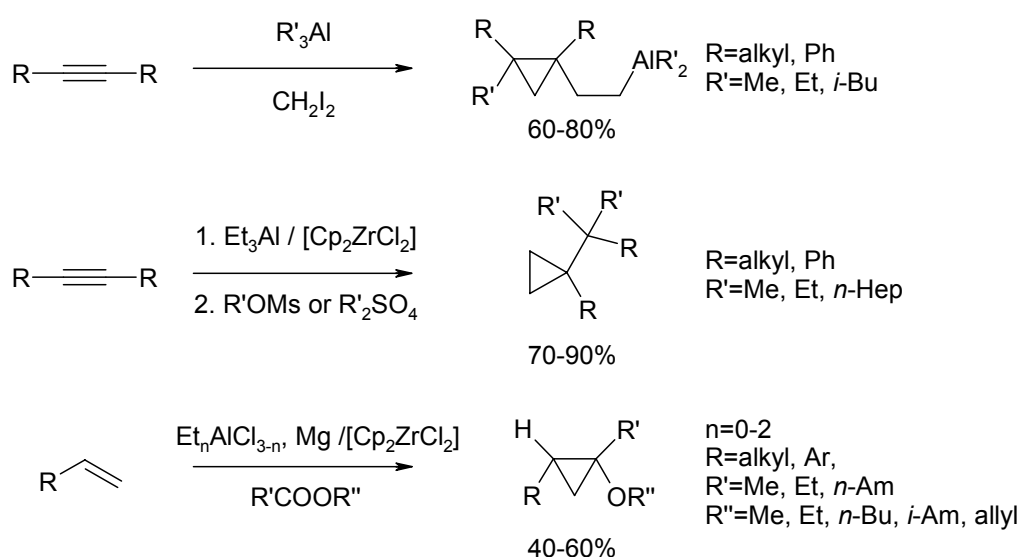
Organometallic compounds, especially of zinc and magnesium, have found wide application in the synthesis of cyclopropanes. The use of organoaluminum compounds in the construction of three-membered ring is very limited. The report will discuss the existing procedures and present new "one-pot" methods to prepare substituted cyclopropanes with the use of alkylaluminums.

Particular attention will be paid to the reaction of mono- and disubstituted alkynes with CH_2I_2 and trialkylaluminums that gives β -iodoethyl-substituted cyclopropanes in the presence of Me_3Al . The use of Et_3Al or *i*- Bu_3Al affords exclusively cyclopropyl organoaluminum compounds.

Otherwise alkynes were converted into 1,1-disubstituted cyclopropanes in high yield via Zr-catalyzed reaction with Et_3Al followed by alkylation by alkyl esters of sulfonic acids. The transformation proceeds via the formation of unsaturated five-membered aluminacycle.

The idea of constructing cyclopropanes by intramolecular rearrangement of five-membered cyclic organometallic compounds was developed in the Zr-catalyzed reaction of α -olefins with $\text{Et}_n\text{AlCl}_{3-n}$ ($n=0-2$) and carboxylic acid esters. A variety of alkoxy cyclopropanes and cyclopropanols were synthesized in moderate yield.

Thus, the report will demonstrate the synthetic potential of organoaluminum compounds in the synthesis of cyclopropanes of different structure.

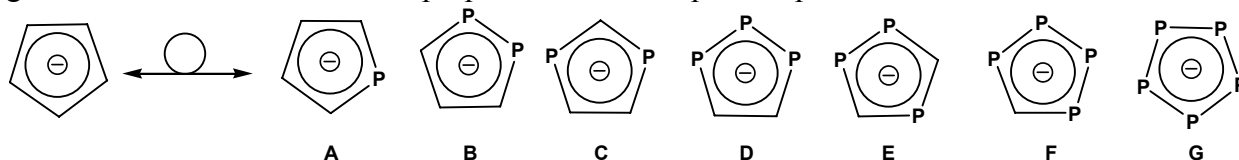


THE 1,2-DIPHOSPHACYCLOPENTADIENIDE-ANIONS IN ORGANIC AND ORGANOMETALLIC SYNTHESIS

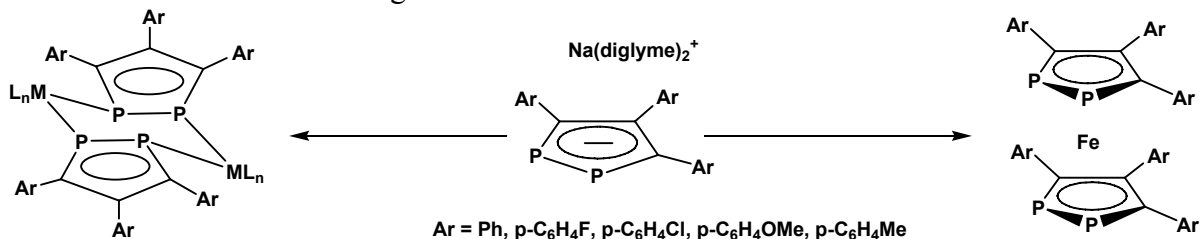
V.A. Miluykov
O.G. Sinyashin

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia
miluykov@iopc.ru

Phosphacyclopentadienide anions (phospholides, $^{\text{P}}\text{Cp}^-$) are isolobal analogues of cyclopentadienide anions Cp^- . However the presence of lone pair on phosphorus causes the significant difference in chemical properties of both $^{\text{P}}\text{Cp}^-$ and Cp^- anions.

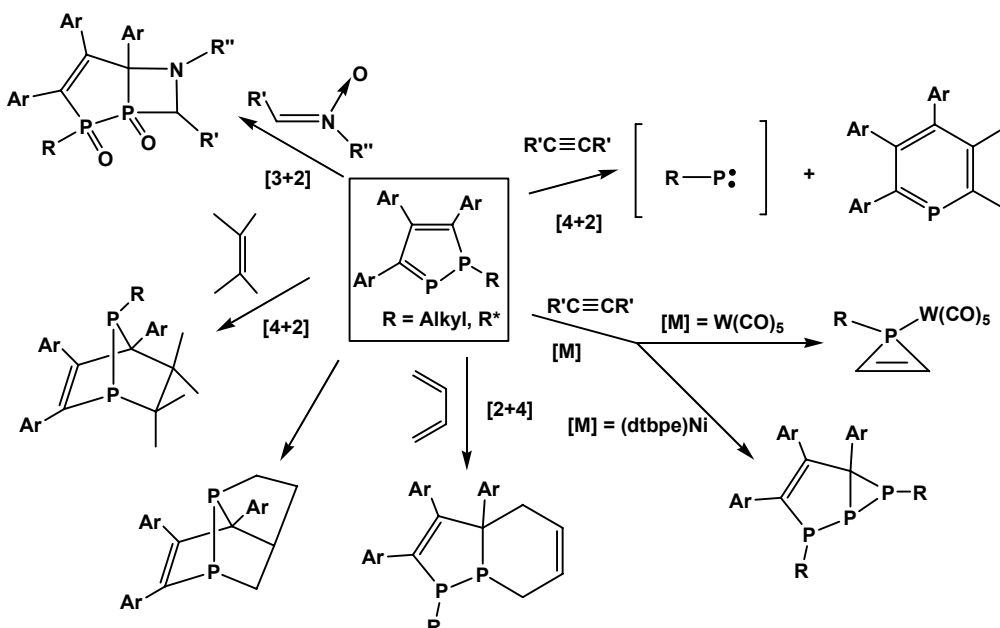


The 1,2-diphospholides **B** have specific interest due to isolobality both Cp^- and pyrazolate that may result two different coordination type in transition metal complexes. The bridged 1,2-diphospholides may act as non-innocent ligands combined ability to metal-to-ligand charge transfer and realized anti-ferromagnetic interactions.



$\text{ML}_n = \text{Mn}(\text{CO})_4, \text{Re}(\text{CO})_4, \text{Ni}(\text{NO})(\text{PPh}_3)$

Alkylation of **B** result formation of stable 1-alkyl-1,2-diphospha-cyclopenta-2,4-dienes (1-alkyl-1,2-diphospholes) combined structural elements both 1H-phospholes and 2H-phospholes and possessing good thermal stability and high reactivity toward dienes, dienophiles and 1,3-dipolar reagents.



Reactions of 1-alkyl-1,2-diphospholes with acetylene proceed with formation of high reactive phosphinidene species in triplet or singlet state depending on reaction conditions.

P.P. Onysko
T.V. Kim
O.I. Kyselyova
Y.V. Rassukana
A.D. Synytsya

BIOMIMETIC TRANSAMINATION IN PHOSPHORYLATED IMINES

Institute of Organic Chemistry, NAS of Ukraine, Kyiv, Ukraine
onysko@rambler.ru

The data on prototropy in imidoylphosphonates containing α -hydrogen atoms in the N-alkyl group of the C=N bond were systematized and generalized. Imidoylphosphonates-alkylideneaminophosphonates interconversions via 1,3-proton transfer are in main focus of the presentation. Central to this endeavour is elucidation of the effect that the phosphonyl moiety exerts on prototropy in the phosphorylated 2-azaallylic triad.

The reversible transformation $A \rightleftharpoons B$ mimics biological transamination, i.e. the enzyme-catalyzed interconversion of α -amino and α -keto carboxylic acids. As imidoylphosphonates are the “oxidized” form of α -aminophosphonates, reduction of the C=N bond (conversion $PC=N \rightarrow PCHN$) is a potential route to their transformation into α -aminophosphonic derivatives.



The recently discovered 1,3-proton transfer in imidoylphosphonates allows this process to be performed in the absence of any external reducing agent.¹ An electron-acceptor phosphoryl group at sp^2 -carbon atom of the C=N-CH triad greatly increases the lability of the proton and thus renders such compounds labile prototropic systems. Generation of a phosphonium center during phosphorylation of imidoyl chlorides with phosphites facilitates rearrangements. The prototropic isomerization in the 1,3-diaryl-1,3-diphosphorylated azaallylic systems is reversible and the equilibrium depends on the polarity properties of substituents in the benzene rings. The elaboration of synthetic approaches to imidoylphosphonates and their 1,3-prototropic isomerizations would open up additional opportunities for preparation of novel biologically active derivatives of α -aminoalkylphosphonic acids and other compounds with acyclic or cyclic structure.

References:

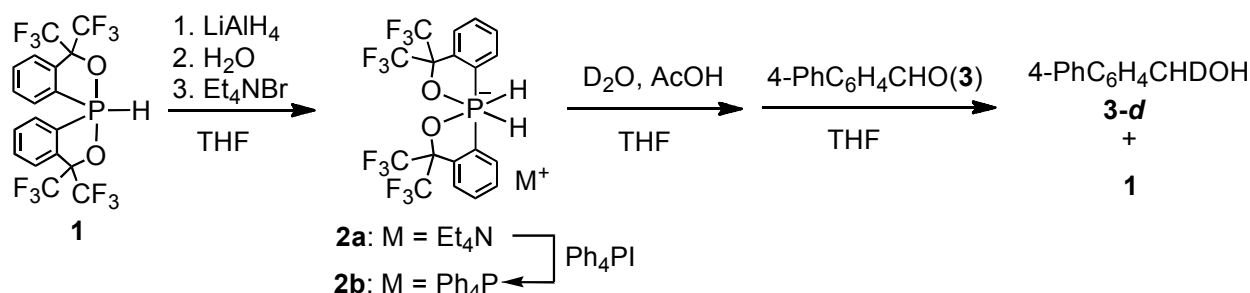
1. Onys'ko, P.P.; Rassukana, Yu. V. ; Synytsya O. A. *Curr. Org. Chem.* **2010**, *14*, 1223-1233.

UMPOLUNG OF A HYDROGEN ATOM OF WATER UTILIZING HEXACOORDINATED DIHYDROPHOSPHATES AND ITS APPLICATION TO ONE-POT DEUTERIDE REDUCTION OF CARBONYL COMPOUNDS

T. Kawashima

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan, Present Address: Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Tokyo 171-8588, Japan
 Takayuki.Kawashima@gakushuin.ac.jp

Umpolung, a reversal of polarity of an atom in a functional group, is one of the most useful methods in organic synthesis. Among umpolung of various functional groups, umpolung of a hydrogen atom is difficult, because a proton source, such as water ($\text{H}^{\delta+}\text{-OH}$), undergoes a reaction with the product of the umpolung ($\text{H}^{\delta-}\text{-Z}$) to give molecular hydrogen. In the course of our study on highly coordinated phosphorus compounds bearing the Martin ligand,¹ we succeeded in synthesizing hexacoordinated dihydrophosphates, which underwent H-D exchange with D_2O and deuteride reduction with carbonyl compounds². Here, we wish to report its details and application to the one-pot reaction.



Dihydrophosphate **2a** was synthesized by the reaction of **1** with LiAlH_4 followed by the cation exchange reaction. The reaction of **2a** with carbonyl compounds in the presence of LiCl or AcOH gave the corresponding alcohols in moderate to high yields together with **1**. The H-D exchange reaction of **2a** gave **2a-d₂**, which underwent deuteride reduction with aldehyde **3** in the presence of AcOH to give the corresponding deuterated alcohol **3-d** with a good yield and D-content. One pot reaction using **2a**, D_2O , and **3** in the presence of AcOH also gave **3-d**, providing novel deuteride reduction method for carbonyl compounds utilizing the umpolung of a hydrogen atom of water. Recently, we succeeded in isolating the geometric isomer **4** of **2a**. X-ray crystal structures of **2b** obtained by the cation exchange of **2a** and **4** and reactivity comparison between **2a** and **4** will also be discussed.

References:

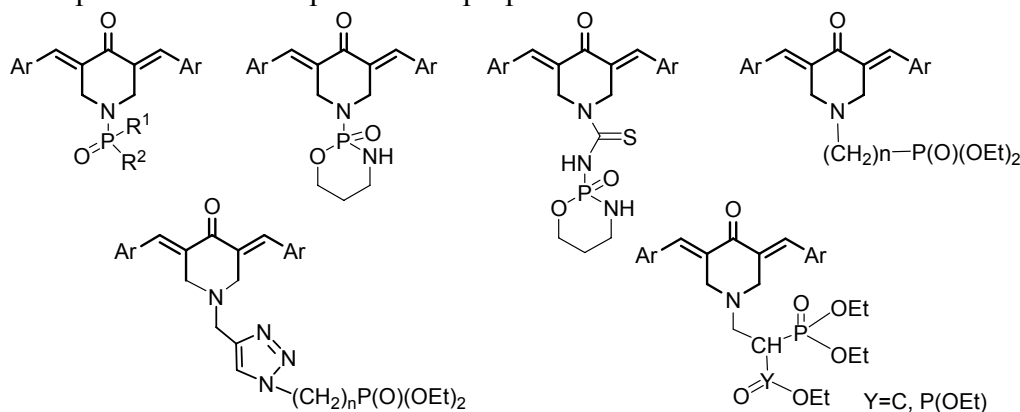
- ¹ Kawashima, T.; Kato, K.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 4008-4010; Kawashima, T.; Soda, T.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1096-1098; Sase, S.; Kano, N.; Kawashima, T. *J. Am. Chem. Soc.* **2002**, *124*, 9706-9707.
- ² Miyake, H.; Kano, N.; Kawashima, T. *J. Am. Chem. Soc.* **2009**, *131*, 16622-16623.

PHOSPHORYLATION OF DIENONE PHARMACOPHORE FOR TARGETED DESIGN OF HIGHLY EFFECTIVE AND FLUORECENT CYTOSTATICS

I.L. Odinets¹
M.V. Makarov¹
E.S. Leonova¹
A.E. Shipov¹
E.Yu. Rybalkina²
T.V. Timofeeva³

1 - A.N. Nesmeyanov Institute of Organoelement Compounds RAS
2 - Institute of Carcinogenesis, N.N. Blokhin Cancer Research Centre, RAMS
3 - New Mexico Highlands University, Las Vegas, NM 87701, USA
odinets@ineos.ac.ru

For years γ -piperidone derivatives have been effectively used as a base for design of a range of pharmacologically active compounds and 3,5-bis(arylidene)-4-piperidones and the related cycloalkanones were found to possess free radical scavenging, α -glucosidase inhibitory, antimycobacterial, and antineoplastic activity. In addition, these compounds have low general toxicity and are considered as free of mutagenic properties characteristic for known alkylating anticancer agents used in current medicine practice.¹ In our study we exploited the idea of introduction of phosphorus-containing groups possessing inherent bioactivity, ability to impart solubility and bioavailability to the molecule structure and improve the capacity of its transportation via a cellular membrane, into 3,5-bis(arylidene)piperid-4-one molecule² and the lecture will discuss the synthetic procedures developed for this purpose.



Ar = 4-NMe₂C₆H₄, 4-MeOC₆H₄, 4-NCC₆H₄, 4-NO₂C₆H₄, 2-NO₂C₆H₄, 3,5-¹Bu-4-OHC₆H₂, 3-Py, 4-Py, 2-Th

This fruitful idea gave rise to a series of phosphorylated compounds either with direct N-P bonding or those in which these atoms were attached to each other via different linker including BPs and PCs derivatives, displaying significantly higher cytotoxicity *in vitro* (IC₅₀ in the range of 1-80 μ M) towards different human carcinoma cell lines, including drug-resistant ones, compared to their starting NH-precursors. Moreover, some products are inclined to photosensibilization and demonstrated fluorescent properties and therefore, may be of interest as biological probes for elucidation of drugs distribution in tissues and cellular uptake.

References:

1. U. Das, R.K. Sharma, J.R. Dimmock. *Curr. Med. Chem.*, 2009, **16**, 2001.
2. a) I.L. Odinets, O.I. Artyushin, E.I. Goryunov, K.A. Lyssenko, E.Yu. Rybalkina, I.V. Kosilkin, T.V. Timofeeva, M.Yu. Antipin, *Heteroatom Chem.* **2005**, 16, 497. b) M.V. Makarov, E.Yu. Rybalkina, G.-V. Röschenhalter, K.W. Short, T.V. Timofeeva, I.L. Odinets, *Eur. J. Med. Chem.* **2009**, 44, 2135. c) M.V. Makarov, E.S. Leonova, E.Yu. Rybalkina, P. Tongwa, V.N. Khrustalev, T.V. Timofeeva, I.L. Odinets, *Eur. J. Med. Chem.* **2010**, 45, 992. d) E.S. Leonova, M.V. Makarov, E.Yu. Rybalkina, S.L. Nayani, P. Tongwa, A. Fonari, T.V. Timofeeva, I.L. Odinets, *Eur. J. Med. Chem.*, **2010**, 45, 5926. e) A.E. Shipov, G.K. Genkina, P.V. Petrovskii, E.I. Goryunov, M.V. Makarov, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, **2011**, 186(4), 945.

**ZIRCONIUM COMPLEX CATALYSIS IN ALKENE
HYDRO-, CARBO- AND CYCLOALUMINATION:
FROM MECHANISM TO CHEMO- AND
ENANTIOSELECTIVITY CONTROL**

L.V. Parfenova
L.M. Khalilov
U.M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of
Sciences, Ufa, Russia
luda_parfenova@mail.ru

Application of transition metal complexes in the chemistry of organoaluminum compounds (OAC) has led to the development of new chemo-, regio- and stereoselective methods for C-H, C-C and M-C bond construction through the formation of new classes of organometallic compounds. Among these methods reactions of hydro-, carbo- and cycloalumination of unsaturated compounds are well known [1].

The report presents the results on studies of the mechanism of Zr catalysis ($L^1L^2ZrCl_2$: $L^1 = L^2 = Cp$, $CpMe$, $CpMe_5$, Ind , Flu , Ind^* (1-neomenthylindenyl); $L^1 = Cp$, $L^2 = Ind^*$; $L^1 = Cp$, $L^2 = Cp'$ (1-neomenthyl-4,5,6,7-tetrahydroindenyl)) in the alkene hydro-, carbo- and cycloalumination reactions [2]. The effect of OAC nature, Zr π - ligand environment, reaction conditions on the process chemo- and enantioselectivity has been investigated. The structures of key intermediates were established by the means of NMR spectroscopy, encounter synthesis and kinetic studies. The geometric and energetic parameters of intermediates and transition states were determined as a result of quantum-chemical modeling.

On the basis of experimental and theoretical investigations a generalized mechanism of Zr catalysis in alkene hydro-, carbo- and cyclometallation, which clarifies the reaction chemo- and stereoselectivity, has been proposed.

References:

- [1] (a) Dzhemilev U.M., Ibragimov A.G. Russ.Chem.Rev., 69 (2000) 121; (b) Dzhemilev U.M., Ibragimov A.G. J. Organomet. Chem. 695 (2010) 1085.
[2] (a) Khalilov L.M., et al, Russ.Chem.Bull., Int. Ed. 49 (2000) 2051; (b) L.V. Parfenova, et al, Russ. Chem. Bull., Int. Ed. 54 (2005) 316; (c) Parfenova L.V., et al. J. Organomet. Chem., 694 (2009) 3725; (d) Pankratyev E.Yu., et al. Organometallics, 28 (2009) 968; (e) Parfenova, L.V., et al, Tetrahedron: Asymmetry 21 (2010) 299.
-

The authors thank the Russian Foundation of Basic Research (Grant No. 11-03-00210-a) for financial support.

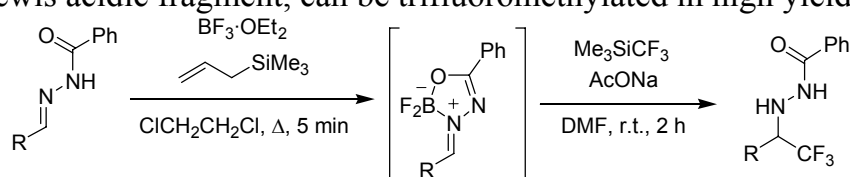
A.D. Dilman
V.V. Levin
A.A. Zemtsov
V.A. Tartakovsky

NUCLEOPHILIC TRIFLUOROMETHYLATION OF C=N AND C=C BONDS

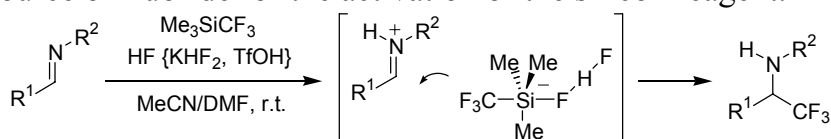
N.D. Zelinsky Institute of Organic Chemistry, Moscow, Russia
dilman@ioc.ac.ru

Nucleophilic trifluoromethylation constitutes a very attractive way for the direct introduction of CF₃-group into organic molecule. We have developed several methods for the addition of CF₃-carbanion to C=N bond using the Ruppert-Prakash reagent (Me₃SiCF₃).¹ These reactions rely on the activation of azomethine fragment by means of Lewis or Brønsted acid.

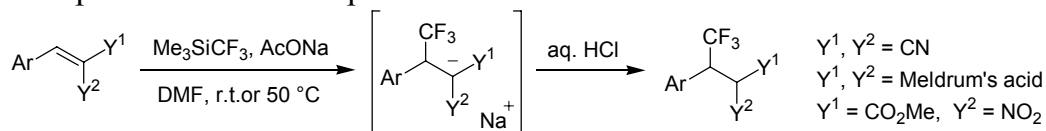
For example, substrates bearing an adjacent functional group, which is capable of coordinating Lewis acidic fragment, can be trifluoromethylated in high yields.



Imines can be trifluoromethylated with Me₃SiCF₃ by using hydrofluoric acid generated *in situ*. It is believed that HF serves as a source of the proton for the activation of imine and as a source of fluoride for the activation of the silicon reagent.³



Trifluoromethylation of C=C bond can be readily achieved by using Me₃SiCF₃ and highly electrophilic Michael acceptors.⁴



References:

1. Dilman, A. D.; Levin, V. V. *Eur. J. Org. Chem.* **2011**, 831.
2. (a) Dilman, A. D.; Arkhipov, D. E.; Levin, V. V.; Belyakov, P. A.; Korlyukov, A. A.; Struchkova, M. I.; Tartakovsky, V. A. *J. Org. Chem.* **2007**, 72, 8604. (b) Dilman, A. D.; Arkhipov, D. E.; Levin, V. V.; Belyakov, P. A.; Korlyukov, A. A.; Struchkova, M. I.; Tartakovsky, V. A. *J. Org. Chem.* **2008**, 73, 5643. (c) Dilman, A. D.; Levin, V. V.; Belyakov, P. A.; Korlyukov, A. A.; Struchkova, M. I.; Tartakovsky, V. A. *Mendeleev Commun.* **2009**, 19, 141.
3. Levin, V. V.; Dilman, A. D.; Belyakov, P. A.; Struchkova, M. I.; Tartakovsky, V. A. *Eur. J. Org. Chem.* **2008**, 5226.
4. (a) Dilman, A. D.; Levin, V. V.; Belyakov, P. A.; Struchkova, M. I.; Tartakovsky, V. A. *Tetrahedron Lett.* **2008**, 49, 4352. (b) Zemtsov, A. A.; Levin, V. V.; Dilman, A. D.; Struchkova, M. I.; Belyakov, P. A.; Tartakovsky, V. A. *Tetrahedron Lett.* **2009**, 50, 2998.

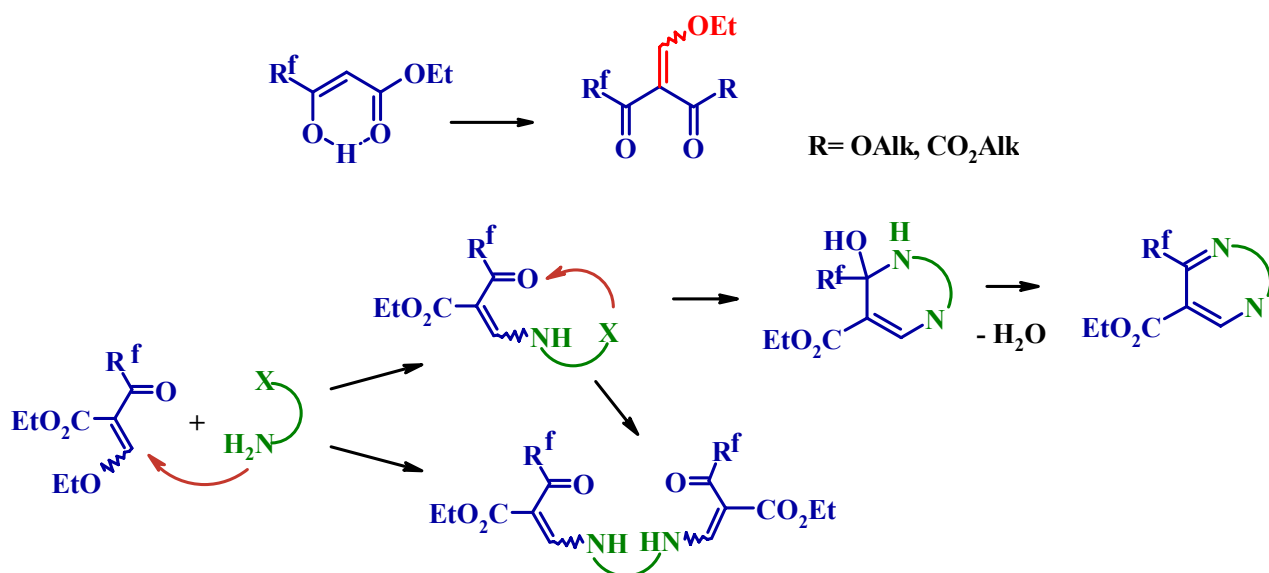
This work was supported by Russian Foundation for Basic Research (projects 08-03-00428, 10-03-91159-GFEN), and Ministry of Science (project MD-1151.2011.3).

V.I. Saloutin
Ya.V. Burgart
M.V. Goryaeva
Yu.S. Kudyakova
O.N. Chupakhin

FLUORINATED 2-ETHOXYMETHYLIDENE-3-OXO ESTERS FOR DESIGN OF HETEROCYCLES AND LIGANDS

Institute of Organic Synthesis UD RAS, Ekaterinburg, Russia
saloutin@ios.uran.ru

We have been developed the synthetic methods for preparation of 2-ethoxymethylidene-3-oxo-3-fluoroalkylpropionates. The polyfluoroalkyl-2-ethoxymethylidene-3-oxo esters were established to be effective matrixes for formation of different heterocycles and ligands. So, condensation at the ethoxymethylidene fragment is the initial process in the reactions with amines. Then in case with alfa-and gem-diamines hetrocyclization at polyfluoroacyl moiety takes place. Sometimes heterocyclization is possible also with the participation of ethoxycarbonyl group. In case with diamines having distant aminogroups open-chain products are formed as a result of another ester molecule condensation.



The research was financed by Russian Foundation for Basic Research (Project No. 09-03-00274), State contract No 02.740.11.0260, Programs of Presidium UD RAS (No 09-P-3-1013, 09-P-3-2001), Supporting program of Leading Scientific School (No 65261.2010.3)

**MOLECULAR HYBRID NANOOBJECTS AS
PERSPECTIVE PLATFORM FOR DRUG DELIVERY
SYSTEMS**

**A.M. Muzafarov
N.V. Voronina
I.B. Meshkov
V.V. Kazakova
A. Zhil'tsov**

N.S. Enicolopov Institute of Synthetic Polymeric Materials of RAS,
Moscow, Russia

The high and regular functionality of the dendrimers allow to consider them as a very attractive carriers of the gene materials and drug delivery systems. The recent investigation of the nanogels representatives from the new group of general polymers classification – Molecular nanobjects - showed great potentials of practical applications. The hybrid nature of this objects and tunable ration between silica core and organic shell allowed to observe very fast transition from macromolecule to nanoparticle [1]. Moving from the model trimethylsilylated systems to the hybrids with shells of different chemical nature one could select appropriate object with needed affinity to the various chemical molecules.

The presentation will cover chemical approach to the synthesis of hybrid molecular systems of different stage of their evolution, comparison new objects with classical dendrimers and results of properties investigation. In final part of presentation prospects of practical applications in biomedical field will be discussed.

References:

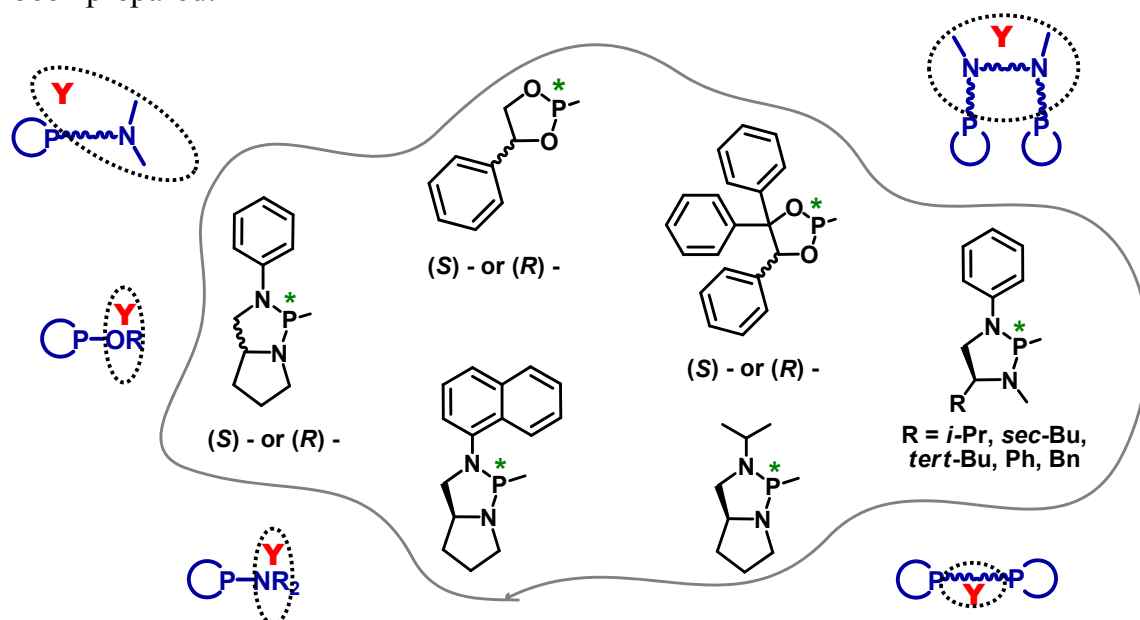
1. N.V. Voronina, I.B. Meshkov, V.D. Myakushev, T.V. Laptinskaya, V.S. Papkov, M.I. Buzin, M.N. Il'ina, A.N. Ozerin, A.M. Muzafarov. "Hybrid Organo-Inorganic Globular Nanospecies: Transition from Macromolecule to Particle". *Journal of Polymer Science: Part A*, **2010**, Vol. 48, 4310–4322

**P*-CHIRAL PHOSPHITE-TYPE LIGANDS AS AN
EFFICIENT STEREOSELECTORS FOR THE
TRANSITION METAL-CATALYZED ASYMMETRIC
REACTIONS**

K.N. Gavrilov¹
N.N. Groshkin¹
O.V. Potapova¹
A.A. Shiryaev¹
I.M. Novikov¹
V.A. Davankov²

1 - Ryazan State University, Department of Chemistry, Ryazan, Russia
 2 - Institute of Organoelement Compounds, Russian Academy of
 Sciences, Moscow, Russia
k.gavrilov@rsu.edu.ru

Preparation of inexpensive starting optically pure synthons, namely 1,2-diols (from (*S*)- and (*R*)-mandelic acid) and 1,2-diamines (from (*S*)- and (*R*)- α -aminoacids) was accomplished in multigram scale. Based on these synthons, novel groups of *P**-mono-, *P**,*N*- and *P**,*P**-bidentate phosphite-type ligands, possessing asymmetric phosphorus atoms, have been prepared:



New stereoselectors provided chemical yields and enantioselectivities >90% in the majority of the key transition metal-catalyzed asymmetric processes. Thus, up 99% *ee* was achieved in the Rh-catalyzed asymmetric hydrogenation of unsaturated acid esters, up to 70% *ee* in the Cu-catalyzed addition of Et₂Zn to cyclohexenone, up to 98% *ee* in the Rh-catalyzed addition of phenylboronic acid to cyclohexenone, up to 99% *ee* in the Pd- and Pt-catalyzed allylation of 1,3-diphenylallyl acetate, and up to 92% *ee* in the Pd-catalyzed alkylation of cyclohex-2-enyl ethyl carbonate with dimethylmalonate. The product of the latter reaction is a key precursor for the synthesis of bioregulators (+)-juvabione and (+)-wine lactone. The practically valuable Pd-catalyzed desymmetrization of *N,N*-ditosyl-meso-cyclopent-4-ene-1,3-diol biscarbamate (provides access to mannostatin A and (-)-swainsonine) has been carried out with 70% *ee*.

We acknowledge the financial support from the Russian Foundation for Basic Research (Grant No. 11-03-00347-a) and a Grant from the President of the Russian Federation for Young Candidates of Sciences (No. MK-3889.2010.3).

SYNTHESIS AND CHARACTERIZATION OF OXIME-PHOSPHAZENES

A.O. Görgülü

Firat University, Department of Chemistry, Elazığ, Turkey
aogorgulu@firat.edu.tr

Phosphazenes are materials with interesting properties. For example, they exhibit fire-retardant properties, have high refractive indices, and might find application in non-linear optics, as ferroelectric materials, as liquid crystals or as photoactive materials. They also possess a number of characteristics such as biomedical properties and applications due to their strong antitumor activity. Their antimicrobial and biological activities on bacterial and yeast cells have been studied. Some applications include model compounds for polyphosphazenes, starting materials for the preparation of cycloliner and/or cyclomatrix phosphazene substrates, commercial polymers with carbon backbones containing pendant cyclophosphazene groups, inorganic hydraulic fluids and lubricants, biologically important substrates such as anticancer agents, insect chemosterilants, pesticides and fertilizers, supports for catalysts, dyes, and crown ether phase transfer catalysts for nucleophilic substitution reactions, core substrates for dendrimers, thermal initiators for anionic polymerization reactions and photosensitive materials [1,2].

In this study, firstly hexachlorocyclotriphosphazene was reacted with 2,2'-dioxibiphenyl ratio 1:2. After obtained compound was treated with different hydroxy aldehyde or ketone, there were prepared oximes. Novel oxime-cyclophosphazenes were synthesized from the reaction of with hydroxylamine hydrochloride in pyridine. Oxime derivatives was obtained from the reactions of oxime-cyclophosphazenes with alkyl halide like methyl iodide, benzyl chloride, and with acyl halide like acetyl chloride, benzoyl chloride, 4-methoxybenzoyl chloride, chloroacetyl chloride, propanoyl chloride, 2-chlorobenzoyl chloride were studied. All products were generally obtained in high yields. The structures of the compounds were proved by elemental analysis, IR, ^1H , ^{13}C and ^{31}P NMR spectroscopy [3-8].

References:

1. Allcock, H. R. Phosphorus-Nitrogen Compounds; Academic Press: New York, 1972.
2. H. R. Allcock, S. R. Pucher, R. J. Fitzpatrick, K. Rashid, *Biomaterials* 1992.
3. G.A. Carriedo, L.F. Catuxo, F.J.G. Alonso, P.G. Elipe, P.A. Gonzalez, *Macromolecules* 29 (1996) 5320.
4. Cil E, M. Arslan, A.O. Gorgulu, *Heteroat. Chem.* 2006, 17, 112–117.
5. Cil E, M. Arslan, A.O. Gorgulu, *Canadian J. Chem.* 2005, 83, 2039–2045.
6. Cil E, M. Arslan, A.O., Gorgulu *Polyhedron* Volume: 25, Issue: 18 Pages: 3526-3532 Published: DEC 25 2006.
7. Cil E, M. Arslan *Inorganica Chimica Acta* Volume: 362, Issue: 5, Pages: 1421-1427, Published: APR 1 2009.
8. Cil E, M. Arslan Turan G, *Acta Chimica Slovenica*, Volume: 55 Issue: 3 Pages: 588-593 Published: 2008.

**MONOTERPENS, TARTRATES,
HYDROXYPHENOLS, ALCOHOLS AND AMINES
WITH CHIRAL CENTERS IN
THIOPHOSPHORILATION REACTIONS**

L.A. Almetkina
I.S. Nizamov
Ye.M. Martianov
G.T. Gabdullina
R.A. Cherkasov

Kazan (Volga region) Federal University, Kazan, Russia
isnizamov@mail.ru

Organic substances with asymmetric centers seem to be convenient substrates for preparing novel organothiophosphorus compounds with appreciate biological activities. We deemed it to be necessary to use chiral natural olefins, alcohols, diols, phenols, dicarboxylic acids and their derivatives as substrates for thiophosphorylation. The reactions of unsaturated monoterpenes such as racemic camphene, *R*-(+)-limonene and (1*S*)-(-)- β -pinene with O,O-dialkyl dithiophosphoric acids have brought about the formation of S-terpenyl esters of dithiophosphoric acids. The reactions studied are facilitated by Lewis acid catalysts (ZnCl₂, NiCl₂, CuCl, CuCl₂, FeCl₃, BF₃·Et₂O, AlCl₃).

Monocyclic monoterpenyl alcohols such as *L*-(-)-menthol and *D*-(+)-menthol were involved in the reactions with tetraphosphorus decasulfide. The corresponding di-*L*-(-)-menthyldithiophosphoric and di-*D*-(+)-menthyldithiophosphoric were prepared in these reactions. 2,4-Diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides undergo coupling with *L*-(-)- and *D*-(+)-isomers of menthol to yield the corresponding O-menthyl arylthiophosphonic acids. In continuation of our approach, we have managed to involve chiral bicyclic monoterpenols such as (1*R*)-*endo*-(+)-fenchyl alcohol, (1*S*)-*endo*-(-)-borneol and (1*R*,2*S*,3*S*,5*R*)-(+)-isopinocampheol into the interactions with tetraphosphorus decasulfide and 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides. On this basis, novel optically active O,O-diterpenyl dithiophosphoric and O-terpenyl arylthiophosphonic acids were obtained. Facile method of synthesizing arylbisdithiophosphonic acids was developed by the reaction of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with tri(ethylene glycol), 1,4-butanediol, *trans*-3,4-pinandiol and (+)-dimethyl *L*-tartrate.

2,4-Diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides reacts with 4,4'-*iso*-propylidenebisphenol, pyrogallol and glycerol to form bis- and trisdithiophosphorylated derivatives. The reactions of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with vitamin B₆ hydrochloride as hydroxyl-containing vitamin and its acetone ester result in the formation of corresponding trisdithiophosphorylated and monodithiophosphorylated derivatives, respectively.

Dithiophosphoric and bisdithiophosphonic acids obtained were transformed into the corresponding ammonium salts including chiral amines. These salts were transformed into the pesticide analogues containing the dithiophosphoric and dithiophosphonic units by the reactions with benzoyl chloride, methyl chloroacetate or epichlorohydrin.

Optically active silyl and plumbyl derivatives of O,O-diterpenyl dithiophosphoric acids were prepared on the basis of the reactions of ammonium salts of corresponding acids with monochloro- and dichlorosilanes, monochloro- and dichloroplumbanes. Chiral silyl and plumbyl derivatives of arylthiophosphonic acids were prepared on the basis of the reactions of ammonium salts of corresponding acids with triorganylechlorosilanes and chloroplumbanes.

New bistriorganylegermyl, stannyl and plumbyl, and cyclic diphenylsilyl and diphenylplumbyl derivatives of arylbisdithiophosphonic acids obtained on the basis of tri(ethylene glycol) and 1,4-butanediol were prepared by the reactions of diammonium salts of corresponding thioacids with triorganylechlorogermane, chlorostannane and chloroplumbane and diphenyl dichlorosilane and diphenyl dichloroplumbane.

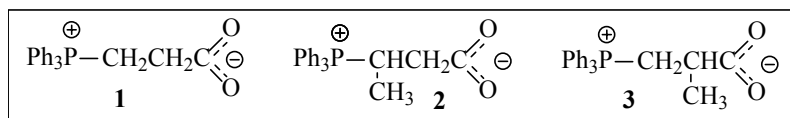
The ammonium salts, S-germyl, S-stannyl and S-plumbyl derivatives of dithiophosphoric, dithiophosphonic and bisarylthiophosphonic acids possess appreciable antimicrobial activity.

Yu.V. Bakhtiyarova
V.V. Stakheev
O.N. Kataeva
V.I. Galkin
I.V. Galkina

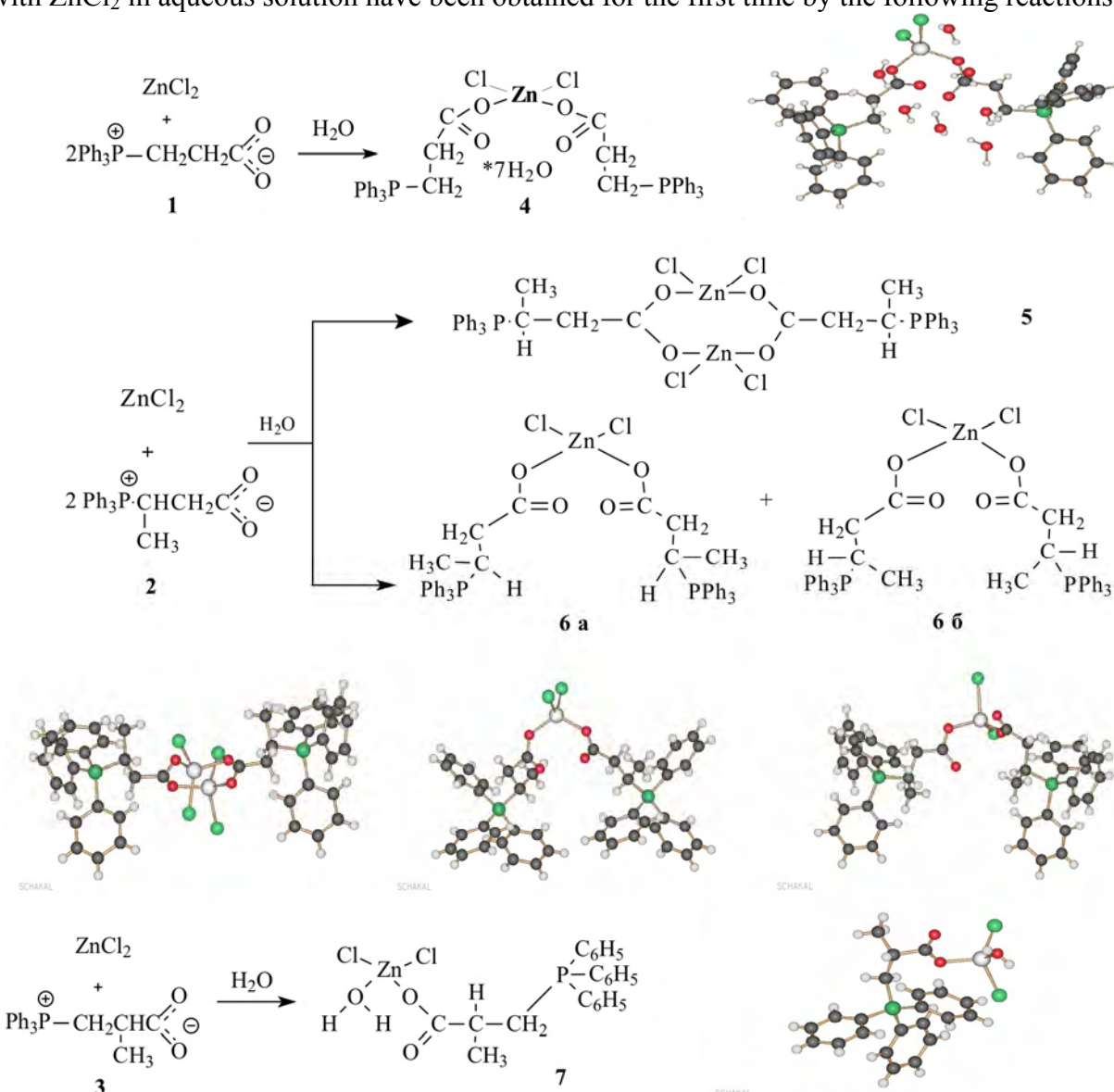
CARBOXYLATE PHOSPHOBETAINES IN COMPLEXES WITH ZnCl₂

Kazan Federal University, A.M. Butlerov Chemistry Institute, Kazan, Russia
vig54@mail.ru

Stable complexes (4-7) of carboxylate phosphobetaines 1, 2 and 3



with ZnCl₂ in aqueous solution have been obtained for the first time by the following reactions:



The structure of the complexes has been determined by NMR and IR spectroscopy, and also by single-crystal X-ray analysis. All compounds obtained showed antimicrobial activity.

The work is realized under financial support of Academy of Sciences of Tatarstan Republic.

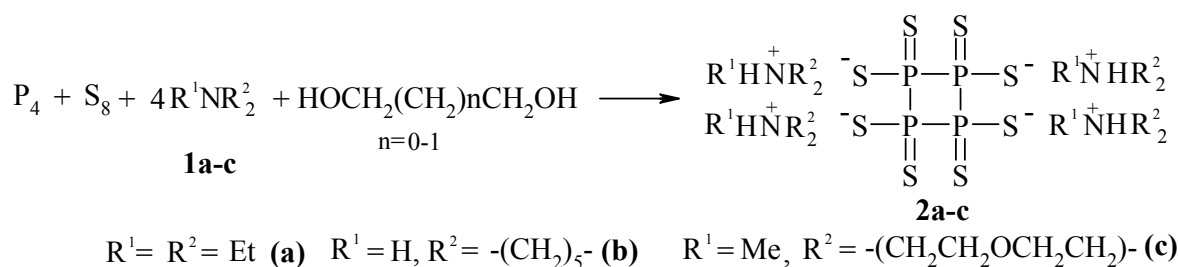
E.S. Batyeva
E.K. Badeeva
E.V. Platova
L.I. Kursheva
O.G. Sinyashin

OCTATHIOTETRAPHOSPHETANES: SYNTHESIS, STRUCTURE AND PROPERTIES

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia
batyeva@iopc.ru

Recently we have reported a new reaction of white phosphorus and elemental sulfur with aliphatic mercaptans in the presence of amines which resulted in the formation of ammonium salts of 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane. According to the X-ray diffraction, the obtained compounds are identified as supramolecular structures formed by realization of intermolecular interactions, including N-H...S and C-H...S ones¹.

In this work we report about the synthesis of octathiotetraphosphetane ammonium salts on the basis of elemental phosphorus, sulfur and amines using diols instead of toxic mercaptans. Thus, the interaction of P₄ with sulfur and 1,3-propylene or ethylene glycols in the presence of amines **1a-c** results in the formation of the corresponding salts **2a-c**.



We investigated the behaviour of the salts **2a-b** in the reaction with copper(I) chloride and obtained the coordination compounds **3a-b**, in which all sulfur atoms of the octathiotetraphosphetane ligands are coordinated by the copper atoms. The comparative IR/Raman spectral analysis in combination with DFT method both the salts **2a-c** and novel Cu(I) chloride complexes **3a-b**, reveals clear spectral features, characteristic for P₄S₈⁴⁻ anion, which are present in the spectra of all obtained compounds, regardless of their character.

References:

1. E.K. Badeeva, E.V. Platova, E.S. Batyeva, L.I. Kursheva, E.E. Zvereva, A.E. Vandyukov, S.A. Katsyuba, V.I. Kovalenko, O.G. Sinyashin // *Heteroatom Chemistry*. – 2011. - V. 22, №.1. - P. 24-30.

Financial support from Russian Foundation for Basic Research (grant no. 09-03-00006-a) is gratefully acknowledged.

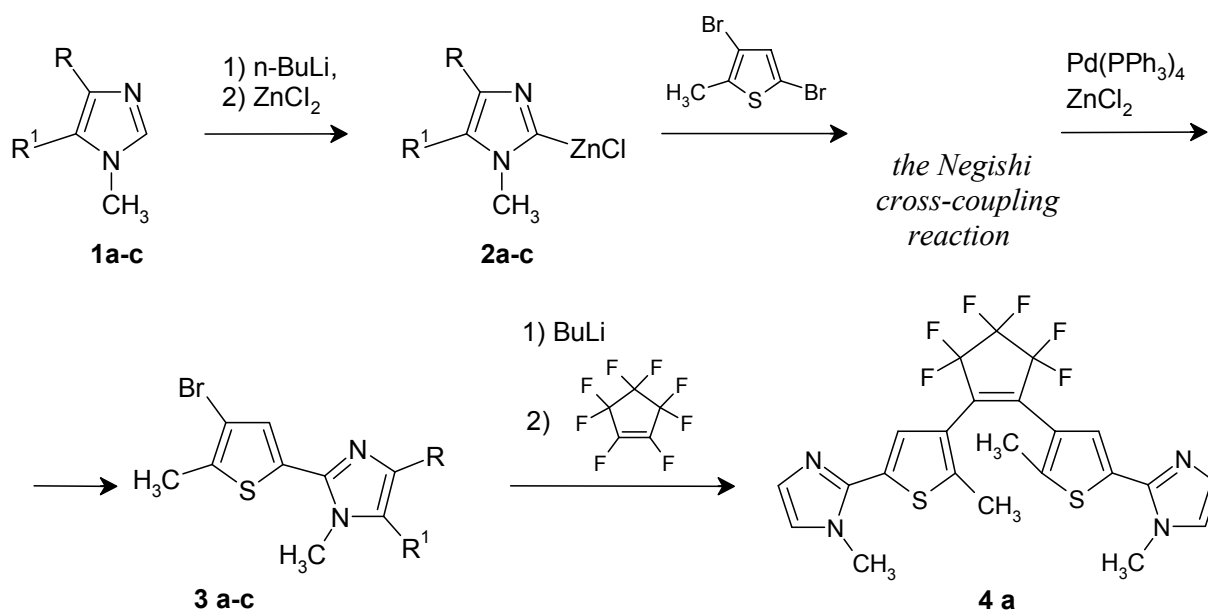
SYNTHESIS OF NOVEL PHOTOCHROMIC DITHIENYLETHENES BASED ON 5-IMIDAZOLYL-3-BROMOTHIOPHENES

A.M. Bogacheva¹
N.N. Mochulskaya¹
V.N. Charushin²

1 - Ural Federal University named after the First President of Russia
Boris N. Yeltsin, Yekaterinburg, Russia
2 - I.Ya. Postovskiy Institute of Organic Synthesis, Ural Division of
the Russian Academy of Sciences, Yekaterinburg, Russia
k-30477@planet-a.ru

Last years photochromic compounds are of great interest due to application of them for creation optoelectronic devices, such as memories and switches. Photochromes based on thiophenes are known to possess optimal spectral characteristics.

The synthesis of 5-imidazolylsubstituted 3-bromothiophenes **3a-c** by means of Negishi Pd-catalysed coupling of imidazolylzinc **2a-c**, which have been obtained from correspondent lithium-derivatives has been realized. The 3-bromothiophene **3a** was lithiated and lithium thiophene derivative was reacted with octafluorocyclopentene at – 78 °C to give 1,2-bis[5-(imidazo-2-yl)thiophen-3-yl]hexafluorocyclopentene **4a**.



(a): $\text{R} = \text{R}^1 = \text{H}$; (b): R and $\text{R}^1 = \text{CH}=\text{CH}-\text{CH}=\text{CH}$; (c): R and $\text{R}^1 = \text{CH}=\text{CF}-\text{CF}=\text{CH}$

The structures of compounds **3a-c**, **4a** was conformed by NMR ^1H and mass-spectra data. Optical properties of compound **4a** are discussed.

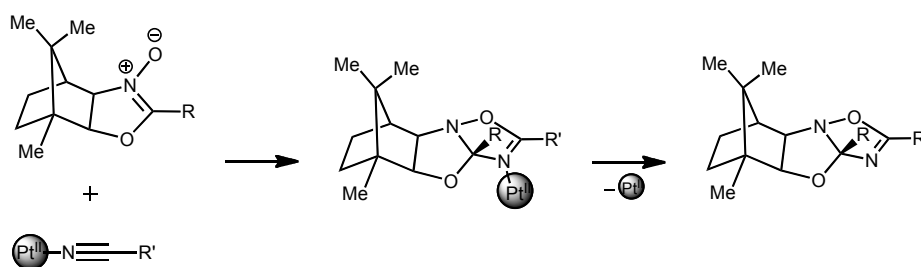
This work was supported by the Russian Foundation for Basic Research (grant 11-03-00718), the Grant of the Progressive Scientific Schools NSh-65261.2010/3 and State Contract GK-02.740.11.0260.

HIGHLY STEREOSELECTIVE PLATINUM-MEDIATED 1,3-DIPOLAR CYCLOADDITION OF NITRONES TO NITRILES

N.A. Bokach
I.A. Balova
V.Yu. Kukushkin

Department of Chemistry, Saint-Petersburg State University, Stary
 Petergof, Russia
 bokach@nb17701.spb.edu

1,3-Dipolar cycloaddition (DCA) form the basis of one of the most important methods for generation of cyclic systems of different sizes. A superior chemical method for enhancing the reactivity of the nitriles in DCA is the introduction of a metal species into the reaction system that allows the generation of heterocycles previously inaccessible (or hardly accessible) by metal-free routes. In CA of nitrones to nitriles, a new asymmetric carbon center is formed, and at least two strategies can be applied to achieve stereoselectivity of these reactions: (i) stereocontrol could be provided by a chiral nitron dipole, (ii) stereocontrol provided by a dipolarophile, when either a metal complex bears both achiral nitrile and chiral supporting ligands, or when a nitrile having chiral substituent is employed.



Two reports related to the stereoselectivity of the metal-mediated nitron–nitrile DCA belongs to type (ii) are known from the literature [1,2]. Rather recently route (i) was explored, by application of the enantiomerically pure asymmetric camphor-based nitrones to provide the stereocontrol of CA (Scheme) [3]. In the report, we discuss a general character of the platinum-mediated reactions, their stereoselectivity, and liberation of the heterocyclic ligand. All complexes were characterized by elemental analyses, high resolution ESI⁺-MS, IR, ¹H and ¹³C NMR spectroscopies, X-ray diffraction, and the liberated heterocycles by high resolution ESI⁺-MS, IR, ¹H and ¹³C NMR spectroscopies.

References:

- (1) A.V. Makarycheva-Mikhailova, J.A. Golenetskaya, N.A. Bokach, I.A. Balova, M. Haukka, V.Y. Kukushkin, *Inorg. Chem.*, 46 (2007) 8323–8331; (2) G. Wagner, M. Haukka, *J. Chem. Soc., Dalton Trans.* (2001) 2690–2697; N.A. Bokach, I.A. Balova, M. Haukka, V.Y. Kukushkin, *Organometallics*, 30 (2011) 595–602.

The Russian Fund for Basic Research (grant 11-03-00262), the Federal Grant-in-Aid Program “Human Capital for Science and Education in Innovative Russia” (contract No P1294 from 09/06/2010) and the Fundação para a Ciência e a Tecnologia (FCT), Portugal – Project PTDC/QUI-QUI/098760/2008 are thanked for support of these studies.

A NEW APPROACH TO THE SYNTHESIS OF SPIROPHOSPHORANES

M.N. Dimukhametov

V.F. Mironov

D.B. Krivolapov

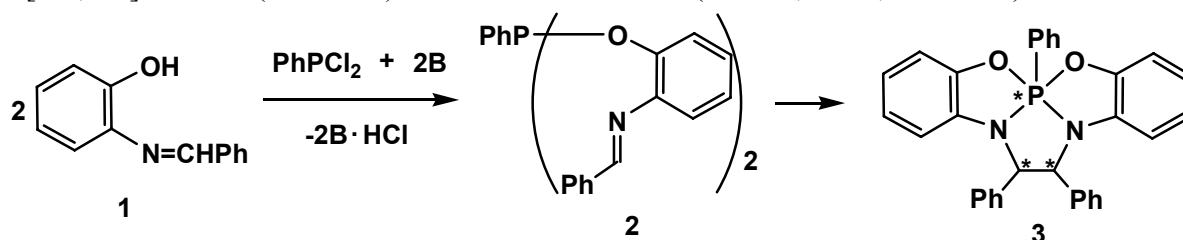
I.A. Litvinov

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia

mudaris@iopc.knc.ru

Pentacoordinated phosphorus derivatives are the key intermediates in phosphorylation and dephosphorylation of the important natural hydroxyl-containing compounds. That is why their synthesis, reactivity, and configurational stability are under intensive study [1-9].

Here we offer a new convenient approach to the synthesis of the pentacoordinated phosphorus species. Bis(2-benzylideneaminophenyl)phosphonite (**2**) (the mixture of a few isomers), obtained in the reaction of dichlorophenylphosphine with two equivalents of 2-benzylideneaminophenol (**1**) in the presence of triethylamine converts almost quantitatively (92.4%) to the spirophosphorane structure (**3**), 1,6,7-triphenyl-3,4,9,10-dibenzo-2,11-dioxo-5,8-diaza-1-phospha[0^{1,5},0^{1,8}]undecan (scheme 1) under mild conditions (solvent, 20°C, 2 months).



Scheme 1.

Compound (**3**) includes three chiral centers and was obtained as a mixture of three diastereoisomers in the ratio of 23 : 67 : 1 (*d,l*- : *meso-1* : *meso-2*). *d,l*-Form has a symmetrical surrounding of the phosphorus atom (δ_P –22.7 ppm), and two non-equivalent *meso*-patterns (*meso-1*, δ_P –23.7 ppm; *meso-2*, δ_P –20.2 ppm) contain a pseudo-chiral phosphorus one. All of them were isolated and their structures were determined by NMR and XRD. Since the other phosphonites obtained react by the similar way it can be held that a new approach to the synthesis of spirophosphoranes was found.

References:

1. R. Holmes. *Acc. Chem. Res.* 1998, **31** (9), 535-542.
2. K.C. Kumara Swamy and N. Satish Kumar. *Acc. Chem. Res.* 2006, **39** (5), 324-333.
3. K. Kajiyama, M. Yoshimune, S. Kojima and K.-y. Akiba. *Eur. J. Org. Chem.* **2006**, (12), 2739-2746.
4. S. Kojima, K. Kajiyama, M. Nakamoto, S. Matsukawa, K.-y. Akiba. *Eur. J. Org. Chem.* **2006**, (1), 218-234.
5. E. Marcos, R. Crehuet, J.M. Anglada, *J. Chem. Theory Comput.* 2008, **4** (1), 49-63.
6. T. Adachi, S. Matsukawa, M. Nakamoto, K. Kajiyama, S. Kojima, Y. Yamamoto, K.-y. Akiba, S. Re, S. Nagase. *Inorg. Chem.* 2006, **45** (18), 7269-7277.
7. X.-D. Jiang, K.-i. Kakuda, S. Matsukawa, H. Yamamichi, S. Kojima, Y. Yamamoto. *Chem. Asian J.* 2007, **2** (2), 314-323.
8. S. Kojima, M. Nakamoto, K.-y. Akiba. *Eur. J. Org. Chem.* **2008**, (10), 1715-1722.
9. X.-D. Jiang, S. Matsukawa, H. Yamamichi, K.-i. Kakuda, S. Kojima, Y. Yamamoto. *Eur. J. Org. Chem.* **2008**, (8) 1392-1405.

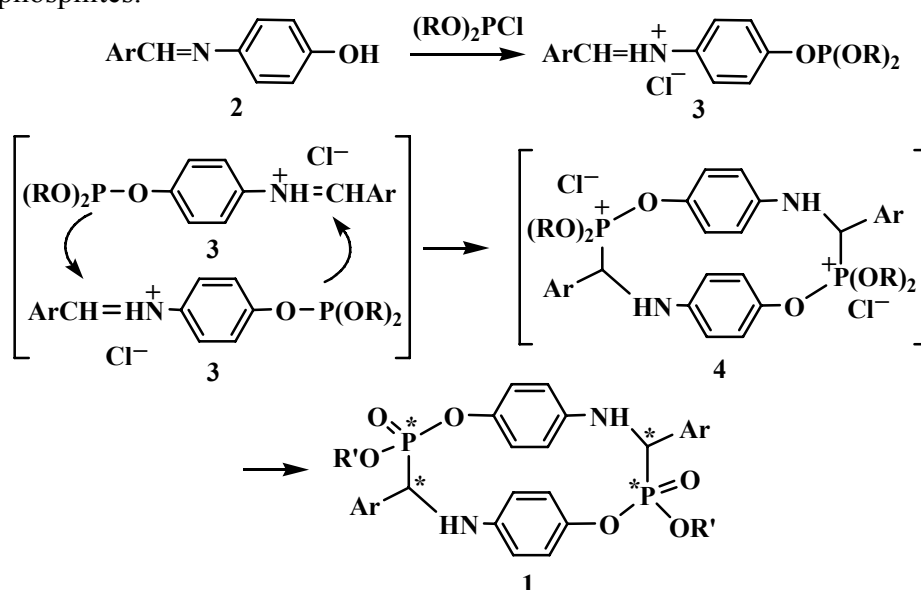
The work is supported by the Russian Foundation for Basic Research (grant 10-03-00525).

A CONVENIENT APPROACH TO THE SYNTHESIS OF 2,7-DIOXA-5,10-DIAZA-3,8-DIPHOSPHA-1,6(1,4)-DIBENZOCYCLODECAPHANES

M.N. Dimukhametov
V.F. Mironov

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
mударis@iopc.knc.ru

Phosphorus-containing macrocycles are of a great interest as the subjects of the supramolecular chemistry for the molecular recognition, complexation etc. [1-7]. We have realized for the first time the synthesis of the sixteen-membered P-macrocycles (**1**) – analogues of [4,4]paracyclophanes – by the reaction of *para*-(*N*-arylidene)aminophenol (**2**) with dialkylchlorophosphites.



R = Et (a); (RO)₂ = O(CH₂)₂O (b), R' = Et (a), (CH₂)₂Cl (b)
Ar = Ph, 4-Br-C₆H₄, 4-MeOC₆H₄, 3-Py

para-Iminoarylphosphites formed at the first stage in these reactions give immonium salts (**3**) with HCl appearing in the course of the reactions. Salts (**3**) are subjected to the cyclocondensation *via* nucleophilic intermolecular attack of phosphorus atoms on electrophilic carbon atoms of the C=N-groups (intermediate **4**) [8] under mild reaction conditions (r.t., stirring for ~5 days). No high dilution is required. Such reactions performed with *meta*-(*N*-benzylidene)aminophenol and dialkylchlorophosphites afford corresponding analogues of [4,4]methacyclophanes. Described approach can be used as a new strategy for the design of various P-macrocyclic species as hosts for some organic molecules.

References:

1. E.N. Tsvetkov, A.N. Bovin, V.Kh. Syundyukova. *Russ. Chem. Rev.* 1988, **57** (8), 776-800.
2. B.P. Friedrichsen, R.P. Powell, H.W. Whitlock. *J. Am. Chem. Soc.* 1990, **112** (24), 8931-8941.
3. A.-M. Caminade, J.P. Majoral. *Chem. Rev.* 1994, **94** (5), 1183-1213.
4. W.D. Habicher, I. Bauer. *Tetrahedron Lett.* 2002, **43** (30), 5245-5248.
5. S. Ekici, M. Nieger, R. Glaum, E. Niecke. *Angew. Chem. Int. Ed. Engl.* 2003, **42** (4), 435-438.
6. S. Cherenok, J.-P. Dutasta, V. Kalchenko. *Curr. Org. Chem.* 2006, **10** (18), 2307-2331.
7. V. Simulescu, G. Ilia. *J. Incl. Phenom. Macrocycl. Chem.* 2010, **66** (1-2), 3-14.
8. M.N. Dimukhametov, V.F. Mironov, R.Z. Musin, *Mendeleev Commun.* 2006, **16** (1), 48-50.

The work is supported by the Federal contract N 02.740.11.0633.

REACTIONS OF 5,7-DICHLORO-4,6-DINITROBENZOFUROXAN AND -FURAZAN WITH TRICYCLOHEXYLPHOSPHINE

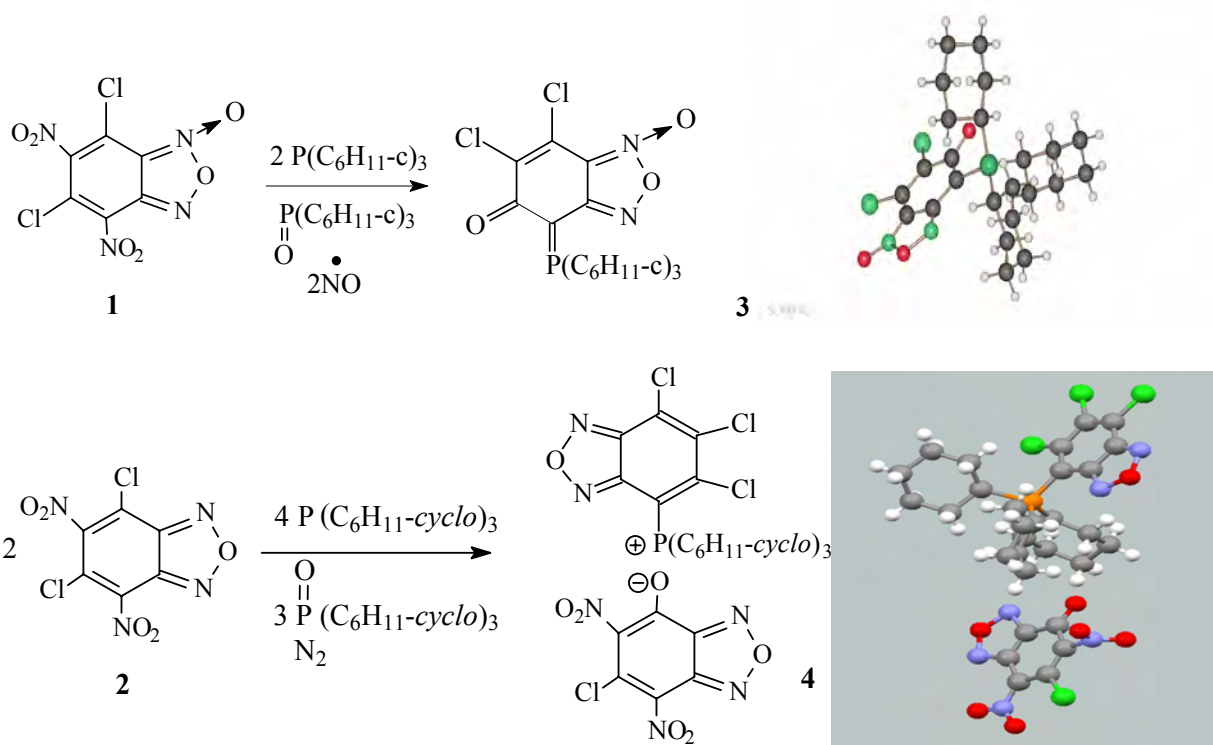
I.V. Galkina¹
E.V. Tudriy¹
O.N. Kataeva²
L.M. Yusupova³
F.S. Levinson³
V.I. Galkin¹

1 - Kazan Federal University, A.M. Butlerov Chemical Institute, Kazan, Russia

2 - A.E. Arbuzov Institute of Organic and Physical Chemistry RAS, Kazan, Russia

3 - Kazan State Technological University, Kazan, Russia
vig54@mail.ru

Benzofuroxan **1** and benzofurazan **2** are of great interest as potential bioactive compounds. Meanwhile, their chemistry, leading to phosphorylated derivatives has not been studied. Here we report about their reactions with tricyclohexylphosphine with the formation of unusual products **3** and **4**:



5,7-Dichloro-4,6-dinitrobenzofuroxan **1** and his deoxygenated analogue **2** react with tricyclohexylphosphine easily at room temperature in absolute ethanol-diethyl ether solvent mixture.

The structure of obtained products **3** and **4** with has been confirmed by X-ray analysis, mass-spectrometry, elemental analysis, NMR ^{31}P , IR, EPR, TG/DSC analysis.

Synthesized products showed high antibacterial and antifungal activity.

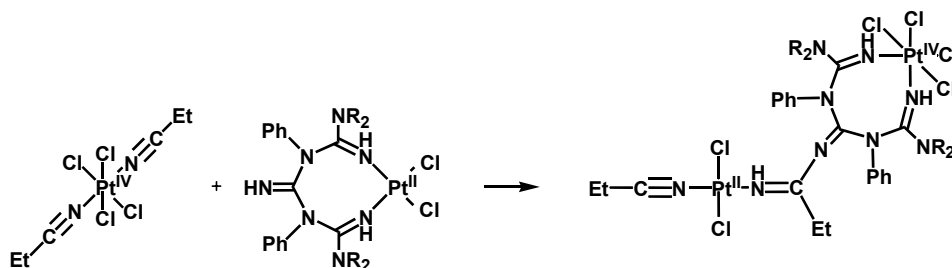
The research is realized under financial support of Academy of Sciences of Tatarstan Republic.

INTEGRATION OF METALLATED TRIGUANIDES WITH BIS-NITRILE PLATINUM COMPLEXES

P.V. Gushchin

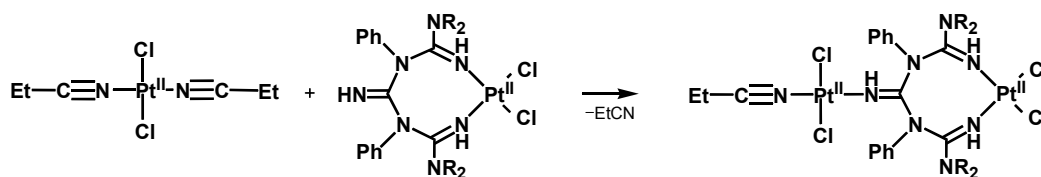
Department of Chemistry, St. Petersburg State University, Stary
Petershof
pvgushchin@gmail.com

It was demonstrated that organonitrile, activated by coordination to platinum(IV) metallocenter, reacts with metallotriguanides $[\text{PtCl}_2\{\text{NH}=\text{C}(\text{R})\text{N}(\text{Ph})\text{C}(=\text{NH})\text{N}(\text{Ph})\text{C}(\text{R})=\text{NH}\}]$ ($\text{R} = \text{NMe}_2, \text{NC}_5\text{H}_{10}, \text{NC}_4\text{H}_8\text{O}$) [1]. This reaction with forming binuclear complexes is accompanied by intramolecular oxidation-reduction process of two metallocenters. The given integration of ligands presents method of assemblage of polynuclear platinum compounds (**Scheme 1**).



Scheme 1

It was studied influence of oxidation degree of metallocenter of nitrile complex on direction of reaction of platinatriguanide with nitrile substratum. It was determined that coupling does not proceed and substitution of nitrile ligand occur in case of platinum(II) nitrile complex in comparison with platinum(IV) compound (Scheme 2).



Scheme 2

References:

[1] Gushchin P. V., Kuznetsov M. L., Haukka M., Wang M.-J., Gribanov A. V., Kukushkin V. Yu. *Inorg. Chem.* 2009, 48, 2583–2592.

This work was supported by Russian Fund for Basic Research (grants 11-03-00483-a, 10-03-90716-mob_st, 11-03-16010-mob_z_ros), the Scientific Council of the President of the Russian Federation (Grant MK-120.2011.3) and Saint-Petersburg Government (The Young Scientist Grant 2010).

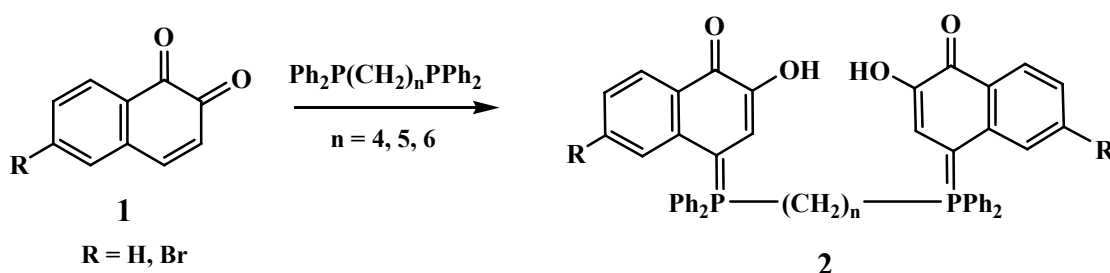
AN EFFICIENT SYNTHESIS OF BIS(PHOSPHONIUM) SALTS, BEARING 1,2-DIHYDROXYNAPHTHYLATE AND 1,2-NAPHTHOQUINONE FRAGMENTS, VIA REACTION OF 1,2-NAPHTHOQUINONES WITH DIPHOSPHINES

N.R. Khasiyatullina
A.V. Bogdanov
D.B. Krivolapov
I.A. Litvinov
V.F. Mironov

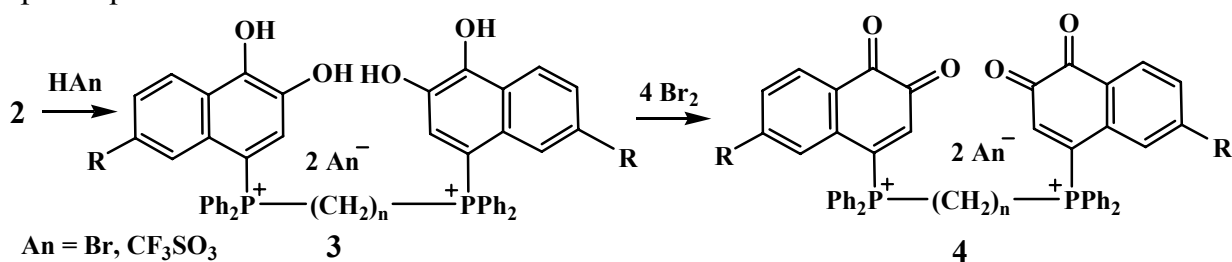
A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
knadya@iopc.ru

Development of the efficient synthesis of multifunctional organophosphorus compounds with P–C bond is one of the important trends of organoelement chemistry. In this respect phosphonium derivatives bearing 1,2-dihydroxyarene or *ortho*-quinone fragments as substituents at phosphorus can be as versatile precursors for the diverse heterocyclic compounds as well as promising ligands for the metal complexes. Such structures are the versatile precursors for the diverse heterocyclic compounds including macrocyclic ones as well as a variety of the metal complexes due to the presence of the chelating 1,2-diketone or 1,2-dihydroxyarene moiety.

In this work we describe the novel phosphonium salt derivatives **3** having the various spacers to combine the phosphorus moieties. The reaction of 1,2-naphthoquinones **1** with bis(diphenylphosphino)alkanes was found to lead to the formation of bis(ylide) structures **2**.



The following modification of phosphobetaines **2** allows to obtain the bis(1,2-naphthoquinone) and bis(1,2-dihydroxynaphthalene) derivatives, containing two phosphonium moieties. Thus, the treatment of bis(ylides) **2** with a dry hydrogen bromide or triflic acid gives more stable bis-1,2-dihydroxynaphthylphosphonium salts **3**. Some of the phosphonium salts are easily oxidized with bromine into the corresponding 1,2-naphthoquinones **4**.



The work is supported by the Federal contract N 02.740.11.0633.

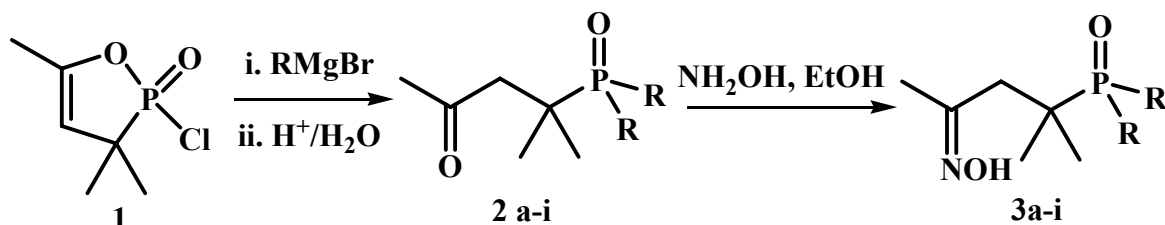
THE SYNTHESIS AND CHEMICAL PROPERTIES OF GAMMA-OXOALKYLPHOSPHINE OXIDES

A.A. Kostin
D.A. Tatarinov
V.F. Mironov
B.I. Buzykin

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
akostin@iopc.ru

The design and synthesis of the new types of the P-ligands containing one or more various functional groups (amino, hydroxy, oxo, etc.) are an important direction of the organophosphorus chemistry. A wide application of these compounds is seriously limited due to the complexity of preparation of phosphine oxides, especially of ones containing additional functional groups. The most well-known procedures require the use of expensive reagents and are complex and laborious. Besides, the isolation of the intermediate and final products is as a rule a difficult problem.

We developed a new approach to the synthesis of a new class of functionally substituted phosphine oxides containing carbonyl group in the γ -position to the phosphorus atom. It includes the reaction of the such P-heterocycles as 3,3,5-trimethyl-2-chloro-1,2-oxaphospholene 2-oxide (**1**) [1-3] with organomagnesium compounds in the 1 : 2 ratio. After hydrolysis of the reaction mixture dialkyl (diaryl) (1-methyl-4-oxopent-2-yl)phosphine oxides (**2**) were isolated with a high yield (above 90 %). Their structure was confirmed by NMR and XRD. The chemical properties of compounds (**2**) were also investigated. So, oximes (**3**) as a mixture of *syn*- and *anti*-isomers were obtained by the treatment of phosphine oxides (**2**) with hydroxylamine.



R = Et (a), Pr (b), C₃H₅ (c), Bu (d), C₅H₁₁ (e), C₆H₁₃ (f), C₈H₁₇ (g), Ph (h), CH₂Ph (i)

References:

1. S.Kh. Nurtdinov, R.S. Khairullin, V.S. Tsivunin, T.V. Zykova, G.Kh. Kamai. *Zh. Obshch. Khim.* 1970, **40**, (11), 2377.
2. K.I. Novitskii, N.A. Razumov, A.A. Petrov. *Khimiya organicheskikh soedinenii fosfora* (Chemistry of Organic Phosphorus Compounds), Leningrad: Nauka, 1967, p. 248.
3. B.A. Arbuzov, V.E. Bel'skii, A.O. Vizel', K.M. Ivanovskaya, G.Z. Motygullin. *Dokl. Akad. Nauk SSSR*. 1967, **176** (2), 323.

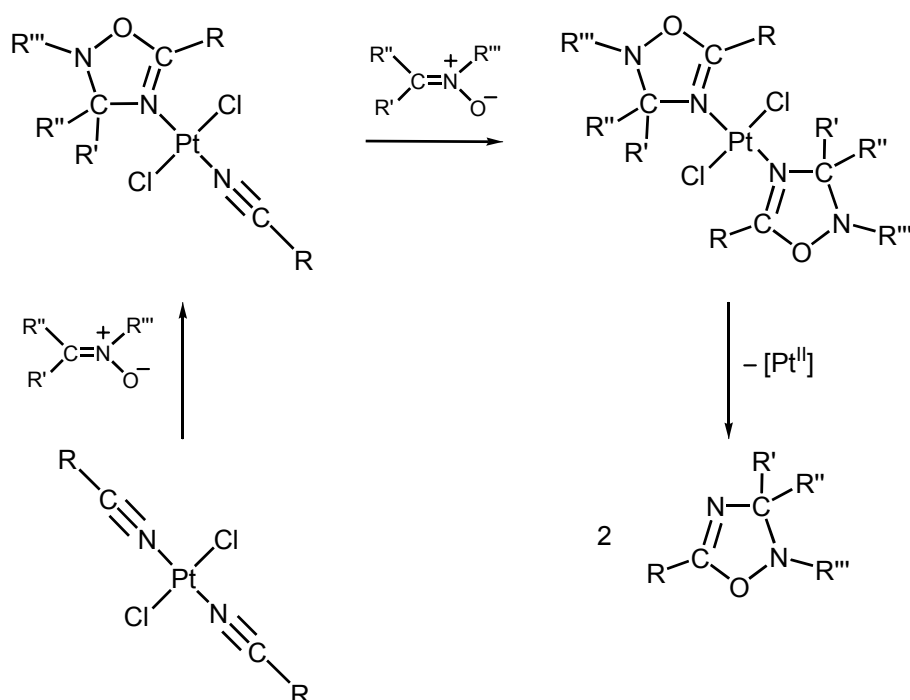
The work is supported by the Russian Foundation for Basic Research – Academy of Sciences of Tatarstan (grant 09-03-97007 p).

TRIARYL KETONITRONES ARE EFFICIENTLY ADDED TO Pt(II)-BOUND NITRILES. RECOGNITION OF REVERSIBILITY OF METAL-MEDIATED CYCLOADDITION

A.S. Kritchenkov
N.A. Bokach
A.P. Molchanov
T.Q. Tung
V.Yu. Kukushkin

Department of Chemistry, Saint-Petersburg State University, Stary
Peterhof, Russia
platinist@mail.ru

Metal-mediated 1,3-dipolar cycloaddition (1,3-DCA) of nitrones to nitriles is an important route for synthesis of 2,3-dihydro-1,2,4-oxadiazoles. The preparation of these heterocycles from *trans*-bis-nitrile Pt(II)-complexes via metal-mediated 1,3-DCA includes: (i) consecutive two-step 1,3-DCA of nitron to each of the nitrile ligands, (ii) liberation of newly formed heterocyclic species from *trans*-bis-oxadiazoline Pt(II)-complexes:



The previous studies demonstrated that the aldonitrones $Z\text{-ArCH=N(O)Alk}$ do not react with alkylcyanide ligands in their Pt^{II} complexes. The aldonitrones give the cycloadducts either with alkylcyanides strongly activated by a Pt^{IV} center, or with more dipolarophilic dialkylcyanamide ligands Alk_2NCN in Pt^{II} complexes. In this work, we found that the ketonitrones $\text{Ph}_2\text{C=N(O)C}_6\text{H}_4\text{R}'$ ($\text{R}' = \text{H, Me, OMe, Cl}$) undergo facile 1,3-DCA to Pt^{II} -bond nitriles RCN such as dialkylcyanamides ($\text{R} = \text{NMe}_2, \text{NEt}_2, \text{NC}_5\text{H}_{10}$) and even alkylnitriles ($\text{R} = \text{Et}$).

Herein we report on the first example of 1,3-DCA of ketonitrones to the $\text{C}\equiv\text{N}$ bond, viz. 1,3-DCA of *C,C,N*-triaryl ketonitrones to alkylcyanide and dialkylcyanamide ligands in their Pt^{II} -complexes. We also report on the reversibility of metal-mediated 1,3-DCA of ketonitrones to nitriles.

References:

A.S. Kritchenkov, N.A. Bokach, M. Haukka, V.Yu. Kukushkin, *Dalton Transactions*, **40** (2011) 4175.

Acknowledgements: Saint-Petersburg State University (research grant 2011–2013), Russian Fund of Basic Research (grant 11-03-00262).

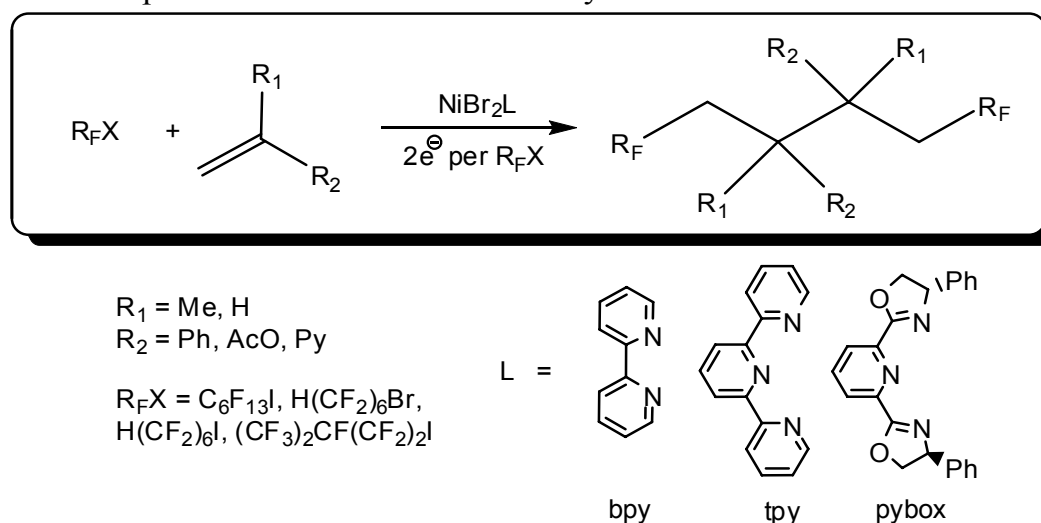
D.Y. Mikhaylov
M.N. Khrizanphorov
T.V. Gryaznova
Y.H. Budnikova
Sh.K. Latypov
O.G. Sinyashin

ELECTROCHEMICAL NICKEL-INDUCED FLUOROALKYLATION: SYNTHETIC, STRUCTURAL AND MECHANISTICAL STUDY

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
dmitrym@iopc.ru

Today, the significant expansion in the use of fluorinated molecules is rooted in the outstanding progress made in the field of synthetic organic chemistry. Indeed, the synthesis of fluorinated molecules is a very challenging area of organic chemistry because the rules that govern the synthesis of non-fluorinated analogs cannot necessarily be transposed to fluorinated compounds. Fluorine is one of the most reactive elements in the periodic table yet some of its compounds are the most stable and least reactive. Many modern pharmaceutical compounds (anti-cancer, antibiotics, anti-malarial etc) include fluorine, or fluorinated groups. Consequently, synthetic methodology to incorporate fluorine synthons must be improved in order to prepare sophisticated organofluorine molecules on a practical scale. Existing methods which employ the addition of fluoroalkyl synthons to different substrates have a number of disadvantages, such as high reaction temperature, low yields, and low selectivities.

We have previously reported our initial findings that electrogenerated nickel can catalyze the addition of perfluoroalkyl halides to olefins to yield new dimeric species. Here we report on the scope of the reaction as well as demonstrate a new method to prevent dimerization and yield monomeric products. This new method opens up the possibility of doing these electrosyntheses asymmetrically. The purposes of the current contribution are to distinguish effects of substrates and catalysts nature on the yields and selectivity of electrocatalytic fluoroalkylation, to manipulate the dimer/monomer formation and to explore the possible reaction pathways. Aiming to identify optimum reaction conditions and to broaden the scope of the electrocatalytic method, a set of experiments with various catalysts, olefins and fluoroalkyl halides was performed (Scheme 1). Several nickel complexes with alpha-diimines were used as catalysts.



Scheme 1. Conditions employed for electrocatalytic fluoroalkylation.

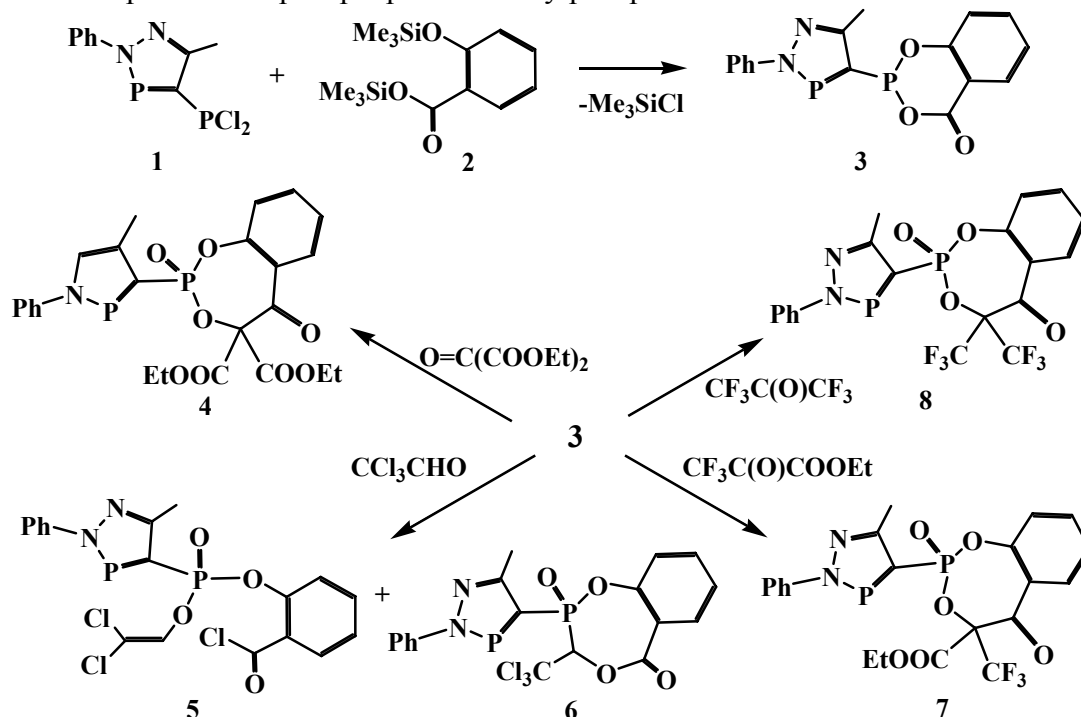
Some details of these intriguing reactions would be discussed.

2-(5-METHYL-2-PHENYL-2H-1,2,3-DIAZAPHOSPHOLE-4-YL)-4H-BENZO[d]-1,3,2-DIOXAPHOSPHORIN-4-ONE – SYNTHESIS AND THE REACTION WITH SOME CARBONYL COMPOUNDS

V.F. Mironov^{1,2}
G.A. Ivkova¹
L.M. Abdrakhmanova²
I.F. Sayfutdinova¹
L.M. Burnaeva¹
I.V. Konovalova¹

1 - Kazan Federal University, Kazan, Russia
2 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia
mironov@iopc.ru

4-(Dichlorophosphino)-2-methyl-5-phenyl-2H-1,2,3σ²-diazaphosphole **1** was obtained for the first time starting from phosphorus trichloride and acetone phenylhydrazone according to data [1] and then 2-[5-Methyl-2-phenyl-2H-1,2,3-diazaphosphole-4-yl]-4H-benzo[d]-1,3,2-dioxaphosphorin-4-one **3** was obtained 2-trimethylsiloxybenzoic acid trimethylsilylic ester and 4-(dichlorophosphino)-2-methyl-5-phenyl-2H-1,2,3σ²-diazaphosphole **1**. The reactivity of initial reagent **3** regarding activated carbonyl compounds (chloral, hexafluoroacetone, diethyl ketomalonate and ethyltrifluoropyruvate) was studied. It was shown that compound **3** reacts with only one equivalent of the carbonyl substrate. The synthetic result is strongly regulated by a bulky diazaphospholic moiety, bonded with a salicylphosphonate fragment, and also depends on the nature of the carbonyl compound. It was shown that both diazaphospholic and salicylphosphonate fragments affect the reactivity of each other, diazaphospholic part remains unchanged. It directs a chemoselectivity of the reaction *via* the six-membered dioxaphosphorinane cycloexpansion [2]. As a final result the products of phosphepine and vinylphosphonate structure were isolated.



References:

- [1] J.H. Weinmaier, G. Brunnhuber and A. Schmidpeter, *Chem. Ber.* 1980, **113**, 2278.
[2] V.F. Mironov, I.A. Litvinov, A.T. Gubaidullin, R.M. Aminova, L.M. Burnaeva, N.M. Azancheev, M.E. Filatov, I.V. Konovalova, *Russ. J. Gen. Chem. (Engl. Transl.)*. 1998, **68**, 1027.
[3] V.F. Mironov, I.V. Konovalova, R.A. Mavleev, A.Sh. Mukhtarov, E.N. Ofitserov, A.N. Pudovik, *Zh. Obshch. Khim. (Russ. J. Gen. Chem.)*. 1991, **61**, 2150.

The work is supported by RFBR (project 10-03-00525).

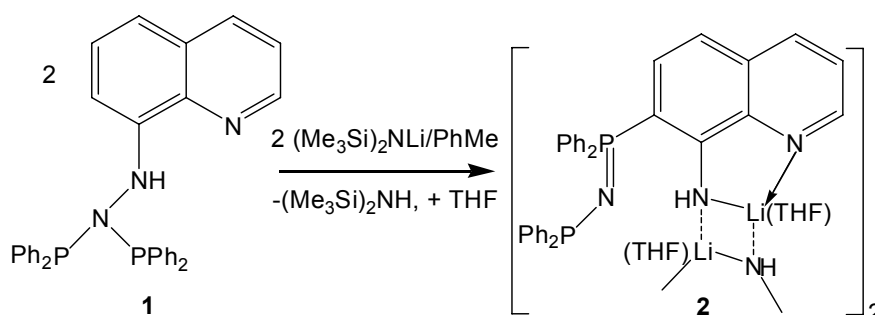
METAL MEDIATED TRANSFORMATION OF ORGANOPHOSPHORUS MOLECULES

J.S. Panova
O.V. Lukoyanova
V.V. Sushev
A.N. Kornev

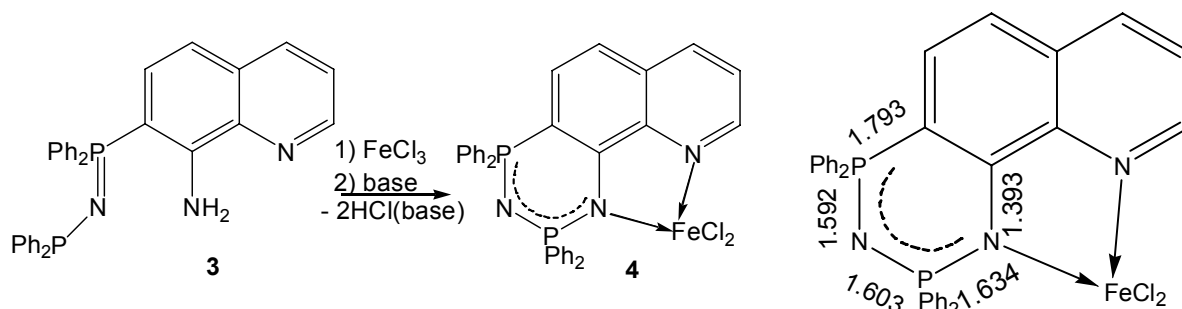
G.A. Razuvaev Institute of Organometallic Chemistry, Rus. Acad. Sci., Nizhny Novgorod, Russia
panovayulya@yandex.ru

Rearrangement of phosphorus-nitrogen ligands in the metal coordination sphere is the important method for synthesis of phosphazene and phosphinoamide of new types.

We found that the interaction of diphosphinohydrazine **1** with $(\text{Me}_3\text{Si})_2\text{NLi}$ results in migration of the $\text{Ph}_2\text{P}-\text{N}=\text{PPh}_2$ -fragment to the nearest carbon atom of the quinolyl ring and gave the lithium salt **2** eventually. Interestingly, lithium atom is chelated by five-membered ring only.



The product of rearrangement **3** reacts with $[\text{Fe}(\text{MeCN})_4]^{2+}[\text{FeCl}_4]^{2-}$ in the presence of base to form phosphorus-nitrogen analog of phenanthroline **4** by the cyclization and deprotonation of the amino group. In this case the metal atom is also chelated by five-membered ring.



The geometry of phosphorus-nitrogen heterocycle in the complex **3** is nearly planar. Notably, there are no alternating single and double bonds in the molecule. The P-N distances increase in series: $\text{P}(1)-\text{N}(3)$ 1.592 Å < $\text{N}(3)-\text{P}(2)$ 1.603 Å < $\text{P}(2)-\text{N}(1)$ 1.634 Å. The nitrogen atom in the iminophosphorus part of **4** forms slightly shorter Fe-N coordination bond than the other one (quinolyl nitrogen). Synthetic and mechanistic aspects are discussed.

This work was supported by The Russian President's program "Leading Scientific Schools" (No. 7065.2010.3) and the Russian Agency for Education

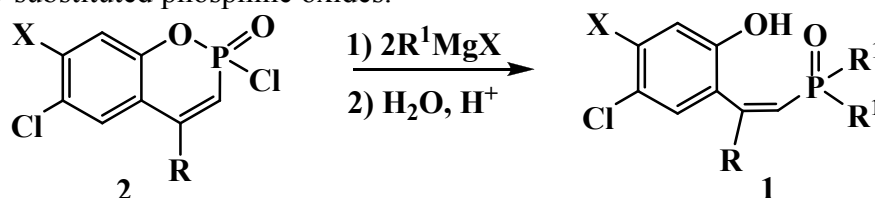
A SIMPLE SYNTHESIS OF HYDROXYPHOSPHINE OXIDES FOR MICELLAR LANTHANIDE'S EXTRACTION

D.A. Tatarinov
A.V. Nemtarev
Yu.G. Elistratova
V.F. Mironov

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan,
Russia
datint@iopc.ru

Phosphine oxides are versatile ligands for the metal complex catalysts [1-3], extracting agents for rare-earth metals [4-6], and materials for a creation of the ion-selective electrodes [7,8]. Phosphine oxides are frequently used for the phosphines synthesis. They are also applied as organocatalysts in some organic reactions [9].

Here we report a simple and effective synthesis of the hydroxyalkenylphosphine oxides (**1**) based on the using of the ready available oxaphosphinine-2-oxide derivatives (**2**) [10] in the reaction with various organomagnesium compounds. This reaction allows synthesizing the phosphine oxides (**1**) with a high yield (80-95 %) and gives a possibility to obtain the wide range of the functionally substituted phosphine oxides.



$R^1 = \text{Aryl, Alkyl}; R = \text{Aryl; Alkyl}, X = \text{H, Me}$

Phosphine oxides (**1**), bearing phosphoryl and hydroxyl groups at the one side of the double bond proved to be the convenient ligands for the rare-earth metals extraction. Obtained phosphine oxides are especially effective for the micellar extraction of some lanthanides from the nitric acid media and show a high extraction degree (in some cases about 100 %).

References:

1. M. Shibasaki, M. Kanai, S. Matsunaga, N. Kumagai. *Acc. Chem. Res.* 2009, **42**, 1117–1127.
2. K. Ishihara, A. Sakakura, M. Hatano. *Synlett*. **2007**, 686–703.
3. M. McConville, O. Saidi, J. Blacker, X. Jian-liang. *J. Org. Chem.* 2009, **74**, 2692–2698.
4. H.H. Dam, D.N. Reinhoudt, W. Verboom. *Chem. Soc. Rev.* 2007, **36**, 367–377.
5. A.S. Aloy, N.B. Sapozhnikova, A.G. Anshitz, K.G. Kudinov, M.V. Burdin, T.D. Tranter, D.A. Knekht, T.A. Todd, L.A. Bechfield. *Russ. Pat. N 2251168* (2005).
6. M.S. Agafonova-Moroz, L.V. Krasnikov, N.E. Mishina, A.Yu. Shadrin, O.V. Shmidt. *Radiochemistry*. 2009, **51**, 403–405.
7. A. Florido, I. Casas, J. Garcia-Raurich, R. Arad-Yellin, A. Warshawsky. *Anal. Chem.* 2000, **72**, 1604–1610.
8. L.J. Charbonniere, R. Ziessel, M. Montalti, L. Prodi, N. Zaccheroni, C. Boehme, G. Wipff. *J. Am. Chem. Soc.* 2002, **124**, 7779–7788.
9. M. Benaglia, S. Rossi. *Org. Biomol. Chem.* 2010, **8**, 3824–3830.
10. V.F. Mironov, A.I. Kononov, I.A. Litvinov, A.T. Gubaidullin, R.R. Petrov, A.A. Shtyrlina, T.A. Zyablikova, R.Z. Musin, N.M. Azancheev, A.V. Il'yasov. *Russ. J. Gen. Chem. (Engl. Transl.)*. 1998, **68**, 1414–1442.

The work is financially supported by the President of the Russian Federation (grant MK-1172.2010.3).

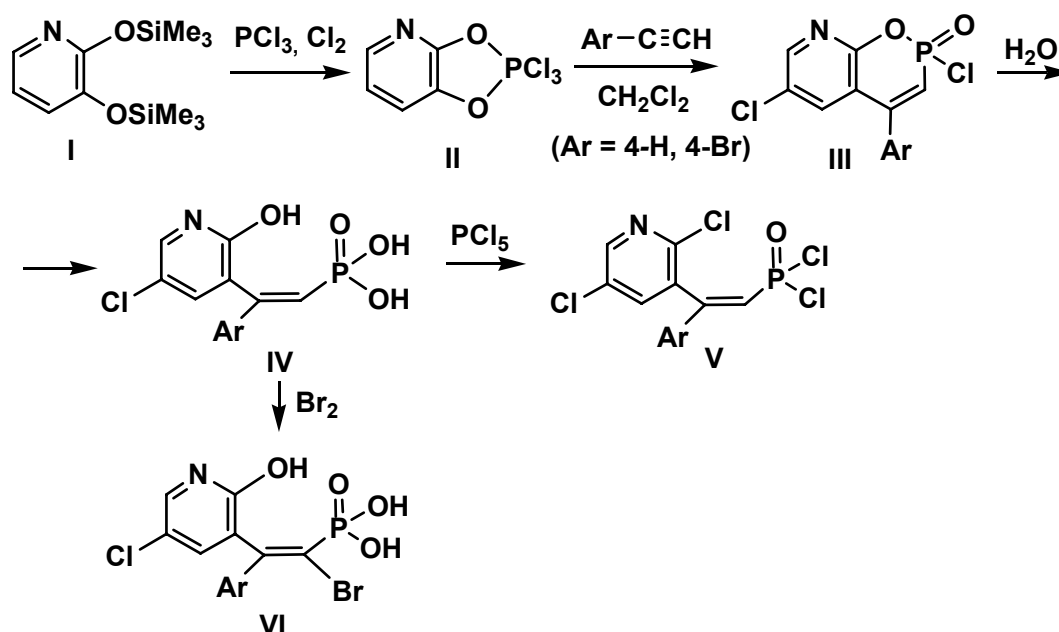
A CONVENIENT WAY TO THE NEW PHOSPHORYLATED PYRIDINE DERIVATIVES – 3- (2'-ARYL-1'-PHOSPHORYLETHEN-2'-YL)-5- CHLORO-2-HYDROXYPYRIDINES

E.N. Varaksina
V.F. Mironov

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
vlena@iopc.ru

Pyridine cycle is the key fragment of a lot of the natural compounds, for example alkaloids, vitamins and others. In spite of the well known range of approaches, such as classical multicomponent condensation methods Krenke, Chichibabin, Gaureshi-Thorpe, Ganch, Fridliander and others, some variants of aza-Baylis-Hilman and Diels-Alder reactions and modern metallic and multimetallic catalyzed cross coupling modification processes are available at present time in the chemists arsenal, the development of selective routes to functionalized pyridine derivatives remains of great importance task.

Here we present a new approach to the 2-hydroxy-3-alkenyl substituted pyridines, which includes a unique transformation of the annelated dioxaphosphole's fragment of phosphorylated dihydroxypyridine (II) to the oxaphosphorinine moiety in the reaction (II) with terminal arylacetylenes under the soft conditions. The main products – heterocycles (III) are obtained with the 60-70 % yields. After hydrolysis they give acyclic phosphonic acids (IV). The halogenation of (IV) was also investigated. The selective formation of (VI) and (V) in the reactions with equimolar amount of bromine or PCl_5 took place at room temperature.



The work was supported by Russian Foundation for Basic Research (grant N 10-03-00525).

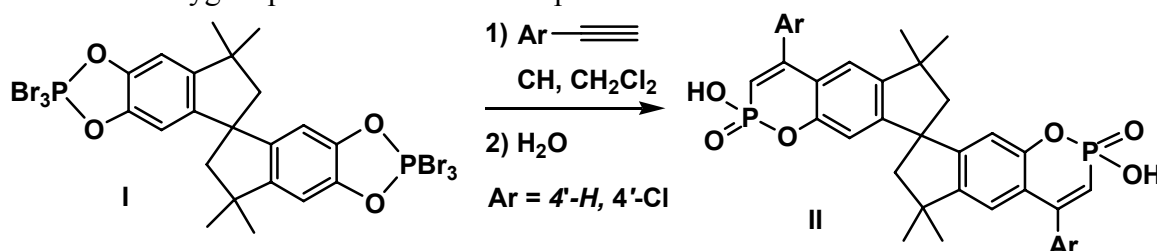
**THE REGIOSELECTIVE SYNTHESIS OF
OXAPHOSPHORININES FUSED WITH
1,1'-SPIROBISINDANES VIA NEW
TRANSFORMATION OF PHOSPHORYLATED
AROMATIC DIOLES WITH ACETYLENES**

**E.N. Varaksina
Sh.K. Latypov
V.F. Mironov**

A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian
Academy of Sciences, Kazan, Russia
vlena@iopc.ru

1,1'-Spirobisindane derivatives attract a great attention both biological active compounds and perspective fragments in the material creation for optical and industrial applications. The selective transformation of its fragment has remained an important goal and a subject of a number of papers and patents within the last few years.

In this work the possibility of an easy selective modification of phosphorylated 1,1'-spirobisindane derivative (I) to the compound (II), in which oxaphosphorinine cycles are fused with 1,1'-spirobisindane moiety, is demonstrated for the first time. The transformation proceeds in the mild conditions and is based on the reaction of bisphosphorane structure (I) with arylacetylene double excess. According to the NMR data the predominantly realization (70-90%) of the only one direction of the oxygen ipso-substitution takes place.



Compounds isolated after hydrolysis have the structures (II). Structures of (II) were definitively proved by NMR correlation experiments. The combination of different 2D experiments (^1H - ^1H COSY, ^1H - ^{31}P HMBC, ^1H - ^{13}C HSQC and HMBC) allowed straightforward identification of the main fragments, assignment all signals of protons and carbons and thus to prove the overall structure. Moreover according to the variety of NMR correlations there is only the *endo* isomer (aromatic substituents *endo*) although the second *exo* regio isomer could not be excluded in advance (Fig. 1). In addition a good correlation of calculated (Gauge-Including Atomic Orbital (GIAO)) versus experimental ^{13}C chemical shifts additionally supports the above conclusions on the structure of these compounds. Finally, variety of ROE's between the key protons unambiguously proves this isomeric structure assignment.

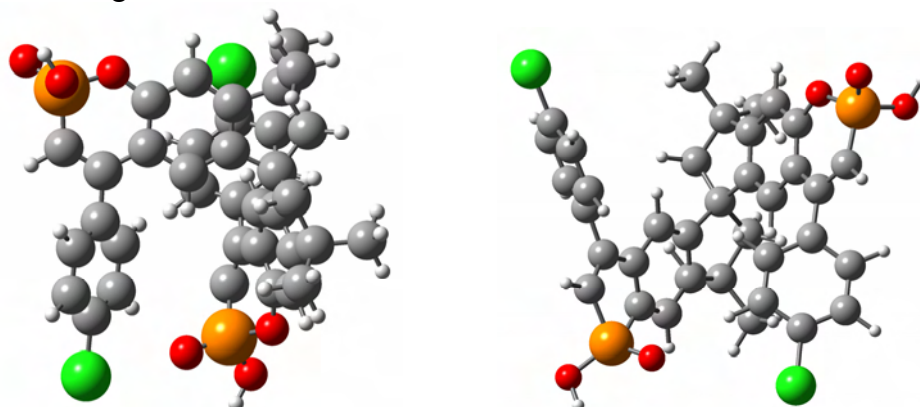


Figure 1. B3LYP/6-31G(d) optimized geometry of (II).

The work was supported by Russian Foundation for Basic Research (grant 10-03-00525).

NEW CADMIUM-PROMOTED REACTION OF A C-NUCLEOPHILE: SYNTHESIS AND X-RAY STRUCTURE OF THE FIRST DICYANOPYRAZINE IRON(II) MACROBICYCLE

Y.Z. Voloshin¹
O.A. Varzatskii²
P.A. Stuzhin³
S.V. Shulga²
S.V. Volkov²
A.V. Vologzhanina¹
E.G. Lebed¹

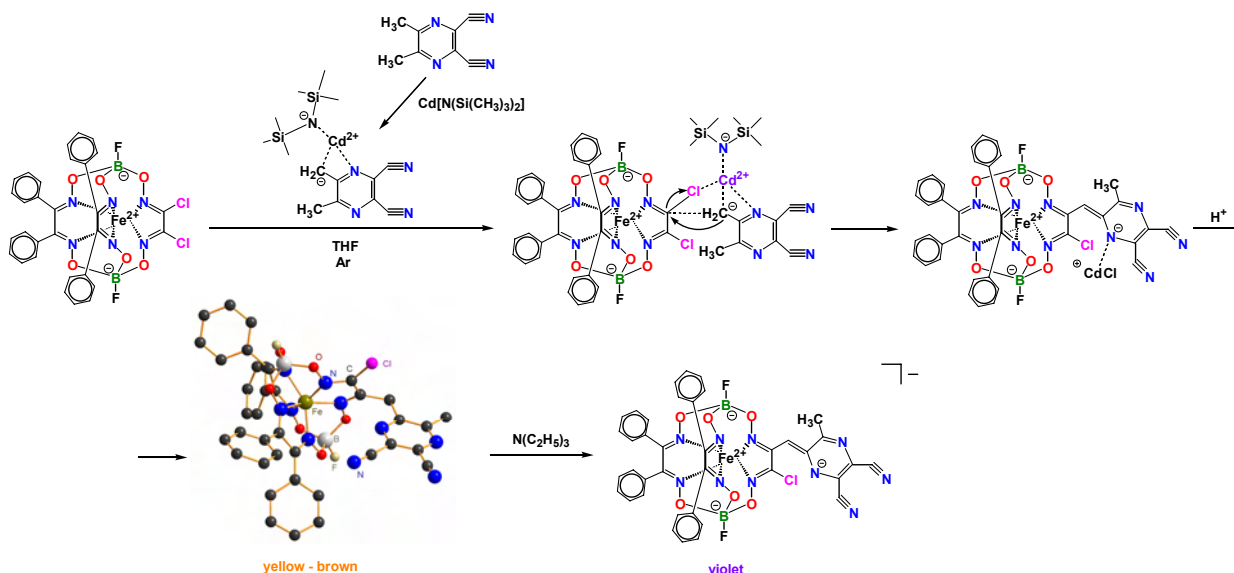
1 - Nesmeyanov Institute of Organoelement Compounds RAS,
Moscow, Russia

2 - Vernadskii Institute of General and Inorganic Chemistry NANU,
Kiev, Ukraine

3 - Ivanovo State University of Chemistry and Technology, Ivanovo,
Russia

voloshin@ineos.ac.ru

The first clathrochelate complex with pendant ribbed dicyanopyrazine substituent was obtained by the new carbanion condensation of the dichloroclathrochelate precursor with 2,3-dicyano-5,6-dimethylpyrazine in the presence of the cadmium(II) amide as a promoter (Scheme). Only one pair of the carbanionic and electrophilic reactive centers is involved in an condensation giving the monosubstituted clathrochelate, whereas the product of the double condensation of its *vic*-dihalogen-containing chelate fragment with *ortho*-dimethylsubstituted pyrazine molecule was not detected. This result is explained by the formation on its first stage of the intermediate dicyanopyrazine carbanion, which is stabilized by the coordination of its heterocyclic nitrogen atom to the cadmium(II) ion (Scheme). The clathrochelate product demonstrates strong CH-acidity: in the presence of strong organic bases its color changes from yellow-brown (Fig 1, **a**) to violet (Fig. 1, **b**) due to the formation of a clathrochelate anion with highly conjugated azapolyene π -system.



Cadmium-promoted condensation is proposed as useful tool to perform other carbanionic reactions as well as to synthesize the functionalized electron-withdrawing heterocycles by alkylation and heteroarylation of their available reactive derivatives.

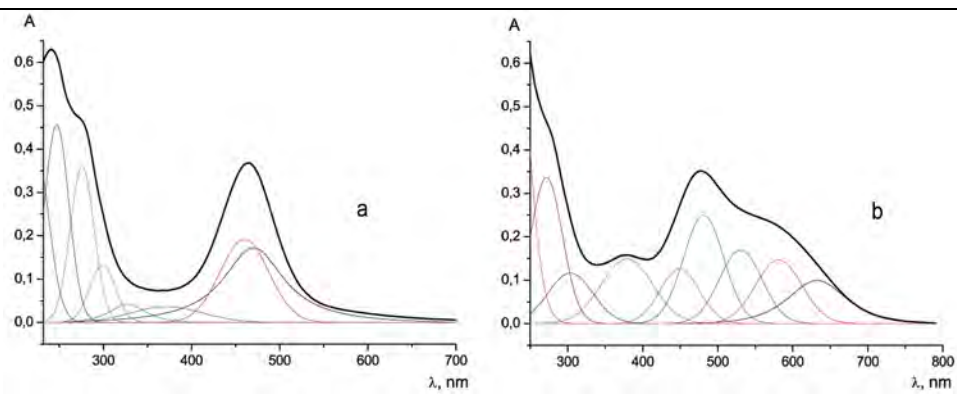


Fig. 1

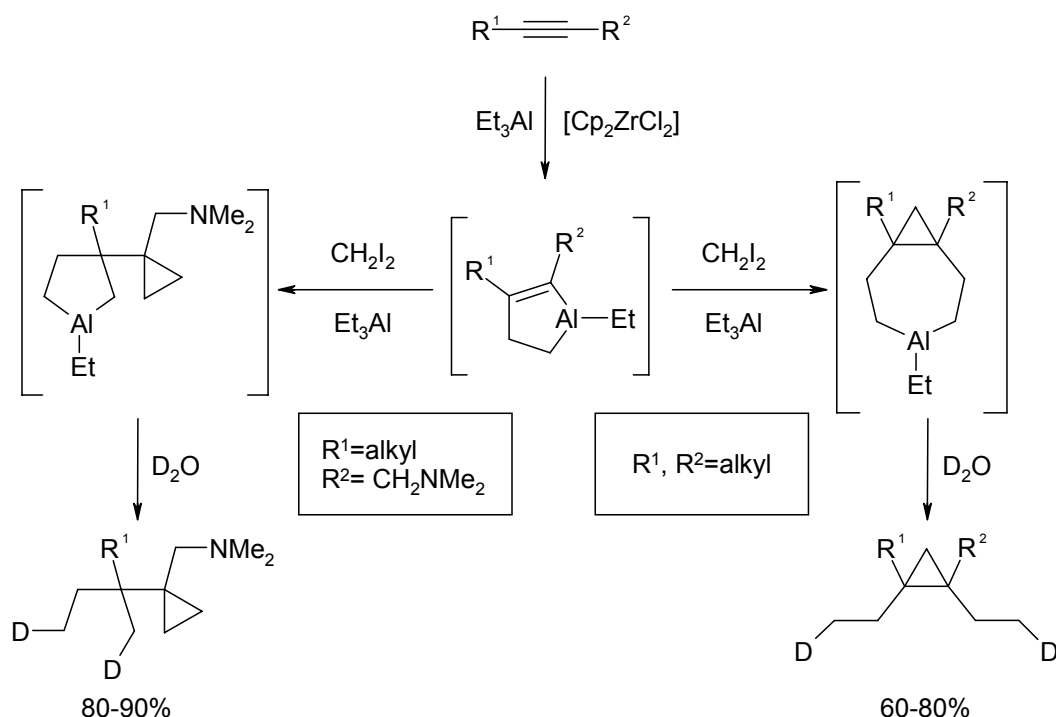
The authors gratefully acknowledge support of the RFBR (grants 09-03-00540, 09-03-00688, 10-03-01069, 10-03-00613 and 10-03-00837) and RAS (programs 6, 7 and P7).

REACTIVITY OF ALUMINUM CARBENOIDS AND MECHANISM OF THE REACTION WITH FUNCTIONALLY SUBSTITUTED OLEFINS

A.V. Yaroslavova
I.R. Ramazanov
U.M. Dzhemilev

Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences, Ufa, Russia
alsu-ufa@inbox.ru

We have studied the reaction of alkenyl derivatives of aluminum, silicon, nitrogen and phosphorus with aluminum carbenoids (R_2AlCH_2I) that were generated *in situ* from CH_2I_2 and R_3Al , where $R=Me, Et, i-Bu$. It was found that alkenyl derivatives of aluminum, silicon and nitrogen give cyclopropane compounds. The structure of the reaction products and the mechanism of their formation are strongly dependent on the nature of the substituents at the double bond. We believe that alkenyl aluminums react with aluminum carbenoids via double bond carboalumination stage with subsequent elimination of the metal iodide and the formation of hard to reach cyclopropyl-containing organometallics. At the same time, the reaction with alkenyl derivatives of silicon and nitrogen proceeds via the addition of methylene group to the double bond. Thus, we found for the first time that the presence of organometallic substituent at the double bond facilitates the carboalumination over methylene transfer process. The report will discuss the scheme of transformation, as well as the factors that determine the pathways of the reaction.

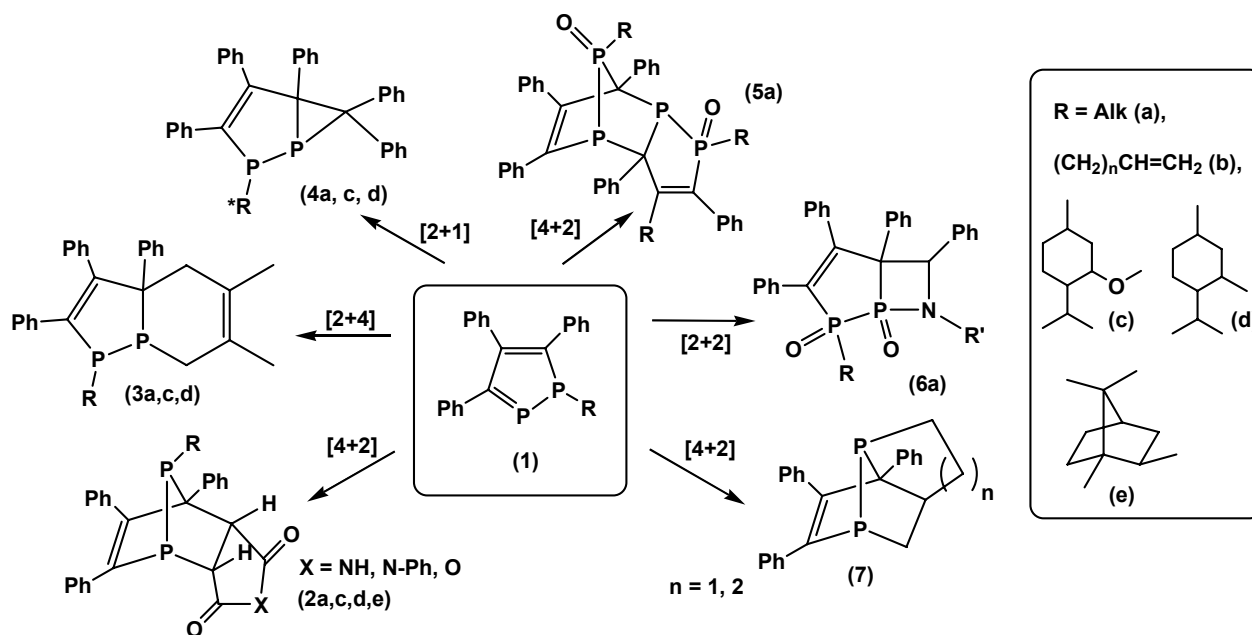


CYCLOADDITION REACTIONS OF 1-ALKYL-1,2-DIPHOSPHOLES

A.A. Zagidullin¹
 V.A. Miluykov¹
 Y.S. Ganushevich¹
 O.G. Sinyashin¹
 E. Hey-Hawkins²

1 - A.E. Arbuzov Institute of Organic and Physical Chemistry RAS,
 Kazan, Russia
 2 - Institut für Anorganische Chemie, Universität Leipzig, Leipzig,
 Germany
 almaz_zagidullin@mail.ru

The cycloaddition reactions of phospholes are convenient tool of molecular design of chiral phosphorus frame ligands which can be employed as weak, highly space filling ligands in homogeneous biphasic and asymmetric catalysis. We have demonstrated that cycloaddition reactions of 1-alkyl-1,2-diphospholes **1** proceed with high regio- and stereoselectivity giving new 1,7-diphosphanorbornenes. New phosphorus frame ligands **2-6** are accessible in high yield as pairs of enantiomers by reacting of 1-alkyl-1,2-diphospholes with maleic acid derivatives, 2,3-dimethylbutadiene, diphenyldiazomethane and nitrones respectively. The 1-alkenyl-1,2-diphospholes **1b** undergo intramolecular cycloaddition reaction to form cage compounds **7**.



The cycloaddition reactions of chiral diphosphole **1c** lead to formation of diastereomers **2c-4c** with ratio 1:1, which were separated with use of inert column chromatography to form pure enantiomers. At the same time chiral diphospholes **1d-e**, containing menthyl and bornyl substituents undergo cycloaddition reactions with high diastereoselectivity (up to 11:1), so chiral compounds **2d,e** were obtained by simple recrystallization.

Section 8.

Symposium “Modern trends in functionalization of C-H bonds in arenes and heteroarenes”

NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN ELECTRON-DEFICIENT ARENES. MISSING PART OF THE AROMATIC SUBSTITUTION PUZZLE

M. Makosza

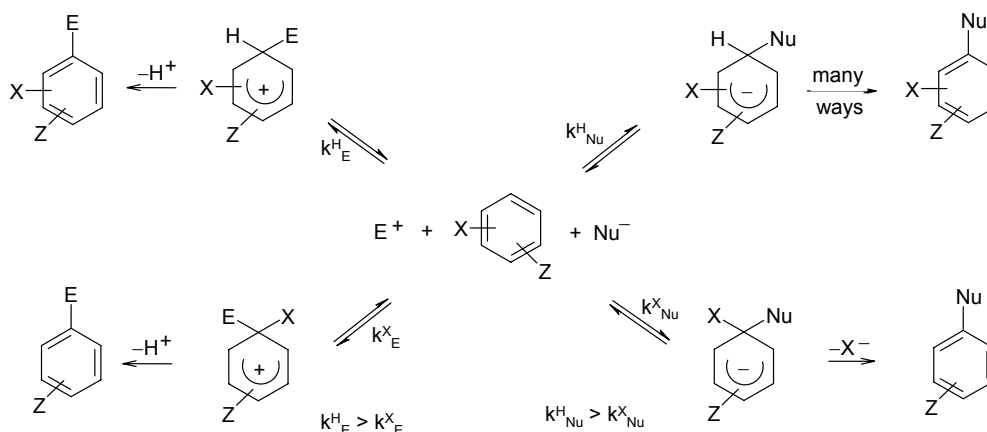
 Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw,
 Poland
 icho-s@icho.edu.pl

Addition of nucleophilic agents Nu^- to nitroarenes proceeds in positions occupied by hydrogen or halogen X to form anionic σ^H and σ^X adducts. Fast spontaneous departure of anions X^- from σ^X adducts results in S_NAr that is well recognized and widely used. Although addition of nucleophiles in positions occupied by hydrogen proceeds much faster but spontaneous departure of hydride anions from initially formed anionic σ^H adducts does not proceed hence they dissociate and S_NAr via slower formation of σ^X adducts is mostly observed.

Nevertheless in recent years a few general ways of conversion of anionic σ^H adducts into products of nucleophilic substitution of hydrogen such as oxidative, vicarious etc substitution were developed.^{1,2} In the lecture general character, great practical value and mechanistic features of these processes and unambiguous evidences that nucleophilic substitution of hydrogen is the major primary process whereas conventional S_NAr of halogen just secondary *ipso* substitution will be discussed.

Similarity electrophilic aromatic substitution of hydrogen that proceeds *via* intermediate cationic σ^H adducts and departure of proton is fast, primary “normal” substitution whereas substitution of other substituents “*ipso*” substitution is slower secondary process.

This analogy between nucleophilic and electrophilic substitution is shown in scheme.



In modern text-books three variants of aromatic substitution are discussed: *normal* and *ipso* electrophilic and *ipso* nucleophilic (S_NAr). Important process of nucleophilic substitution of hydrogen is not presented, thus appropriate corrections should be introduced into text-books and teaching of chemistry of arenes.² Nucleophilic substitution of hydrogen is therefore the missing part of aromatic substitution puzzle.

References:

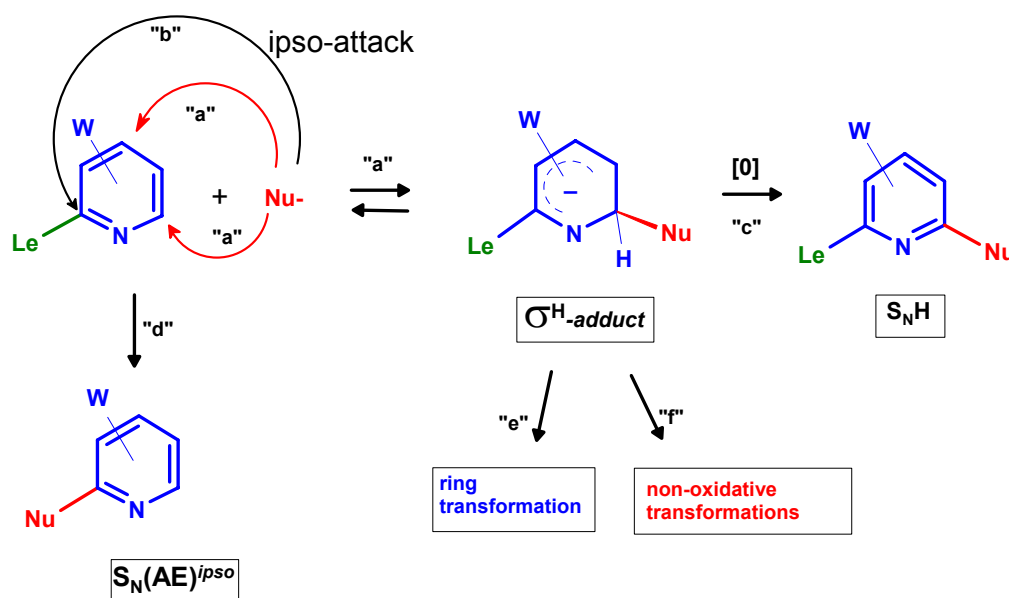
1. M. Makosza, K. Wojciechowski, *Chem. Rev.*, **2004**, *104*, 2631.
2. M. Makosza, *Chem. Soc. Rev.*, **2010**, *39*, 2855.
3. M. Makosza, *Synthesis*, **2011**, in print

DIRECT NUCLEOPHILIC FUNCTIONALIZATION OF THE C-H BOND IN AZINES

G.L. Rusinov
O.N. Chupakhin
V.N. Charushin

I.Ya. Postovsky Institute of Organic Synthesis of the Russian
Academy of Sciences
rusinov@ios.uran.ru

The reactions of azines and azoloazines bearing a bridge nitrogen atom with nucleophiles have been studied. A number of pathways for direct C-C coupling reactions of hetarenes with C nucleophiles based on a nucleophiles attack on unsubstituted carbon in azaaromatics (path a) have been developed. Activation of azaaromatic systems and structural effects, including azoloannulation and influence of substitutes, have been elucidated. Novel oxidative (path c) and non-oxidative transformations of σ^H -adducts (paths b,e,f) have been found.



The work was financially supported by the Russian Academy of Sciences (grants 09-I-3-2004, 09-P-3-2001, 09-II-3-1015, 09-T-3-1016, 09-T-3-1022), the Russian Foundation for Basic Research (grant 11-03-00545-a), the State Contract (02.740.11.0260), and the State Program for Supporting of Leading Scientific Schools of Russian Federation (grant NSh-65261.2010.3).

NEW ADVANCES IN SELECTED TRANSITION
METAL-CATALYZED TRANSFORMATIONS

V. Gevorgyan

University of Illinois at Chicago, Chicago, USA
vlad@uic.edu

A set of novel efficient transition metal-catalyzed methodologies for synthesis of multisubstituted carbo- and heterocycles has been developed [1-10]. Commonly, regioselective synthesis of carbo- and heterocycles possessing various functional groups is not a trivial task. We have shown, however, that incorporation of migrating step(s) in the cyclization cascade often helps solving this problem. Thus, it was found that in the presence of Cu-, Ag-, and Au catalysts, a number of groups, such as Hal-, RS-, AcO-, TsO-, Ar-, and SiR₃ could undergo 1,2- or 1,3-migration, or in some cases even double migration, which allows for expeditious synthesis of densely-functionalized carbo- and heterocycles, which are not easily accessible via existing techniques.

We have also explored a direct Pd-catalyzed C-H functionalization approach toward synthesis of multisubstituted aromatic and heteroaromatic molecules [11-16]. Thus, a novel silicon-tether approach for the Pd-catalyzed C-H arylation of phenols has been developed. Next development involved employment of the PyDipSi-, a Si-tethered directing group in the Pd-catalyzed C-H acyloxylation and halogenation reactions. The PyDipSi group is traceless or can easily be converted into a variety of useful functionalities.

The scope of these transformations will be demonstrated and the mechanisms will be discussed.

References:

- [1] Kel'in, A. V.; Sromek, A. W.; Gevorgyan, V. *J. Am. Chem. Soc.* **2001**, *123*, 2074-2075.
- [2] Kim, J. T.; Kel'in, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2003**, *42*, 98-101.
- [3] Sromek, A. W.; Kel'in, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 2280-2282.
- [4] Sromek, A. W.; Rubina, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, *127*, 10500-10501.
- [5] Seregin, I.; Gevorgyan, V. *J. Am. Chem. Soc.* **2006**, *128*, 12050-12051.
- [6] Dudnik, A. S.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2007**, *46*, 5195-5197.
- [7] Schwier, T.; Sromek, A. W.; Yap, D. L. M.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 9868-9878.
- [8] Xia, Y.; Dudnik, A. S.; Gevorgyan, V.; Li, Y. *J. Am. Chem. Soc.* **2008**, *130*, 6940-6941.
- [9] Dudnik, A. S.; Sromek, A. W.; Rubina, M.; Kim, J. T.; Kel'in, A. V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2008**, *130*, 1440-1452.
- [10] Dudnik, A. S.; Xia, Y.; Li, Y.; Gevorgyan, V. *J. Am. Chem. Soc.* **2010**, *132*, 7645-7655.
- [11] Seregin, I. V.; Ryabova, V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 7742-7743.
- [12] Chernyak, N.; Gevorgyan, V. *J. Am. Chem. Soc.* **2008**, *130*, 5636-5637.
- [13] Huang, C.; Gevorgyan, V. *J. Am. Chem. Soc.* **2009**, *131*, 10844-10845.
- [14] Dudnik, A. S.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 2096-2098.
- [15] Chernyak, N.; Dudnik, A. S.; Huang, C.; Gevorgyan, V. *J. Am. Chem. Soc.* **2010**, *132*, 8270-8272.
- [16] Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729-8732.

**FUNCTIONALIZATION OF CARBO-, N-, O-
CONTAINING HETEROAROMATIC SYSTEMS**

A.D. Kotov
V.Yu. Orlov

Yaroslavl State University, Department of Organic and Biochemistry,
Yaroslavl, Russia
kot@bio.uniyar.ac.ru

We studied the peculiarities of the interaction nitroarenes with arylacetonitriles and the possibility of modifying formed compounds. Realization the reaction in medium of aliphatic alcohols in the presence of alkali in case of *para*-substituted nitroarenes leads to the corresponding 2,1-benzoxazoles. The data on the influence of several factors on the process, carried out quantum-chemical modeling of possible directions, identified minor products, was concluded on the mechanism of the process and key stages. Established that the formation of target structures includes the step of formation of *ortho*-arylcyanometilenquinonmonooxysims that exist in several stereoisomeric forms. *Para*-unsubstituted nitroarenes under these conditions always form arilcyanometilen *para*-quinonmonooxysims also exist in several stereoisomeric forms. Realized S_NAr^H reaction in the absence of solvent, but for the *para*-substituted nitroarenes heterocyclization does not happen, and highlights the resinous substance. Thus, in the synthesis of 5-*R*-3-aryl-2,1-benzoxazoles by S_NAr^H method solvent has a key role on the stage of cyclization.

Discussed the ways of modifying 5-*R*-3-aryl-2,1-benzoxazoles. The direction of the interaction antraniles with nitrating reagents depends on applied reaction conditions. Carrying out the reaction in a medium of concentrated sulfuric acid and sodium nitrate using or nitric acid leads to the formation of 5-chloro-7-nitro-3-(4-nitrophenyl)-2,1-benzoxazoles, while the interaction with nitric acid environment of chloroform or methylene chloride at room temperature formed 2-chloro-4-nitro-9,10-dihydro-9-akridinon. In the use of solid-phase nitration reaction system is transformed, leading to a 2-chlorakridinon.

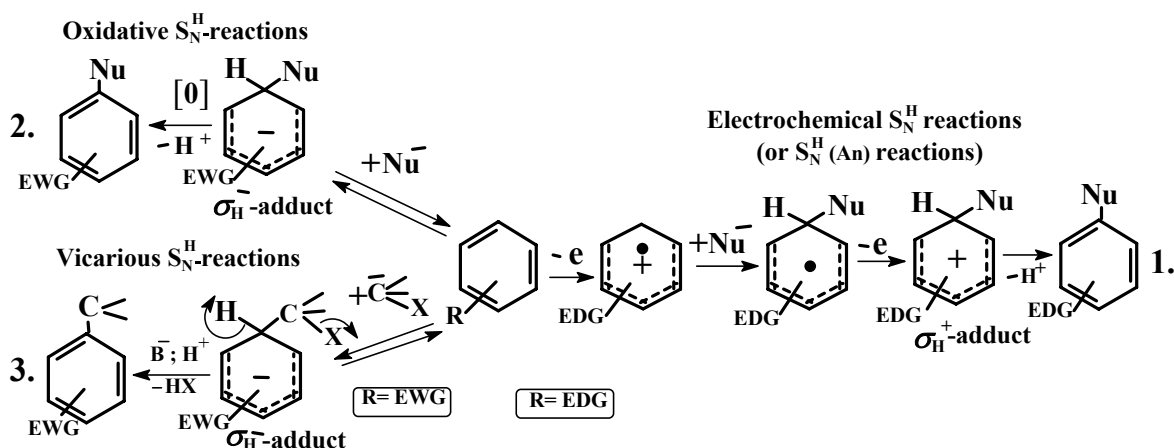
The direct amination of 5-*R*-3-aryl-2,1-benzoxazoles in the reaction system hydroxylamine sulfate / concentrated sulfuric acid / vanadium oxide (V) (catalyst) was realized.

ANODIC AND CHEMICAL AROMATIC
SUBSTITUTION

V.A. Petrosyan

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of
Sciences, Moscow, Russia
petros@ioc.ac.ru

Analysis of anodic (electro-oxidative) aromatic substitution reactions allows a specific group of reactions involving direct nucleophilic replacement of hydrogen atom at the aromatic ring to be singled out. These reactions, which we call $S_N^H(\text{An})$ reactions¹ (Scheme, pathway 1), occur *via* an intermediate σ^+ adducts, represent a versatile type (the hydrogen atom that is easily removed as a proton) of S_N^H reactions that are being studied intensely. It is quite obvious that a direct S_N^H process is unlikely since it would involve hydrogen abstraction from a σ_H^- adduct as a hydride ion. However, a number of “indirect” methods for performing this task are known, the main ones involving the addition – oxidation $S_N^H(\text{AO})$ (pathway 2) and addition – elimination $S_N^H(\text{AE})$ (pathway 3) processes². The $S_N^H(\text{An})$ reactions do not involve the removal of nucleofugal groups (*cf.* $S_N^H(\text{AE})$ reactions) and the electron transfer successfully works instead of an oxidant ($S_N^H(\text{AO})$ reactions). It should be noted that $S_N^H(\text{An})$ reactions use arenes with electron-donating substituents as the main starting compounds. However, due to the polarity inversion (“umpolung”) the starting nucleophilic arene is converted to a cation radical (pathway 1) to become an electrophile, which, in turn, efficiently adds nucleophilic reagents. This fact expands considerably the scope of arenes that can undergo S_N^H reactions. Both mechanisms of $S_N^H(\text{An})$ reactions and examples of their synthetic application has been described.



Scheme

References:

1. Vladimir A. Petrosyan. *Mendeleev Commun.*, 2011, **21**, 115.
2. Valery N. Charushin and Oleg N. Chupakhin, *Mendeleev Commun.*, 2007, **17**, 249.

C-N BOND FORMATION VIA THE NUCLEOPHILIC AROMATIC SUBSTITUTION OF HYDROGEN: OXIDATIVE ALKYLAMINATION AND ARYLAMINATION OF NITROARENES

A.V. Gulevskaya¹
B.U.W. Maes²
S. Verbeeck²
I.N. Tyaglivaya¹

1 - Southern Federal University, Department of Chemistry, Rostov-on-Don, Russia

2 - University of Antwerp, Department of Chemistry, Organic Synthesis, Antwerp, Belgium
agulevskaya@sfsedu.ru

The synthesis of functionalized aromatic and heteroaromatic amines is of great interest, due to their importance as building blocks for pharmaceuticals, agrochemicals, polymers, and materials. The classical strategy for their preparation is based on nucleophilic displacement reactions involving good leaving groups. Harsh reaction conditions and strong dependence on the substitution pattern of the arene substrate are drawbacks limiting its application. A more general approach is Pd-catalyzed coupling between aryl halides and amines (Buchwald-Hartwig amination). In cases of electron-deficient azaheteroaromatics (azines and their nitro derivatives), direct oxidative amination and alkylation with $\text{KNH}_2/\text{NH}_3/\text{KMnO}_4$ or alkylamine/ KMnO_4 , pioneered by van der Plas, is an attractive alternative because no classical leaving group is required.

Reports on oxidative (alkyl)amination of polynitroarenes, which also possess a rather high π -deficiency, are very scarce. We have studied the viability of the oxidative alkylation process for the derivatization of electron-deficient carboaromatics. 1,3-Dinitrobenzene, 3-nitrobenzo-nitrile, 1-nitro-3-(trifluoromethyl)benzene, 1-nitronaphthalene, and 1,5-, 1,8- and 2,7-dinitro-naphthalenes have shown to react with a wide range of alkylamines in the presence of an oxidant (KMnO_4 , AgMnO_4 , $\text{AgPy}_2\text{MnO}_4$) giving access to the corresponding *N*-alkyl-nitroarene-amines. The rate-limiting step of the mechanism for some substrate/alkylamine combinations was determined. With the use of ^1H NMR spectroscopy thermodynamic properties of σ^H -adduct formation were deduced and the effect of additives on the adduct formation was investigated.

Unfortunately, the oxidative alkylation procedure is not suitable for arylamination because of the low nucleophilicity and high sensitivity of arylamines towards oxidation. This is why S_N^H -arylation reactions are still rare. We have shown that *N*-aryl-2,4-dinitroanilines and *N*-aryl-5-nitropyridin-2-amines can be easily obtained from 1,3-dinitrobenzene and 3-nitropyridine, respectively, through oxidative nucleophilic substitution of hydrogen, using the metal amides of a range of aryl(heteroaryl)amines as reactants. The nitroarene plays a dual role in this reaction, acting as the substrate and oxidizing agent.

**REDUCTIVE ACTIVATION OF
AREN CARBONITRILES FOR THE FORMATION OF
CARBON-CARBON BOND**

**E.V. Panteleeva
T.A. Vaganova
V.D. Shteingarts**

N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian
Division of the Russian Academy of Science, Novosibirsk, Russia
shtein@nioch.nsc.ru

The results are reported of the development of a general approach to the activation of aromatic nitriles for the formation of carbon-carbon bond on the aromatic skeleton, based on the substrate single- or two-electron reduction in liquid ammonia to form long-lived anionic species (radical anions, dianions or cyclohexadienyl anions), involved further as anionic synthons in alkylation or biaryl coupling. The revealed structural regularities of these reactions (the product nature, regioselectivity) are correlated with the results of studying their mechanism implemented on the base of the structural approach (the use of mechanism-specific modeling reagents) in a context of the competition of a mechanism of the one-step carbon-carbon bond formation and a two-step mechanism involving the single electron transfer.

**POSITIONAL SELECTIVITY IN ELECTROPHILIC
SUBSTITUTION IN π -EXCESSIVE
HETEROAROMATICS****L.I. Belen'kii
N.D. Chuvylkin**N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of
Sciences, Moscow, Russia
libel@ioc.ac.ru

The trend of positional selectivity (α : β -ratios) in electrophilic substitution reactions in the series furan > selenophene $\geq$ thiophene > pyrrole don't correlate with known order of substrate selectivity: pyrrole $\gg$ furan > selenophene > thiophene. The mentioned discrepancy manifests in reactions of parental heterocycles, their substituted derivatives, and corresponding benzannulated systems [1]. To interpret the experimental data, the hypothesis was proposed that the trend of positional selectivity under discussion correlates with the change of relative stabilities of onium states of elements ($O^+ < Se^+ \leq S^+ < N^+$) and reflects the dominant role of heteroatoms in stabilization of σ -complexes formed in β -substitution. The positive charge in the latter is distributed between heteroatom and one of α -carbon atoms (in α -isomers, four atoms of the ring take part in delocalization of the charge) [2]. This interpretation was confirmed by *ab initio* MP2/6-31G and DFT B3LYP/6-31G quantum chemical calculations of model cationic σ -complexes (2*H*- and 3*H*-hetarenium ions) [3]. However, using the simplest 2- and 3-protonated molecules as models, more delicate differences manifested in reactions of *N*-substituted pyrroles could not be explained [4]. Considering σ -complexes formed on attack of five-membered ring by cations corresponding to respective electrophiles (Me^+ , Me_3Si^+ , Br^+ , NO_2^+ , $MeCO^+$, SO_3) we revealed three reasons of the formation of β -isomers as preferable or single products: steric effects of the substituent at nitrogen atom, polar effects of the latter, and isomerization of the α -substituted derivative primarily formed into more thermodynamically preferable β -isomer [1, 5, 6].

References:

1. L. I. Belen'kii, *Adv. Heterocycl. Chem.*, **99**, 143 (2010).
2. L. I. Belen'kii, *Khim. Geterotsikl. Soed.*, 1587 (1980).
3. L. I. Belen'kii, I. A. Suslov, and N. D. Chuvylkin, *Khim. Geterotsikl. Soed.*, 38 (2003).
4. L. I. Belen'kii, T. G. Kim, I. A. Suslov, and N. D. Chuvylkin, *ARKIVOC*, xiii, 59 (2003).
5. L. I. Belen'kii, N. D. Chuvylkin, A. I. Serykh, and I. A. Suslov, *Zh. Org. Khim.* **41**, 1362 (2005).
6. L. I. Belen'kii, I. D. Nesterov, and N. D. Chuvylkin, *Khim. Geterotsikl. Soed.*, 1645 (2008).

STABLE CRYSTALLINE σ -COMPLEXES OF 4,6-DINITROBENZOFUROXAN AND AMINES

V.I. Galkin¹
 E.V. Tudriy¹
 G.L. Takhautdinova¹
 L.M. Yusupova²
 D.B. Krivolapov³
 I.A. Litvinov³
 I.V. Galkina¹

1 - Kazan Federal University, A.M. Butlerov Chemistry Institute, Kazan, Russia

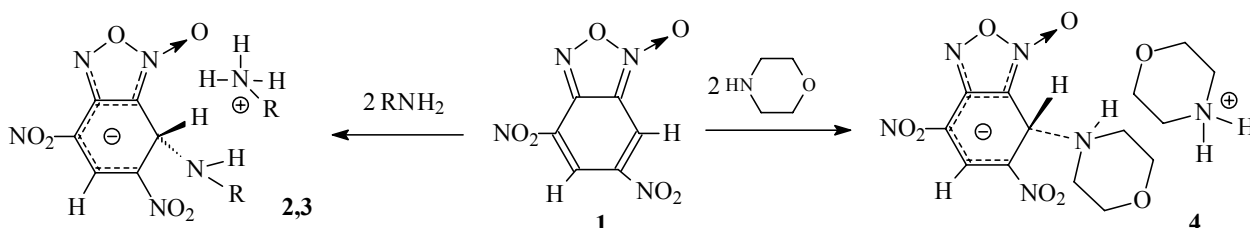
2 - Kazan State Technological University, Kazan, Russia

3 - A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia

vig54@mail.ru

A crystalline stable σ -complexes of superelectrofilic 4,6-dinitrobenzofuroxan **1** with three amines have been prepared and characterized by single-crystal X-ray analysis. All of the compounds – stable Meisenheimer σ -complexes (**2-4**) – were readily available through straightforward nucleophilic aromatic substitution reactions of 4,6-dinitrobenzofuroxan **1** with dodecylamine, cyclohexylamine and morpholine in a mixture of 30% EtOH-70% Et₂O (v/v) as solvent at 20°C (*Scheme I*).

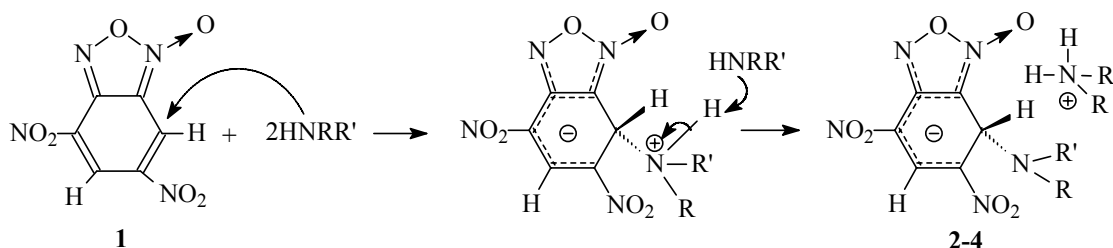
Scheme I



R = C₁₂H₂₅ (**2**); C₁₆H₃₃ (**3**)

A reasonable mechanism, which could account for the formation of these products (**2-4**), is shown in *Scheme II*.

Scheme II



The single crystal X-ray structure of complexes **2-4** are presented on Fig. 1-3.

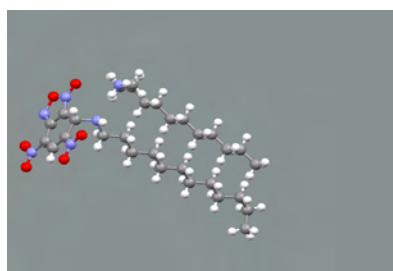


Fig.1. Molecular geometry of complex **2**

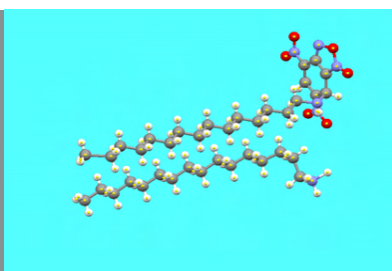


Fig.2. Molecular geometry of complex **3**

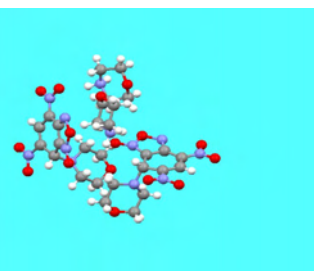


Fig.3. Molecular geometry of complex **4**

A.V. Pestov
P.A. Slepukhin
Yu.G. Yatluk
V.N. Charushin
O.N. Chupakhin

SYNTHESIS OF CHELATING POLYMER SORBENTS BY USING THE S_N^H METHODOLOGY

I.Ya. Postovsky Institute of Organic Synthesis UB RAS, Russia
pestov@ios.uran.ru

Recently we had developed a new synthetic approach to modify the structure of phenol-formaldehyde resins, which enables one to functionalize a polymer matrix by using the S_N^H (nucleophilic aromatic substitution of hydrogen) methodology [1]. This paper is dedicated to further development of the S_N^H methodology for polymer transformations of resorcinol-formaldehyde resins, elucidation of sorption characteristics for the modified polymers, and coordination structure of the chelating unit on the basis of model low-molecular weight compounds.

Direct heteroarylation of phenol (resorcinol) fragments in polymer chains with 1,2,4-triazine derivatives illustrates a new synthetic method in the polymer chemistry. The feature of this methodology is that it provides an opportunity to accomplish direct one-pot polymer transformations by incorporating of rather complicated chelating groups through the displacement of hydrogen in phenol moieties. It has been shown that in order to obtain chemically modified polymers on the basis of phenol-formaldehyde and resorcinol-formaldehyde resins with a high degree of substitution with chelating units, a polymer matrix has to react with 3-(pyridin-2'-yl)-1,2,4-triazin-5(2*H*)-one. Also, it has been found that polymer sorbents with a high selectivity can be obtained by using the template method [2].

Targeted synthesis of model compounds (1-acetyl-3-(pyridin-2'-yl)-6-(3',5'-dimethyl-4'-hydroxyphenyl)-1,2,4-triazin-5(2*H*)-one), as structural units of the chelating polymers, and elucidation of the structure of their complexes with copper (II) ions using X-ray analyses have shown that the most plausible type of coordination is formation of the bridge 1:1 complexes of the α,α' -bipyridinyl type. Structural elucidation of the complex has shown that besides one molecule of the ligand, the acetate and hydroxide ions are involved. Thus, only one chelating ring is formed in the complex by coordinating with nitrogen atoms of pyridine and triazine rings. Contrary to expectations, the hydroxy group of phenol fragments does not participate in complexing. Based on the data obtained for model compounds one can assume that in the process of sorption the attached ligand fragments of polymer exhibit coordination properties like α,α' -bipyridinyl, while phenol hydroxy groups are not involved in the complex formation.

References:

- [1] O.N. Chupakhin, A.V. Pestov, Yu.G. Yatluk, // Russ. Chem. Bull. (2009) 256-257.
- [2] A.V. Pestov, P.A. Slepukhin, Yu.G. Yatluk, V.N. Charushin, O.N. Chupakhin // J. Appl. Polym. Sci., 2011, submitted

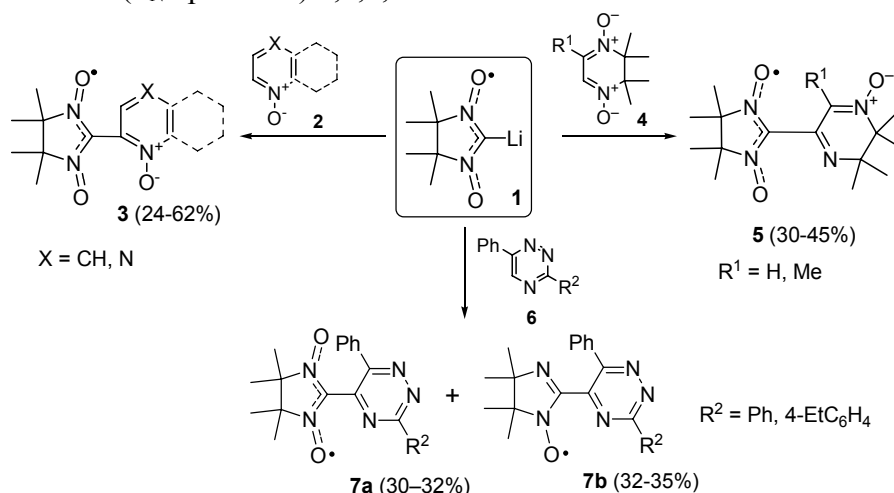
O.N. Chupakhin¹
 M.V. Varaksin¹
 I.A. Utepova¹
 E.V. Tretyakov²
 G.V. Romanenko²
 A.S. Bogomyakov²
 D.V. Stass³
 V.I. Ovcharenko²

THE METHODOLOGY OF NUCLEOPHILIC SUBSTITUTION OF HYDROGEN (S_N^H) IN THE SYNTHESIS OF NITROXIDE RADICALS

1 - Ural Federal University, Ekaterinburg, Russia
 2 - International Tomography Center, Novosibirsk, Russia
 3 - Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia
 chupakhin@ios.uran.ru

The development of new approaches for the synthesis of the previously unavailable spin-labeled compounds based on stable organic radicals is an advanced area in the chemistry of magnetically active substances.¹

For the synthesis of the heterocyclic 2-imidazoline nitroxide derivatives a convenient synthetic approach based on the interaction of nitroxide lithium derivative **1** with various nitrogen-containing heterocycles (π -deficient heteroarenes **8** and their *N*-oxides **2** as well as non-aromatic nitron **4**) has been developed. As a result, a series of polyfunctional magnetically active nitronyl and iminonitroxide radicals (S_N^H products) **3,5,7,9** has been obtained.^{2,3}



The magnetically active metal complexes differ in structure and geometry have been synthesized on the basis of heteroaromatic nitroxides obtained. In the structure of coordination heterospin compounds azinylnitroxides were found to perform a function of effective channels through which the exchange interaction between paramagnetic centers was transmitted.⁴

References:

- Miller, J. S.; Drillon, M.; Eds. *Magnetism: Molecules to Materials, I-V*; Wiley-VCH: Weinheim, Germany, 2001-2005.
- Chupakhin, O. N.; Utepova, I. A.; Varaksin, M. V.; Tretyakov, E. V.; Romanenko, G. V.; Stass, D. V.; Ovcharenko, V. I. *J. Org. Chem.* **2009**, 74(7), 2870-2872.
- Tretyakov, E. V.; Utepova, I. A.; Varaksin, M. V.; Tolstikov, S. E.; Romanenko, G. V.; Bogomyakov, A. S.; Stass, D. V.; Ovcharenko, V. I.; Chupakhin, O. N. *Arkivoc* **2011**, 8, 76-98.
- Chupakhin, O. N.; Tretyakov, E. V.; Utepova, I. A.; Varaksin, M. V.; Romanenko, G. V.; Bogomyakov, A. S.; Veber, S. L.; Ovcharenko, V. I. *Polyhedron* **2011**, 30, 647-653.

The research was financially supported by the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-65261.2010.3, Grant MK-1901.2011.3) and RFBR (10-03-00756-a) and CRDF (REC-005).

**SODIUM AZIDE IN POLYPHOSPHORIC ACID –
A NEW REAGENT FOR DIRECT ELECTROPHILIC
AMINATION OF AROMATIC COMPOUNDS AND
ANNULATION METHODS OF PYRROLE,
PYRIMIDINE AND PYRIDINE RINGS DEVELOPED
ON ITS BASIS**

A.S. Lyakhovnenko¹A.V. Aksenov¹I.V. Aksenova¹V.I. Goncharov²

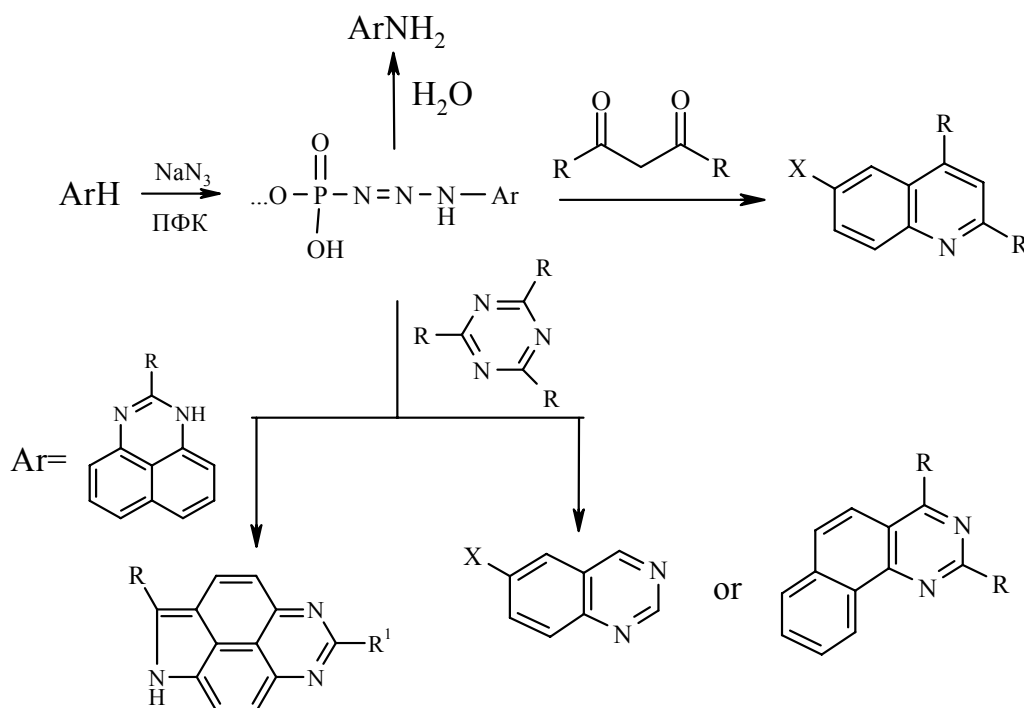
1 - Stavropol State University, Organic Chemistry, Stavropol, Russia

2 - Stavropol State Medicinal Academy, Basic and Bioorganic
Chemistry, Stavropol, Russia*k-bochem-org@stavsru.ru*

Aromatic amines are important synthetic intermediates. A standard method of their synthesis is a sequence of both nitration and reduction of the nitro-derivatives¹ forming at the first stage.

A direct one-step amination is known but it proceeds with low yields² because in many cases the initial aromatic compound is used as a solvent. The known amination agents include: hydroxylamine^{2b,c}, alkylhydroxylamines^{2d}, hydroxylamine-*O*-sulfoacid^{2e}, and hydrazoic acid^{2f} in the presence of Lewis acids. Later Olah used for such purpose hydrazoic acid^{2g} and trimethylsilylazide^{2h} in the presence of superacids. The latter is the most effective reaction system, yields counting on azide are around 90% but owing to a great excess of aromatic compound, a conversion degree does not exceed 10%.

In this message we present a new method of aromatic compounds amination based on application of a new reagent system – sodium azide/PPA³.



Using this method and a subsequent reaction of intermediates with 1,3,5-triazines a

new method for earlier unknown 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes synthesis has been developed⁴. Anisole, phenol and naphthalene under these conditions forms quinazolines^{3c,5}. A new method for quinolines synthesis was development by reaction of anisole and phenol with sodium azide in PPA and then with 1,3-dicarbonyl compounds⁶.

References:

2. Schroter, R.; Mtiller, E. *Houben-Weyl Methoden der Organischen Chemie*, Thieme Verlag: Stuttgart, **1957**; Vol. XI/I, pp 341-488.
3. (a) Kovacic, P. *Friedel-Crafts and Related Reactions*, Interscience Publishers: New York, **1964**; Vol. 111/2, p 1493; (b) Graebe, C. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 1778; (c) Kovacic, P.; Bennet, R.P.; Foote, J.L. *J. Am. Chem. Soc.* **1962**, *84*, 759; (d) Kovacic, P.; Foote, J.L. *J. Am. Chem. Soc.* **1961**, *83*, 743; (e) Kovacic, P.; Bennet, R.P. *J. Am. Chem. Soc.* **1961**, *83*, 221; (f) Kovacic, P.; Russell, R.L.; Bennett, R.B. *J. Am. Chem. Soc.* **1964**, *86*, 1588; (g) Mertens, A.; Lammertama, K.; Arvanaghi, M.; Olah, G.A. *J. Am. Chem. Soc.* **1983**, *105*, 5657; (h) Olah, G.A.; Ernst, T.D. *J. Org. Chem.* **1989**, *54*, 1203.
4. (a) Aksenov, A.V.; Lyakhovnenko, A.S.; Karaivanov, N.C. *Chem. Heterocycl. Compd.* **2009**, 871. (b) Aksenov, A.V.; Lyakhovnenko, A.S.; Karaivanov, N.C.; Levina I.I.; *Chem. Heterocycl. Compd.* **2010**, 468. (c) Aksenov, A.V.; Lyakhovnenko, A.S.; Kugutov, M.M.; *Chem. Heterocycl. Compd.* **2010**, 1262. (d) Lyakhovnenko, A.S.; Aksenov, A.V.; Kugutov, M.M.; *Chem. Heterocycl. Compd.* **2010**, 1138.
5. (a) Aksenov, A.V.; Lyakhovnenko, A.S.; Andrienko, A.V.; Levina I.I.; *Tetrahedron Lett.* **2010**, 2406. (b) Aksenov, A.V.; Lyakhovnenko, A.S.; Andrienko, A.V.; *Chem. Heterocycl. Compd.* **2010**, 1266.
6. Aksenov, A.V.; Lyakhovnenko, A.S.; Kugutov, M.M.; *Chem. Heterocycl. Compd.* **2010**, 125.
7. Ляховненко, А. С.; Кугутов, М. М.; Аксенов, А. В.; *Известия Академии наук. Серия химическая*, **2011**, 757.

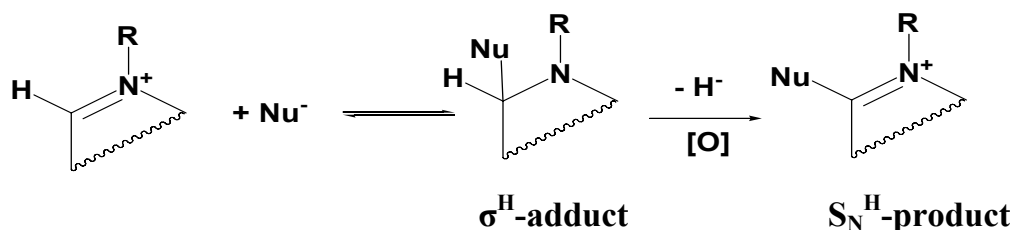
This work was supported by Russian Foundation for Basic Research (Grant No.10-03-00193a).

THE ROLE OF ELECTRON TRANSFER IN S_N^H REACTIONS IN AZINES

A.I. Matern

Urals Federal University, Analytical Chemistry Department,
Yekaterinburg, Russia
a.i.matern@ustu.ru

During the last decade the renaissance came into the azine chemistry, due to the progress in supramolecular chemistry, development of bio- and nanotechnologies and introduction of new synthetic methodologies and detection methods. Azagroups as π -acceptors provide the electron deficient character for the whole heteroaromatic system, thus making azines and especially azine cations to be susceptible towards the direct substitution of hydrogen by nucleophile residues (S_N^H reactions). The most common for those processes is the “addition-elimination” mechanism accompanied by the formation of σ^H -intermediates – dyhydroazines.



Until now the actual matter for discussions is the mechanism of the oxidative aromatization of σ^H -adducts as that mechanism originates from the nature of the biochemical action of nicotinamide conferments. There are hundreds of publications in a literature, concerning the hydride transfer events in the series of pyridines and acridines.

It worth to mention that in most cases dyhydroazines, having electron-donating groups or not having any substituent next to the sp^3 -hybrid carbon atom, were only utilized. At the same time, there is no data about the influence of electron-withdrawing groups next to the hydrogen atom on the lability of hydride ion. Those groups can dramatically affect the whole process and even alter the hydration mechanism.

This work presents some new evidences for single electron transfer in S_N^H reactions based on the comparing results of experiments to NMR, EPR, MS and electrochemical studies on the nucleophile addition step and oxidative aromatization step in reactions of azine cations with nucleophiles.

NITROALKANES IN POLYPHOSPHORIC ACID – A NEW REAGENTS FOR ACETAMIDATION AND CARBOXYAMIDATION OF AROMATIC COMPOUNDS AND SYNTHETIC METHODS DEVELOPED ON ITS BASIS

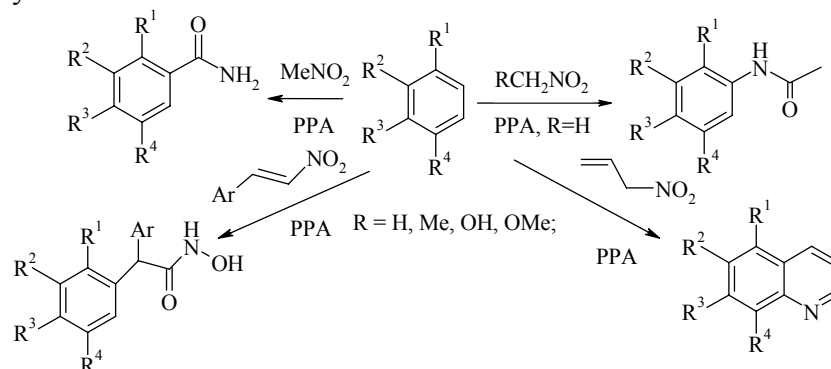
A.V. Aksenov
N.A. Aksenov
O.N. Nadein
I.V. Aksenova

Stavropol State University, Organic Chemistry, Stavropol, Russia
alexaks05@rambler.ru

Amides are compounds of current industrial interest as intermediates in the production of pharmaceuticals and dyes. For example, Lidocaine is a widely used anesthetic.¹

Amides can be prepared by several well-established procedures including acylation of amines, hydrolyses of nitriles and rearrangement reactions such as the Schmidt and Beckmann procedures². In synthetic purposes it is more efficient to start directly from arenes rather than from amines or ketones, thereby bypassing some steps. A direct arylamidation procedure has been reported, in which arenes can condense with a hydroxamic acid^{3a,b} or *N*-tosyloxypthalimide^{3c} but this reaction has a limited scope of applications.

In the current poster we propose a new method of acetamidation or carboxyamidation of aromatic compounds based on the usage of nitroethane or nitromethane in polyphosphoric acid (PPA). The reaction of arenes with nitroethane in 86% PPA at 100–110 °C leads to formation of acetanilides with yields 63–92%⁴.



The reaction of arenes with nitromethane in 86% PPA at 90–95 °C leads to formation of benzamides with yields 46–71%⁵. Arenes containing electron-giving groups such as hydroxy-, alkoxy-, alkyl- as well as benzene itself participates in this reaction.

References:

- 1) (a) Zhang, Z.; Yin, A.; Kadow, J. F.; Meanwell, N. A.; Wang, T. J. *J. Org. Chem.* **2004**, *69*, 1360; (b) Lidocaine. In *Merck Index*, 12th ed.; Budavari, S., Ed.; Merck, **1996**; Vol. 5505, p 936;
- 2) (a) Beckwith, A. L. J. *The Chemistry of Amides*; Zabicky, J., Ed.; Interscience: London, **1970**, p. 73; (b) Vogel, A. *Practical Organic Chemistry*; Langman Scientific & Technical and Wiley: New York, 1989; pp 708–710. (c) Katritzky, A. R.; He, H.-Y.; Suzuki, K. *J. Org. Chem.* **2000**, *65*, 8210. (d) Cacchi, S.; Misiti, D. *Synthesis*, **1980**, 243. (e) Cablewski, T.; Gum, P. A.; Raner, K. D.; Strauss, Ch. R. *J. Org. Chem.* **1994**, *59*, 5814.
- 3) (a) Wassmundt, F. W.; Padegimas, S. J. *J. Am. Chem. Soc.* **1967**, *89*, 7131. (b) March, J.; Engenito, J. S. *J. Org. Chem.* **1981**, *46*, 4304. (c) Cadogan, J. I. G.; Rowley, A. G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1069.
- 4) Aksenov, A. V.; Aksenov, N. A.; Nadein, O. N.; Aksenova, I. V.; *Synlett*, **2010**, 2628.
- 5) Aksenov, A. V.; Aksenov, N. A.; Nadein, O. N.; Aksenova, I. V.; *SynCom*. **2011**, (in press).

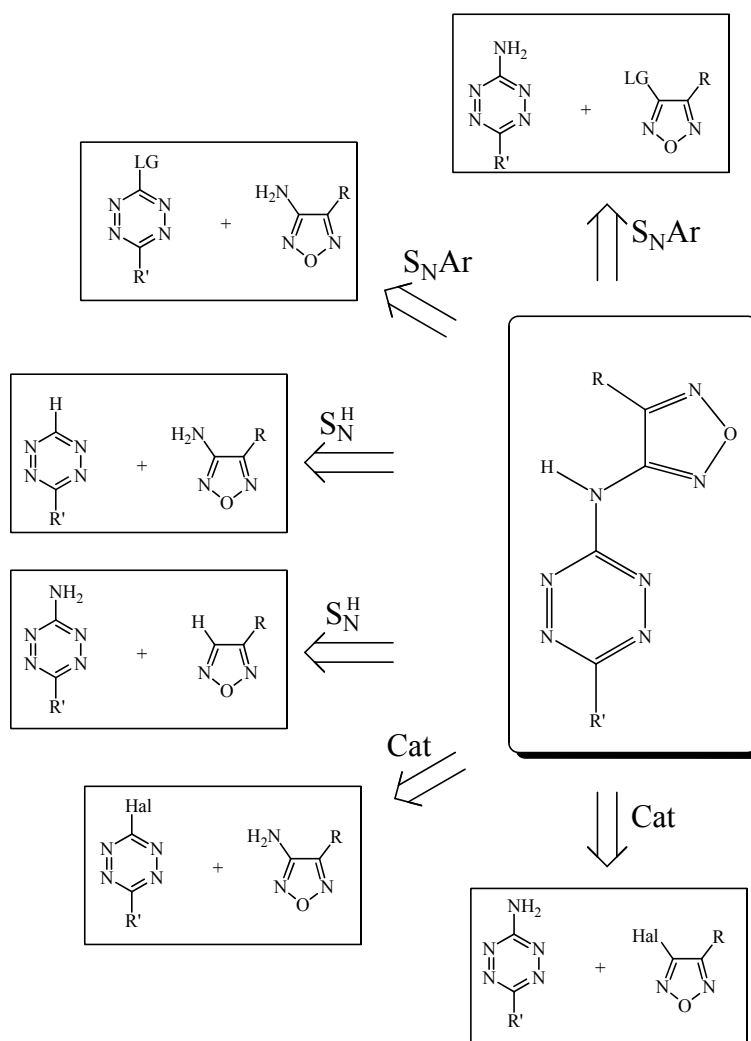
This work was supported by the Federal Program “Scientific and scientific-pedagogical personnel of innovative Russia” (Grant No. 16.740.11.0162) and Russian Foundation for Basic Research (Grant No.10-03-00193a).

DEVELOPMENT OF FLEXIBLE STRATEGIES TOWARDS DIHETARYAMINE CONSTRUCTIONS. SYNTHESIS OF COMPOUNDS WHEN FURAZAN AND S-TETRAZINE RINGS BRIDGED THROUGH THE NH-SPACER

A.B. Sheremetev
N.V. Palysaeva

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia
sab@ioc.ac.ru

Alternative approaches to construction of secondary amines incorporated furazan (1,2,5-oxadiazole) and s-tetrazine (1,2,4,5-tetrazine) bridged by NH-spacer have been investigated. Traditional nucleophilic displacement S_NAr , nucleophilic aromatic displacement of hydrogen S_N^H and metal-catalyzed cross-coupling reaction were utilized in the study.

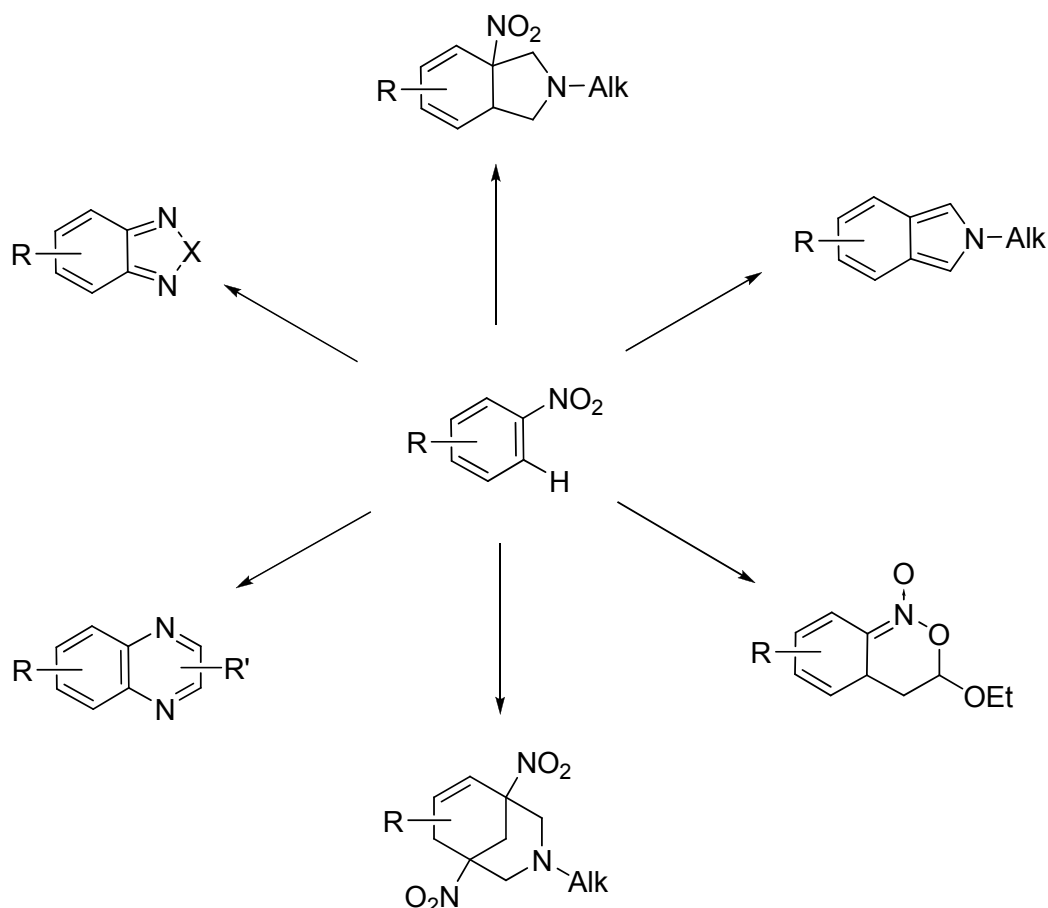


NITROARENES AS A BASIS FOR THE SYNTHESIS OF BENZO-FUSED N-HETEROCYCLES

A.M. Starosotnikov
S.A. Shevelev

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia
alexey41@list.ru

Nitrogen heterocycles play an important role in medicinal chemistry as well as in chemistry of natural compounds. Therefore the development of novel, efficient and convenient methods of their synthesis is still of interest. In this presentation, a new versatile methodology for the synthesis of benzo-fused N-heterocycles will be discussed on the basis of transformations of aromatic nitro compounds. The general pathways for the construction of N-heterocyclic nucleus will be considered: nucleophilic aromatic substitution of hydrogen (S_N^H), pericyclic [3+2]- and [4+2]-cycloaddition reactions of nitroarenes, and cyclocondensations of hydride σ^H -adducts.



This work was supported by the Russian Foundation for Basic Research (Project No. 10-03-00185a) and the President of the Russian Federation (The program of state supporting for young chemists, Project MK-220.2011.3)

A NEW METHOD FOR SIX AND SEVEN-MEMBER RING ANNULATION TO INDOLES BY THERE REACTION WITH ALIPHATIC NITROCOMPOUNDS

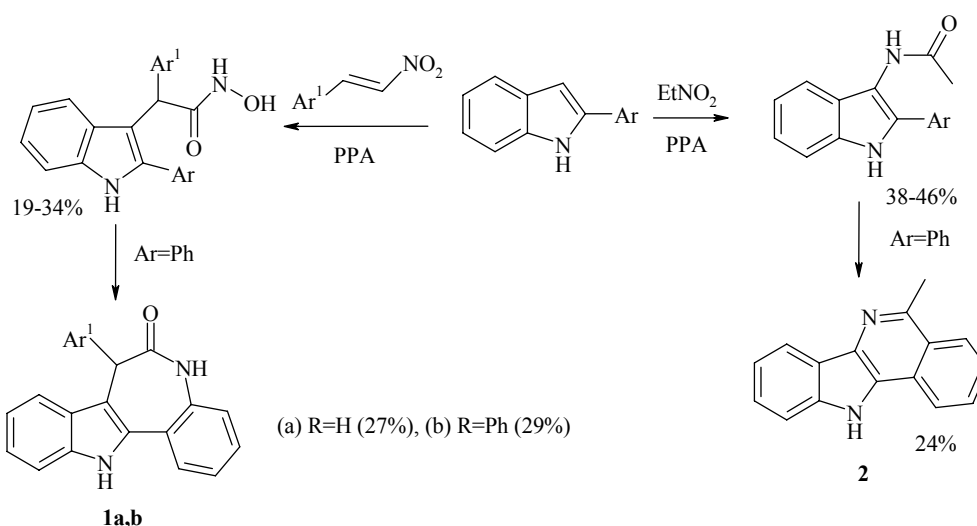
N.A. Aksenov
A.V. Aksenov
A.N. Smirnov
O.N. Nadein

Stavropol State University, Organic Chemistry, Stavropol, Russia
alexaks05@rambler.ru

It is difficult to overestimate the significance of indole derivatives amongst biologically active substances.

Yearly same methods for six- and seven-member ring annulations can be development, for example, Pictet-Spengler reaction.

In the current poster we propose a new method of acetamidation, acetocarboxylation of indoles and six- and seven-member ring annulations to indole derevatives based on the usage of nitroethane and unsaturated nitrocompounds in polyphosphoric acid (PPA).



The reaction of indoles with nitroethane in 86% PPA at 95–105 °C leads to formation of 3-acetamidoindoles with yields 38–46%¹. With nitrostyrenes correspondent hydroxamic acids can be prepared with yields 19–34%. If reaction mixture temperature is increased to 130 °C, polynuclear compounds **1a,b** or **2** are formed with yields 27-29% or 24%.

References:

- 6) Aksenov, A. V.; Aksenov, N. A.; Nadein, O. N.; Aksenova, I. V.; *Synlett*, **2010**, 2628.

This work was supported by the Federal Program "Scientific and scientific-pedagogical personnel of innovative Russia" (Grant No. 16.740.11.0162).

M.V. Berezin
E.V. Verbitskiy
Yu.A. Titova
P.A. Slepukhin
O.N. Zabelina
G.L. Rusinov
V.N. Charushin

SYNTHESIS OF NOVEL 3,3-DI(HTERO)ARYL SUBSTITUTED BINAPHTHYL DERIVATIVES AS EFFICIENT CHIRAL CATALYSTS

I.Ya. Postovsky Institute of Organic Synthesis, Ekaterinburg, Russia
berezin@ios.uran.ru

3,3'-Disubstituted 2,2'-binaphthol derivatives have attracted much attention as chiral modifiers in Lewis acid catalyzed reactions. We have recently discovered a new synthetic approach to the family of 3,3'-di(hetero)aryl substituted binaphthyl derivatives **2a-c** when exchanging $-B(OH)_2$ and halogen functionalities in the Suzuki cross-coupling reaction under of microwave irradiation. Boronic acids **1** were used for preparations of chiral (*R*)- or (*S*)-1,1'-binaphthyl-2,2'-diyl,3,3'-bis(heteroaryl) hydrogen phosphate **4** (Scheme 1). The structure of catalysts was established by X-ray crystallography for 5,5'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)dipyrimidine **2** (see Figure 1).

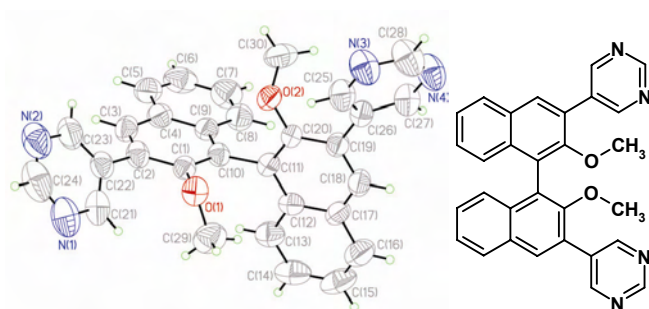
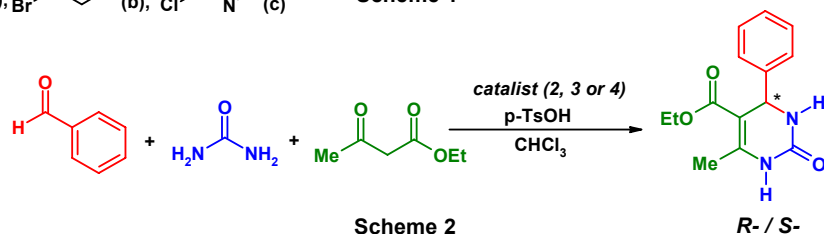
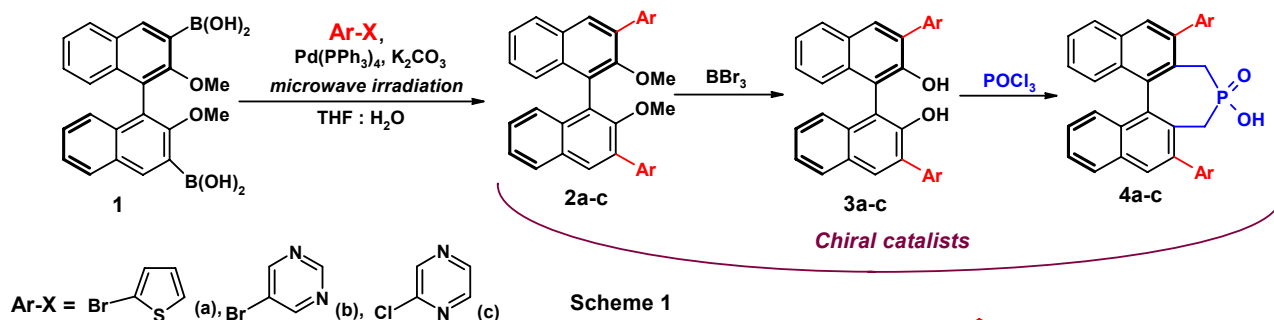


Figure 1. The X-ray structure of compound **2**

Catalytic activities of compounds **2-4** were examined on a model Biginelli reaction by using chiral HPLC analysis (Scheme 2). It has been established that compounds **2-4** are able to promote the Biginelli reaction, thus exhibiting with excellent yields and high stereoselectivities.

This work was supported by the Programs of Ural Division of RAS 09-II-3-2004, 09-II-3-1015, 09-T-3-1022, State Contract № 02.740.11.0260., the Russian Foundation for Basic Research (grant no. 10-03-96078-r_ural_a) and the State Program for Supporting Leading Scientific of the Russian Federation (grant no. NSh-65261.2010.3).

SYNTHESIS OF NOVEL ETHYL 7,8-DICYANOPYRIMIDO[2,1-b][1,3]BENZOTHAZOL-3-CARBOXYLATE

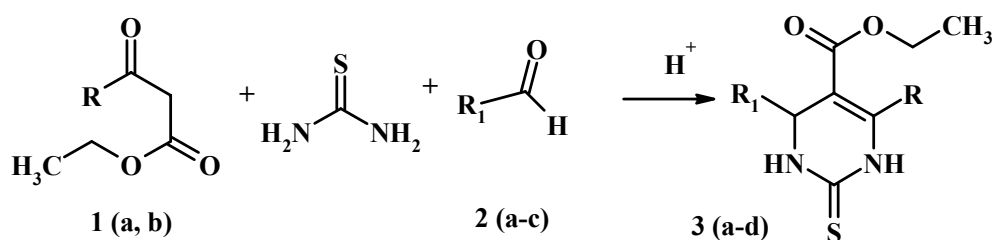
Zh.V. Chirkova
S.I. Filimonov
V.S. Sharunov
I.G. Abramov

Yaroslavl State Technical University, Department of General and Physical Chemistry, Yaroslavl, Russia
chirkovazhv@ystu.ru

Biginelli compounds are objects of intense research, due to their exhibited high biological activity. Pyrimidinethions derivatives are used in pharmacology, as antiviral, antibacterial, anticancer and anti-inflammatory drugs.

The reaction of 4-bromo-5-nitrophthalonitrile (BNFN) with esters of 2-thioxo-1,2,3,4-tetrahydropyrimidin-5-carboxylic acids is of some practical interest, leading to the formation of ethyl 7,8-dicyanopyrimido [2,1-b][1,3]benzothiazole-3-carboxylates. We have developed a two-stage method for the synthesis of novel heterocyclic pyrimido[2,1-b][1,3]benzothiazol compounds.

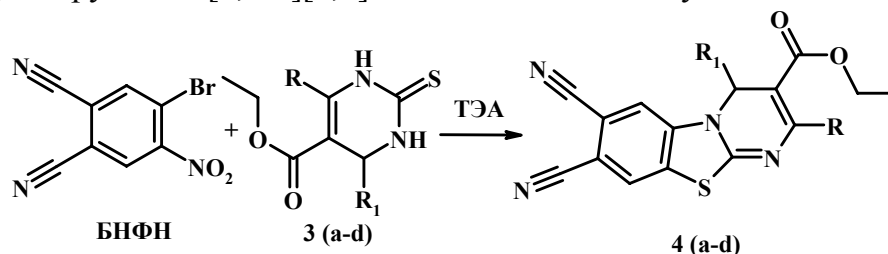
At the first stage pyrimidintions are synthesized by three-component Biginelli reaction, using 1, 3-dicarbonyl compounds, aldehydes and thiourea, with 67-75 % yield.



1 a – R=CH₃, b – R=C₆H₅. 2 a – R₁=C₆H₅; b – R₁=4-CH₃OC₆H₄; c – R₁=2-thienyl.

3 a – R=CH₃, R₁=C₆H₅; b – R=CH₃, R₁=4-CH₃OC₆H₄; c – R=CH₃, R₁=2-thienyl,
d – R=C₆H₅, R₁=4-CH₃OC₆H₄

At the second stage BNFN was interacted with synthesized substituted pyrimidinethions, using TEA as deprotonating agent, leading to the formation of substituted ethyl 7,8-dicyano-pyrimido [2,1-b][1,3]benzothiazol-3-carboxylates with 65-78 % yield.



3, 4 a – R=CH₃, R₁=C₆H₅; b – R=CH₃, R₁=4-CH₃OC₆H₄; c – R=CH₃, R₁=2-thienyl,
d – R=C₆H₅, R₁=4-CH₃OC₆H₄

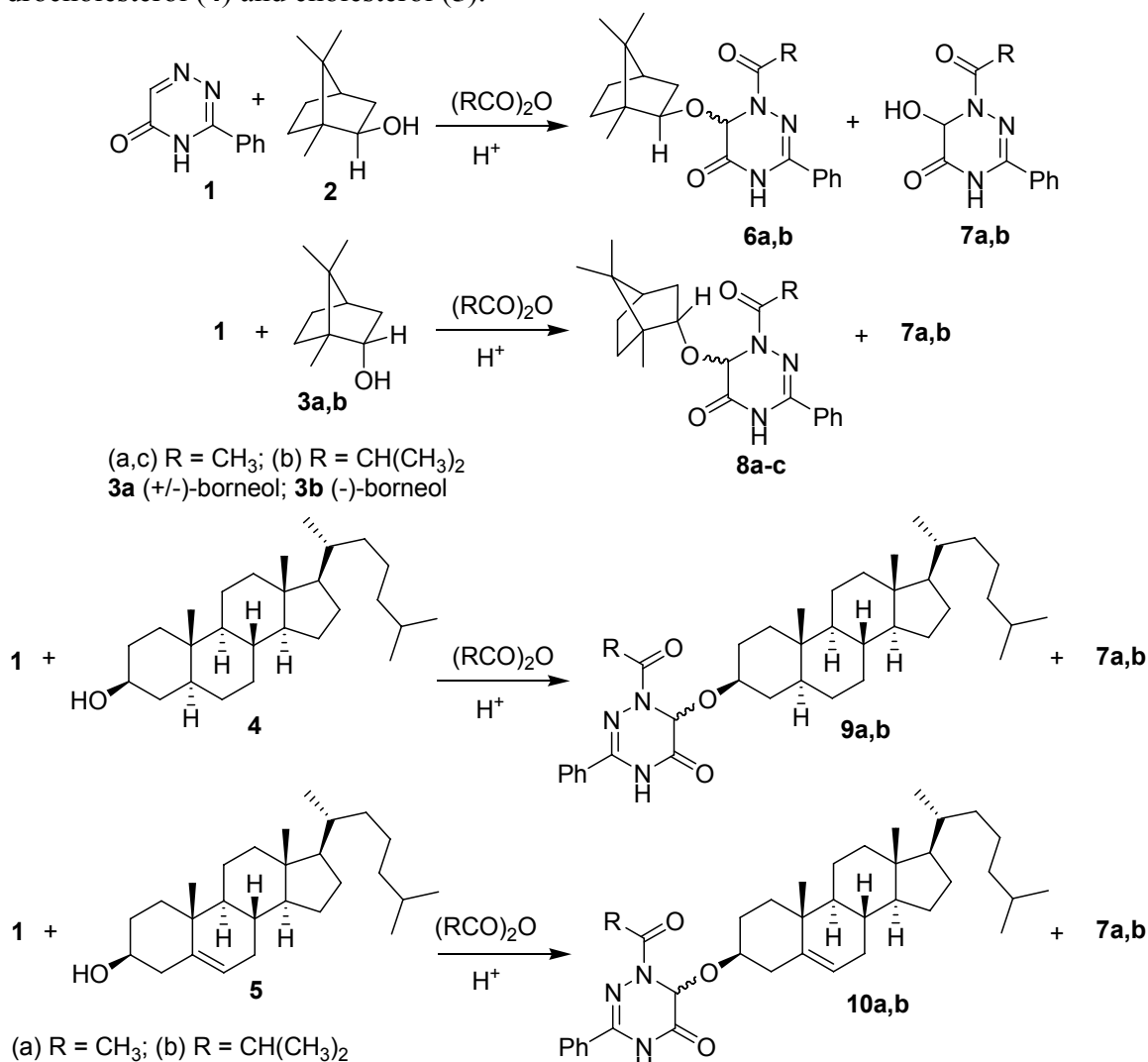
The structure of synthesized compounds is confirmed by data collection of mass spectrometry and IR, NMR spectroscopy, including two-dimensional correlation NOESY-spectroscopy.

8. S_N^H Symposium: Poster presentation P-227
INTERACTION OF 3-PHENYL-1,2,4-TRIAZIN-5(4H)-ONE WITH NATURAL CHIRAL ALCOHOLS

I.N. Egorov¹
T.A. Tseitler¹
G.V. Zyryanov²
V.L. Rusinov¹
O.N. Chupakhin²

1 - Ural Federal University, Department of Organic Chemistry, Ekaterinburg, Russia
2 - Ural Federal University, Department of Organic Chemistry, Institute of Organic Synthesis, Ural Branch of Russian Academy of Sciences, Ekaterinburg, Russia
i.n.egorov@gmail.com

Chiral derivatives of azines are of considerable interest. Many works in the synthesis of bornyl derivatives of bipyridines, terpyridines and bis-pyridilamine as catalysts for asymmetric synthesis were proceeded in the last time. Besides, it is known, that bornyl and isobornyl derivatives of azines show antiviral activity. In this work was investigated possibility of asymmetric synthesis of O-nucleophiles addition products to the C=N bond of 3-phenyl-1,2,4-triazin-5(4H)-one (**1**) with using of easily accessible natural alcohols such as isoborneol (**2**), borneol (**3**), dihydrocholesterol (**4**) and cholesterol (**5**).



It was shown that addition of the chiral alcohols **2-5** to 3-phenyl-1,2,4-triazin-5(4H)-one (**1**) in the solution of acetic or isobutyric anhydrides does not proceed diastereoselectively. The obtained compounds show weak antiviral activity on influenza A/S.Peterburg/5/09 A(H1N1v) and A/Victoria/35/72 A(H3N2).

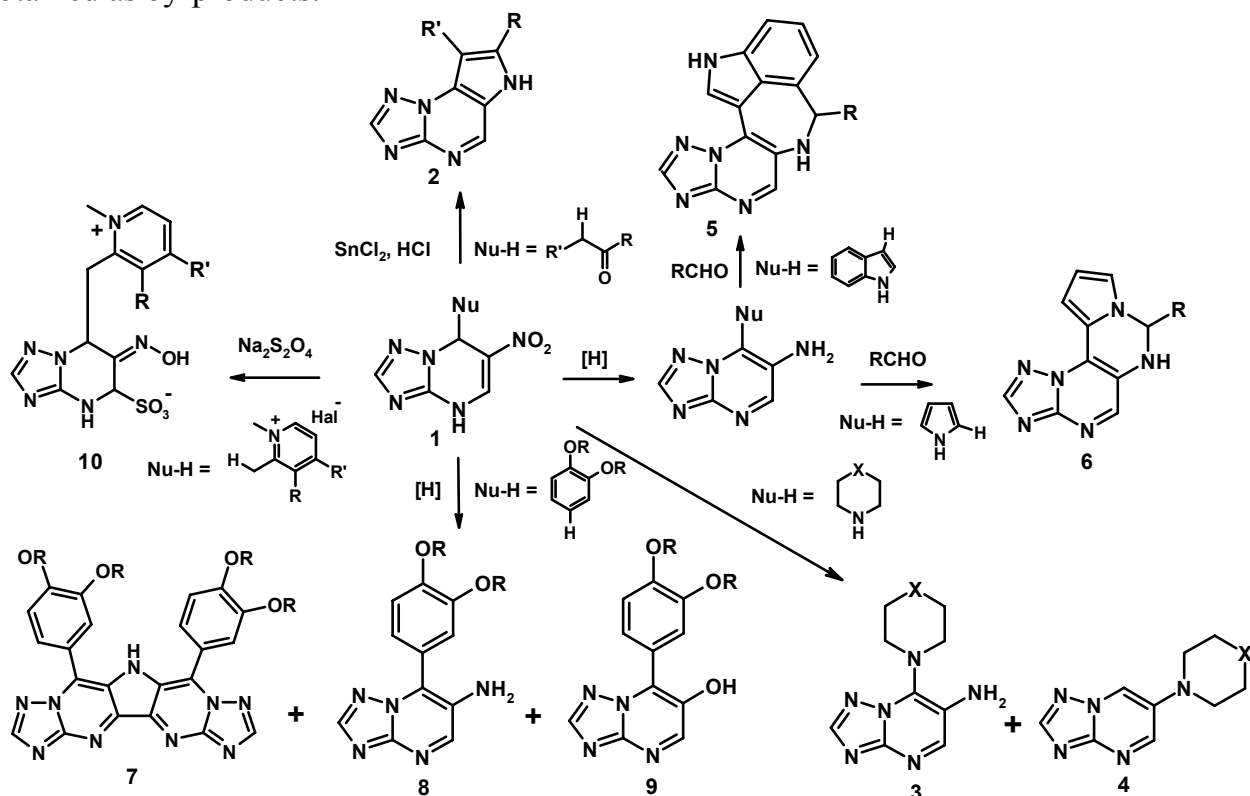
Ye.B. Gorbunov
G.L. Rusinov
O.N. Zabelina
O.N. Chupakhin
V.N. Charushin

NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN 6-NITROAZOLO[1,5-a]PYRIMIDINE ASSISTED BY REDUCTION OF THE NITRO GROUP

I.Ya. Postovsky Institute of Organic Synthesis, Ekaterinburg, Russia
nitro@ios.uran.ru

Electron-deficient 6-nitroazolo[1,5-a]pyrimidines have been shown to react with C-, S-, N-, O-, P-nucleophiles into the corresponding σ^H -adducts **1**. The presence of the nitro group appears to facilitate nucleophilic substitution of hydrogen since reduction of the nitro group in the adducts is accompanied by aromatization of the pyrimidine ring. The reaction pathways depend on the nature of nucleophiles used. In the reaction with α -carbonyl compounds the derivatives of condensed systems **2** are formed, while in the reactions with primary and secondary phosphines and mercaptans 6-amino-7-R-azolo[1,5-a]pyrimidines are formed. In case of σ^H -adducts with secondary amines 6-amino-7-R-azolo[1,5-a]pyrimidines **3** or the transamination product **4** have been obtained depending on the reaction conditions.

Hetarylamines which are derived from these reactions are prone to undergo intramolecular condensations. Also they can react with aldehydes to give heterocyclic systems **5** and **6**. Dimerization (**7**) and hydroxydesamination (**9**) compounds have also been obtained as by-products.



This work was supported by the Presidium of RAS (grants 09-P-3-1015, 09-T-3-1022, the State Program for Supporting Leading Scientific Schools of the Russian Federation (grant no. NSh-65261.2010.3) and the State Contract № 02.740.11.0260.

NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN NITROARENES AS A NEW APPROACH TO THE SYNTHESIS OF FLUORINATED BENZAZINES AND BENZAZOLES

V.N. Charushin¹
O.N. Chupakhin¹
S.K. Kotovskaya²
G.A. Zhumabaeva²

1 - Institute of Organic Synthesis, Ekaterinburg, Russia

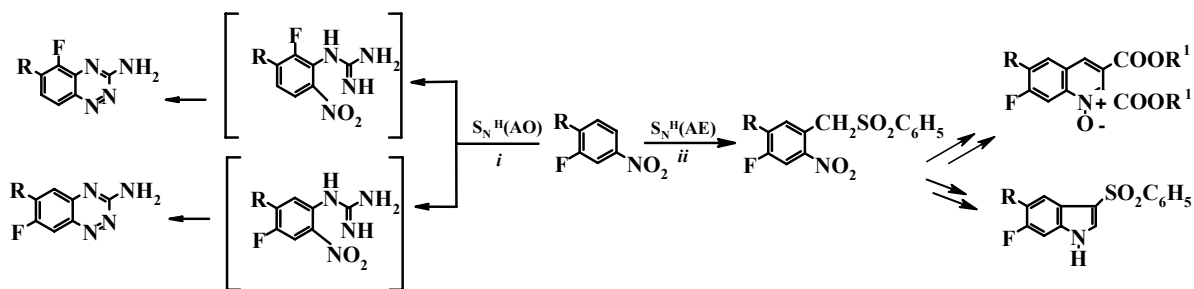
2 - Ural Federal University, Ekaterinburg, Russia

kotovskaya@mail.ustu.ru

New methods of the construction fluorinated azaheterocycles with especial physical, chemical properties and biological activities have always attracted attention of heterocyclic and medicinal chemistry [1].

Nucleophilic substitution of hydrogen (S_N^H) represents the effective method of functionalization of electrondeficient nitroarenes, S_N^H -process is the key stage of synthesis for construction of condensed compounds based on nitroarenes. On the one hand, the nitrogroup activates the aromatic substrate to nucleophilic attack, on the other hand, itself can participate in formation of heterocycle. This circumstance allows to use nitroarenes for synthesis of benzoannelated azoles or azines by nucleophilic substitution of hydrogen (S_N^H) in eliminative (vicarious) or oxidative variants.

In continuation of our research studies [2] a new approaches to the synthesis of inaccessible earlier fluorinated derivatives of 1,2,4-benzotriazines, quinolines and indoles by substitution reactions of electrondeficient nitroarenes will be discussed in these work.



i: $H_2NC(=NH)NH_2$, HCl, Bu^tOK , THF; ii: $ClCH_2SO_2C_6H_5$, KOH, DMSO

A new synthesis of 5- and 7-fluorinated derivatives of 1,2,4-benzotriazines is based on the tandem reactions of the corresponding nitroarenes with guanidine followed by cyclocondensation with participation of nitro group. For the first time vicarious nucleophilic substitution of hydrogen in fluorinated derivatives of nitroarenes with chloromethyl phenyl sulfone have been realized. As result, have been seen effective methods of the construction fluorinated derivatives quinolines N-oxides and 3-sulfonylindoles.

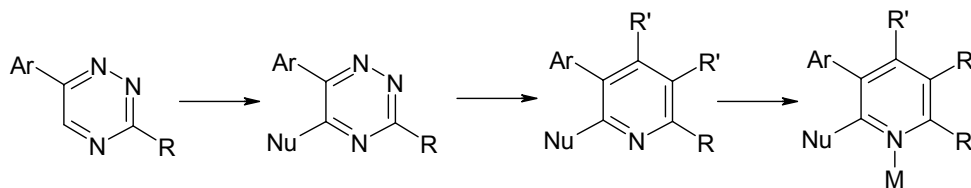
Advantage of S_N^H -methodology is that in a case of nitroarenes both versions of S_N^H -reactions allow to keep fluorine atoms that opens wide opportunities for the further transformations.

References:

1. V.T. Welch, S. Eswarakrishnan, Fluorine in Bioorganic Chemistry. Wiley -Interscience. New-York. 1991.
2. E.V. Nosova, N.N. Mochul'skaya, S.K. Kotovskaya, G.N. Lipunova, V.N. Charushin, Heteroatom Chemistry, 2006, 17, 6, 579.

S_N^H REACTIONS OF 1,2,4-TRIAZINES IN DESIGN OF NEW LIGANDS FOR TRANSITION METAL COMPLEXES**D.N. Kozhevnikov**I. Postovsky Institute of Organic Synthesis, Ural Federal University,
Ekaterinburg, Russia
dnk@ios.uran.ru

Design of organic ligands is the most powerful tools for tuning properties of transition metal complexes: from luminescence and catalysis to liquid crystallinity and solubility. High reactivity of 1,2,4-triazines in S_N^H reactions and the Diels-Alder reactions can be successfully used for the synthesis of functionalized bi- and terpyridines and their azaanalogs. The synthetic strategy includes 3 general steps: 1) synthesis of 3-pyridyl-1,2,4-triazines and their 4-oxides; 2) introduction of residues of various nucleophiles (thiophenes, indoles, carboranes, phenols, cyanide, acetylenes) into the triazine ring through C,C-bond formation; 3) transformation of new 1,2,4-triazines to target substituted bipyridines *via* cycloaddition reactions.



M = Zn(II), Ru(II), Pt(II), Eu(III), Tb(II)

Residues of the nucleophiles or products of their chemical transformations can be further involved in a metal co-ordination, *e.g.* thienylpyridines form cyclometallated Pt(II) complexes; transformations of the cyano group give new ligands for luminescent Eu(III) complexes, including neutral complexes soluble in organic solvents *etc.* Introduced electron donating (hetero)aromatic substituents determine intermolecular interactions of complexes of substituted triazines and pyridines due to π,π -interactions. Influence of the resulting structures of new ligands on properties of their metal complexes will be discussed.

UNEXPECTED SYNTHESIS OF PYRAZINO[2,3-*b*]PYRAZINES FROM FURAZANOPYRAZINES BY COMBINATION OF S_N^H METHODOLOGY AND CROSS-COUPLING REACTIONS

Yu.A. Kvashnin
E.V. Verbitskiy
P.A. Slepukhin
G.L. Rusinov
V.N. Charushin

I.Ya. Postovsky Institute of Organic Synthesis, Ekaterinburg, Russia
Kvashnin@ios.uran.ru

A new method for the synthesis of symmetric tetra-substituted pyrazine[2,3-*b*]pyrazines has been discovered. These heterocyclic derivatives proved to exhibit a strong orange luminescence and are of interest as ligands for organometal complexes.

Compounds **1** were found to react with 2,5-dibromothiophene into unexpected 5-(5-bromothiophen-2-yl)-6-(hetero)aryl-1,2,5-oxadiazolo[3,4-*b*]pyrazines **2**, which can be regarded as products of *ipso*-substitution of bromo in 2,5-dibromothiophene by action of the NH- pyrazinium cation generated from **1** in acetic acid.

Furazanopyrazines **2** are further involved into the Suzuki cross-coupling reaction by action of arylboronic acids under microwave conditions. The intermediate **3** is supposed to be transformed into pyrazine[2,3-*b*]pyrazines **4**. The structure of substances **4** was established by X-ray crystallography for 2,7-bis-(3-nitrophenyl)-3,6-bis(phenyl-thiophen-2-yl)-pyrazino[2,3-*b*]pyrazine **4ab'** (Figure 1) obtained in 24% yield.

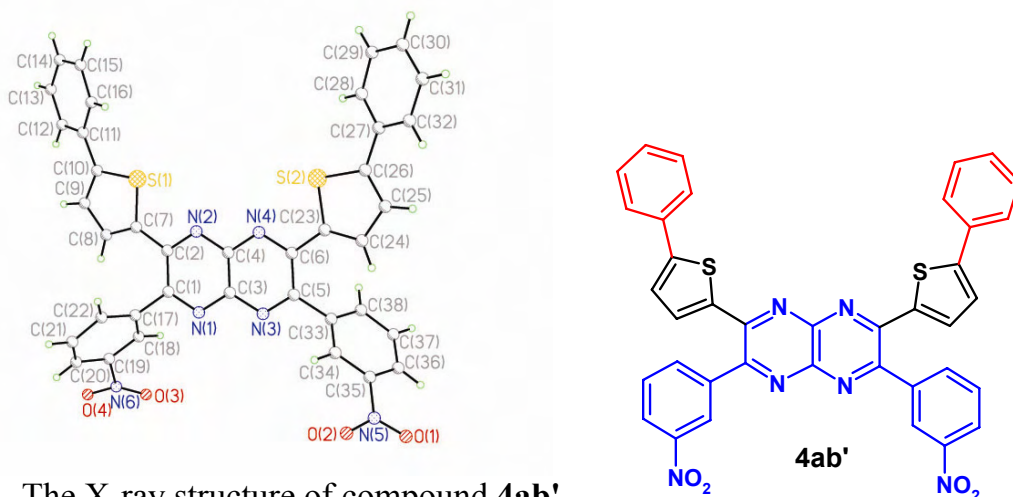
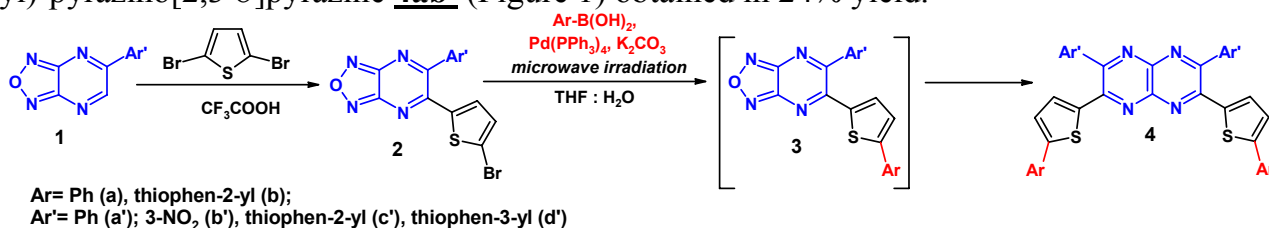


Figure 1. The X-ray structure of compound **4ab'**

This work was supported by the Programs of Ural Division of RAS 09-II-3-2004, 09-II-3-1015, 09-T-3-1022, State Contract № 02.740.11.0260., the Russian Foundation for Basic Research (grant no. 10-03-96078-r_ural_a) and the State Program for Supporting Leading Scientific of the Russian Federation (grant no. NSh-65261.2010.3).

MODIFICATIONS OF 6-(HET)ARYLFURAZANO[3,4-*b*]PYRAZINES BY USING THE METHODOLOGY OF NUCLEOPHILIC DISPLACEMENT OF HYDROGEN

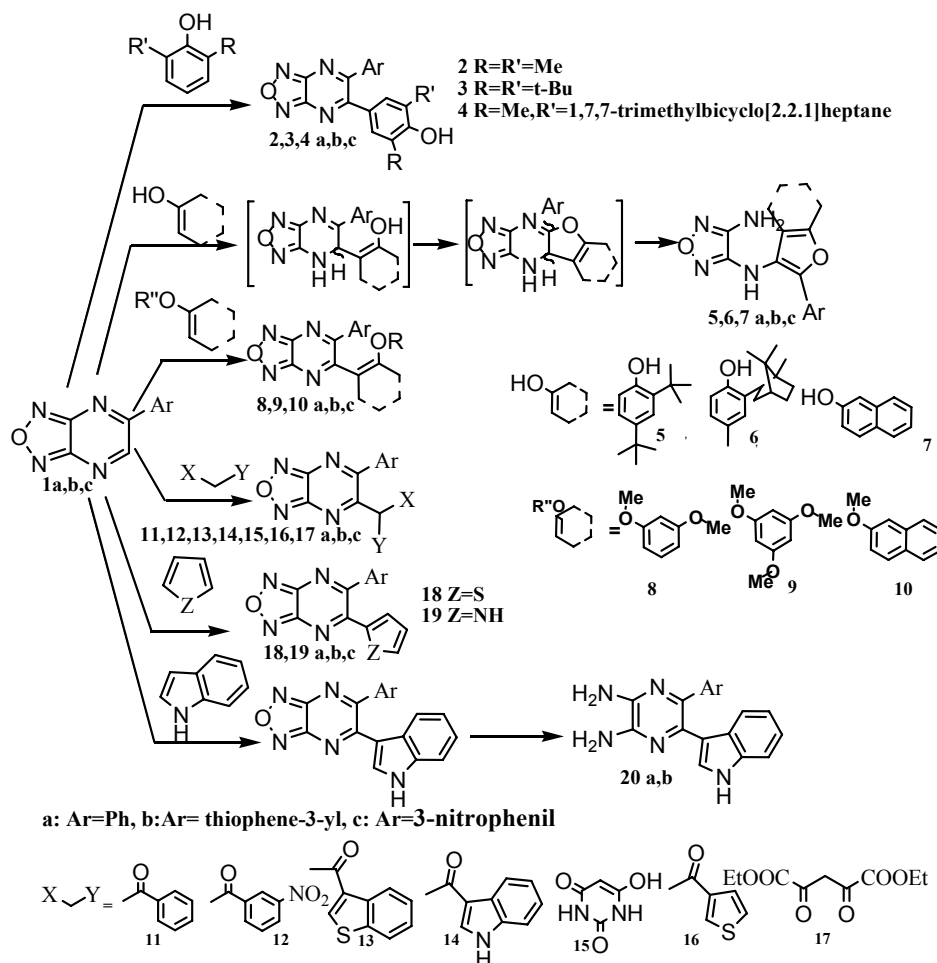
Y.A. Kvashnin
G.L. Rusinov¹
A.V. Kuchin²
O.N. Chupakhin¹
V.N. Charushin¹

1 - I.Ya. Postovsky Institute of Organic Synthesis, Ekaterinburg,
Russia

2 - Institute of Chemistry of Komi Branch of RAS, Russia
kvashnin@ios.uran.ru

The reactions of 6-(het)arylfurazano[3,4-*b*]pyrazines with a series of 2,6-disubstituted phenols and their O-alkyl ethers have been shown to afford the products of nucleophilic aromatic substitution of hydrogen in the pyrazine ring **2-4** and **8-10**, while in case of 2-*ortho* unsubstituted phenols the unexpected tandem reaction takes place leading to the ring trans-formation compounds **5a,b,c**, **6a,b,c** and **7a,b,c**.

Also CH-active acetophenones and other acetyl aromatics, as well as pyrroles, indoles and thiophenes appear to be appropriate C-nucleophiles to modify 6-(het)arylfurazano[3,4-*b*]pyrazines into the corresponding S_N^H products **11-20**. Reduction of **20a,b** with hydrogen on a palladium catalyst provided 2,3-diamino-5,6-disubstituted pyrazines **21a,b** in good yields.



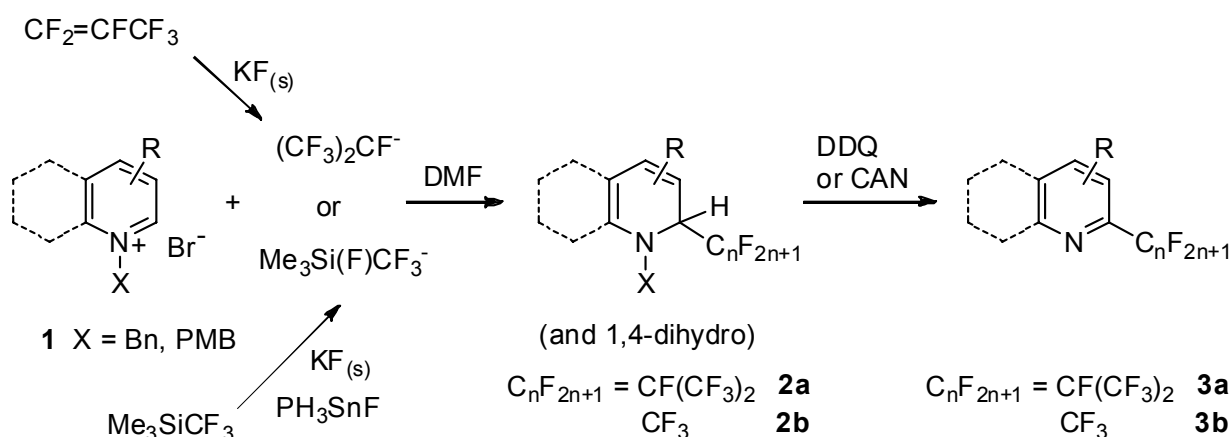
This work was supported by the Programs of Ural Division of RAS 09-II-3-1015, 09-T-3-1016, 09-T-3-1022, State Contract № 02.740.11.0260.

SYNTHESIS OF PERFLUOROALKYL-SUBSTITUTED HETEROCYCLES VIA NUCLEOPHILIC SUBSTITUTION OF HYDROGEN

R.A. Loska
M. Makosza

Institute of Organic Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01-224, Warsaw, Poland
rloska@gazeta.pl

Perfluoroalkyl-substituted heterocyclic compounds are of significant importance being widely applied as agrochemicals and pharmaceuticals.¹ We report an efficient two-step procedure for synthesis of perfluoroalkyl-substituted pyridines, quinolines and other azines starting from the corresponding azinium salts **1**. Reaction of *N*-benzyl- or *N*-p-methoxybenzylazinium salts with perfluoroisopropyl carboanions, generated from HFP and solid potassium fluoride, gives isolable and reasonably stable 1,2-dihydro-2-perfluoroisopropyl azines **2a**. Similarly, reaction with Ruppert reagent, Me_3SiCF_3 gives trifluoromethyl analogues **2b**. These compounds undergo deprotection-rearomatisation when oxidized with DDQ or CAN to provide the final azines containing $(\text{CF}_3)_2\text{CF}$ or CF_3 groups (**3**) in the ring positions originally occupied by hydrogen.



The process is of general character with respect to substituents R. This reaction can be considered as an example of oxidative nucleophilic substitution of hydrogen.²

References:

1. (a) Chambers, R. D. *Fluorine in Organic Chemistry*, Blackwell Publishing, Oxford, 2004. (b) Kirsch, P. *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, 2004.
2. Makosza, M.; Wojciechowski, K. *Chem. Rev.* **2004**, *104*, 2631.

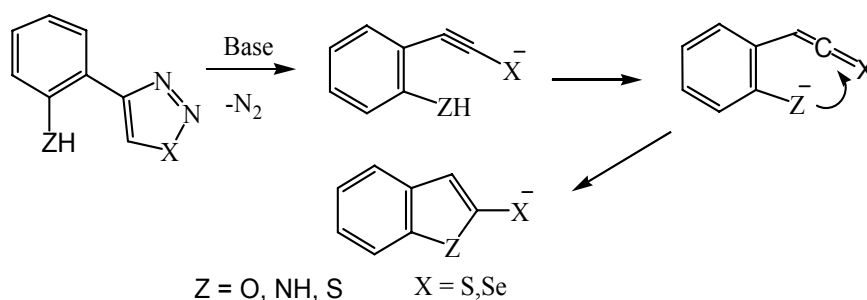
4-ARYL-1,2,3-THIA- AND –SELENADIAZOLES: SYNTHESIS, REACTIVITY AND APPLICATIONS IN HETEROCYCLIC CHEMISTRY

M.L. Petrov
A.G. Lyapunova
F.S. Teplyakov
D.A. Androssov

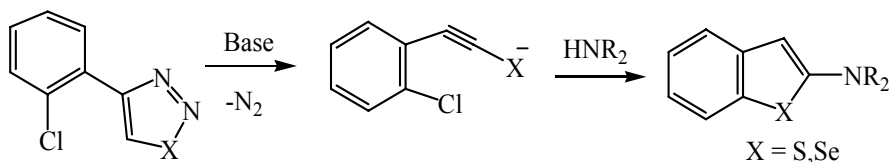
Saint-Petersburg State Institute of Technology, Department of Organic Chemistry, Saint-Petersburg, Russia
mlpetrov@lti-gti.ru

We offer new methods of synthesis benzofuranes, indoles, benzothio- and selenophenes on the basis of transformations of easily accessible 4-aryl-1,2,3-thia- and selenadiazoles.

This approach is based on the transformation of 4-aryl-1,2,3-thia- and selenadiazole having hydroxy or amino substituent in *ortho* position to the heterocyclic ring. Base-induced opening of heterocyclic ring resulted in formation of active thioketene or selenoketene intermediate which reacted with *ortho*-hydroxy or –amino group in an intramolecular manner. 4-(2-Arylthiol)-1,2,3-thiadiazoles decompose under the action of bases and the subsequent alkylation of intermediates converts them into 2-alkylsulfanylbenzothiophenes.



4-(2-Chloroaryl)-1,2,3-thia- and selenadiazoles decompose under the action of bases and the subsequent nucleophilic ipso-cyclization of intermediates in excess of amine converts them into 2-dialkylaminobenzothio- and selenophenes.

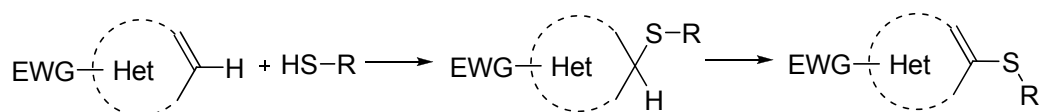


N.A. Rasputin
Y.A. Kvashnin
G.L. Rusinov
O.N. Chupakhin
V.N. Charushin

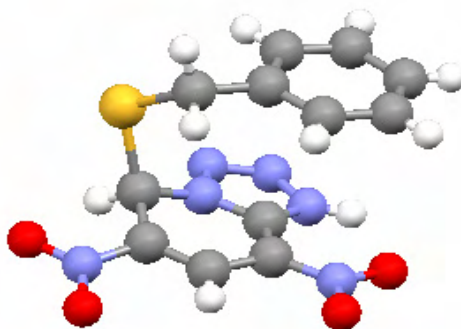
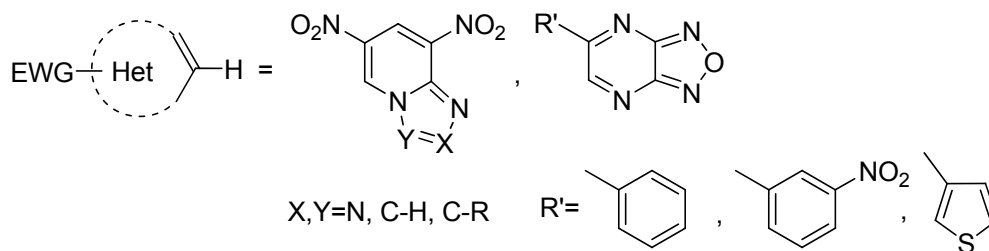
DIRECT MODIFICATION OF PYRIDINES AND PYRAZINES WITH S-NUCLEOPHILES

I.Ya. Postovsky Institute of Organic Synthesis of RAS, Ekaterinburg, Russia
nar@ios.uran.ru

The reactions of 6-(het)aryl[1,2,5]oxadiazolo[3,4-*b*]pyrazines and 6,8-dinitrotetrazolo[1,5-*a*]-pyridine with a number of S-nucleophiles have been studied. The methodology of nucleophilic aromatic substitution of hydrogen S_N^H has been successfully exploited to obtain a series of heterocyclic thia derivatives.



R = *i*-Pr-, Bz-, Ph-, Bu-, Allyl-.



Oxadiazolopyrazines have been established to react with S-nucleophiles into the S_N^H products, while dinitrotetrazolopyridine proved to give rather stable σ^H -adducts due to addition of thiols at the carbon atom adjacent to the tetrazole ring, as indicated by x-ray studies.

This work was supported by the Programs of Ural Division of RAS 09-II-3-1015, 09-T-3-1016, 09-T-3-1022, State Contract № 02.740.11.0260.

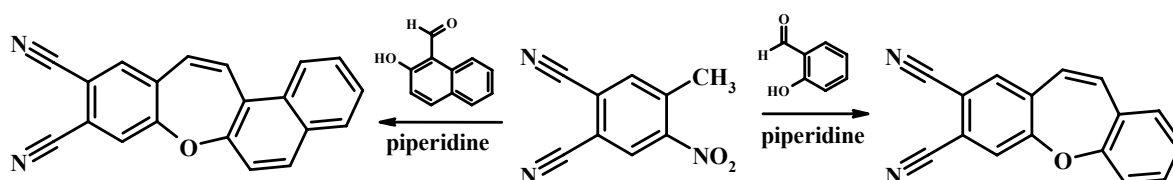
SYNTHESIS OF SEVEN-MEMBERED BENZOANNULATED HETEROCYCLES ON BASIS OF 4-METHYL-5-NITROPTALONITRILE

V.S. Sharunov
Zh.V. Chirkova
S.I. Filimonov
I.G. Abramov

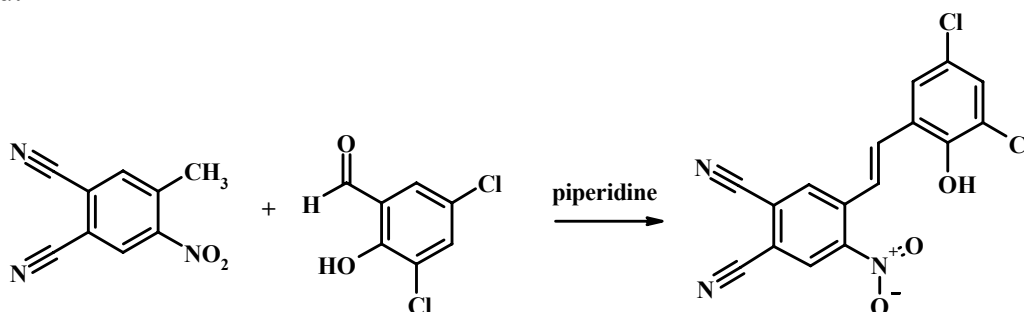
Yaroslavl State Technical University, General and Physical Chemistry,
Yaroslavl, Russia
sharunovvs@ystu.ru

Synthesis of seven-membered benzoannulated heterocyclic systems, containing oxygen, is of special interest, because synthetic dibenzo[b,f]oxepine derivatives display different biological activity – anti-inflammatory, neuroleptic, etc. We develop synthesis methods of new ptalonitriles, condensed with oxepine and oxazepine fragments, with the use of 4-methyl-5-nitroptalonitrile as substrate.

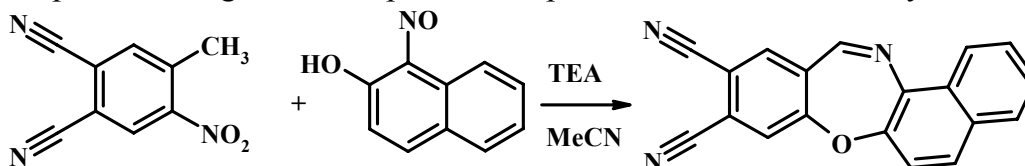
Condensation reaction of 4-methyl-5-nitroptalonitrile with salicylic aldehydes proceeds in isopropylalcohol by base catalysis, as a result of which target dibenzo[b,f]oxepine-2,3-dicarbonitriles are formed with 47-55 % yield.



If using aldehyde with electron-withdrawing substituents (for example, 3,5-dichlorosalicylic aldehyde), instead of expected cyclic product the acyclic structure is generated.



When coupling 4-methyl-5-nitroptalonitrile with α -nitroso- β -naphthol in acetonitrile at room temperature, target benzonaphthooxazepine is formed with 19 % yield.

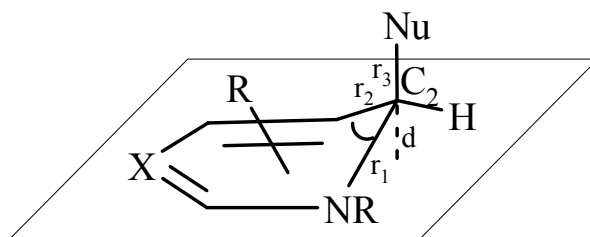


Structure of synthesizing compounds is confirmed by data collection of IR, NMR spectroscopy and mass spectrometry.

X-RAY STUDIES ON THE STRUCTURE OF σ^H -ADDUCTS DERIVED FROM THE NUCLEOPHILIC ADDITION REACTIONS IN THE SERIES OF AZINES

P.A. Slepukhin
G.L. Rusinov
V.N. Charushin
O.N. Chupakhin

I. Postovsky Institute of Organic Synthesis (Ural Division of the Russian Academy of Sciences), Russia
slepukhin@ios.uran.ru



X-Ray elucidation into the structure of σ^H -adducts derived from the reactions of azines (1,3- and 1,4-diazines, 1,2,4-triazines and the corresponding azinium salts) with C-, O-, N- and P-nucleophiles has been performed. It has been shown that these adducts proved to be in two conformations: in the cover-like one or in the conformation of a sheet bent across the axis $C_2 \dots X$. In all dihydroazine systems studied a nucleophilic fragment proved to be in the *pseudo*-axial position. Bond lengths r_1 , r_2 and r_3 have been shown to be in a good agreement with the standard values for single bonds; they do not exhibit any serious distortions, apparently due to the influence of the conjugated heterodiene system. At the same time, the distance between the sp^3 -atom C_2 and the least-squares azine plane d , and also values for the angle $r_1 C_2 r_2$ are varied significantly, thus depending on an azine structure.

Molecular packages for the crystals the σ^H -adducts, usually presented in a racemic form, belong to one of symmetric space groups. However, in a number of cases the crystals exhibit chirality due to the presence of the asymmetric C_2 atom, thus forming an appropriate group of the symmetry.

This work was supported by the Programs of Ural Division of RAS 09-II-3-2004, 09-II-3-1015, 09-T-3-1022, State Contract № 02.740.11.0260., the Russian Foundation for Basic Research (grant no. 09-03-12242-ofi_m) and the State Program for Supporting Leading Scientific Schools of the Russian Federation (grant no. NSh-65261.2010.3)

S.G. Tolshchina
I.N. Ganebnykh
A.V. Korotina
R.I. Ishmetova
N.K. Ignatenko
G.L. Rusinov
O.N. Chupakhin
V.N. Charushin

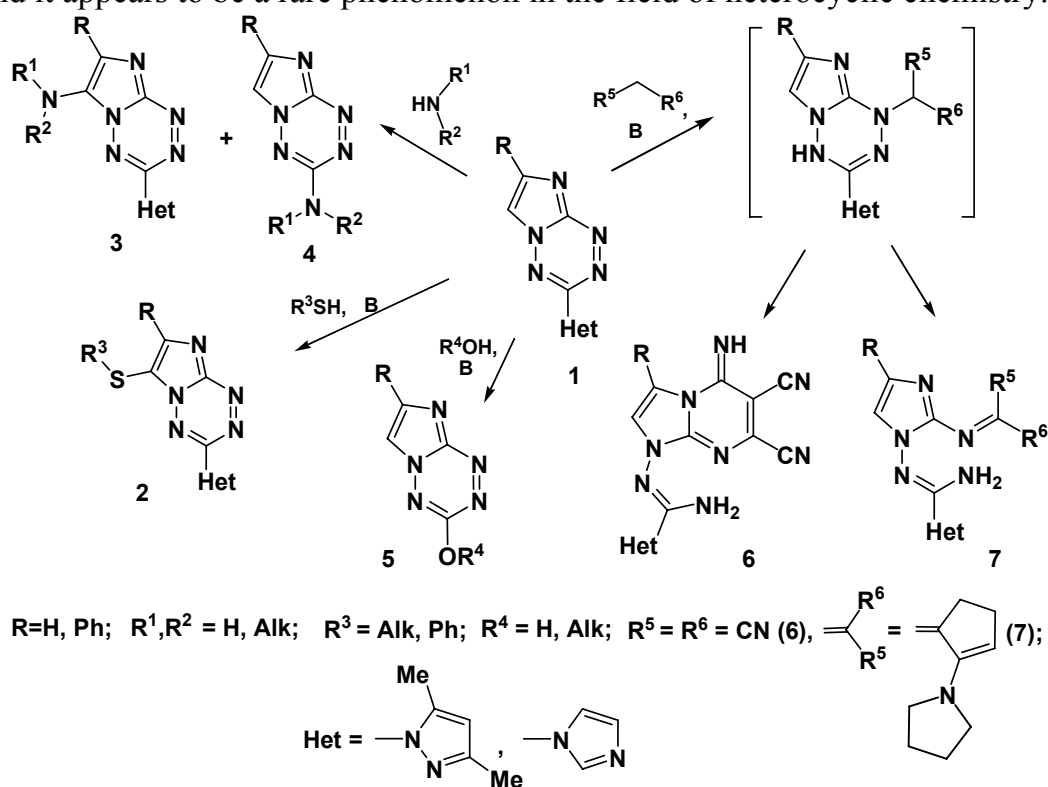
NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN IMIDAZO[1,2-*b*][1,2,4,5]TETRAZINES

I.Ya. Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences, Ekaterinburg, Russia
tolshchina@ios.uran.ru

An opportunity for nucleophilic substitution of hydrogen in imidazo[1,2-*b*][1,2,4,5]tetrazines (**1**) by S, N, O and C nucleophiles has been elucidated. It has been found that the reactions of **1** with thiols proceed regioselectively to give the products of nucleophilic substitution of hydrogen in the azole moiety, namely 6-substituted imidazo[1,2-*b*][1,2,4,5]tetrazines **2**. The reactions of **1** with N nucleophiles resulted in the formation of S_N^H -products **3** concurrently to ipso-substitution compounds **4**.

In the reaction of imidazotetrazines **1** with O nucleophiles (aliphatic alcohols and water) only ipso-substitution of the heterocyclic fragment in the tetrazine ring has been observed.

Malononitrile and 1-pyrrolidinocyclopentene proved to react with imidazo[1,2-*b*][1,2,4,5]tetrazines into imidazo[1,2-*a*]pyrimidine and imidazole derivatives (**6** and **7**). The formation of these products can be explained by attack of C nucleophile at the nitrogen atom, and it appears to be a rare phenomenon in the field of heterocyclic chemistry.



The work was financially supported by the Russian Academy of Sciences (grants 09-I-3-2004, 09-P-3-2001), the Russian Foundation for Basic Research (grant 11-03-00545-a), the State Contract (02.740.11.0260), and the State Program for Supporting of Leading Scientific Schools of Russian Federation (grant NSh-65261.2010.3).

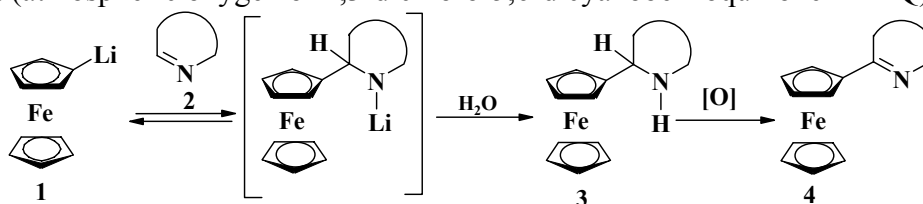
THE METHODOLOGY OF NUCLEOPHILIC SUBSTITUTION OF HYDROGEN (S_N^H) AS A TOOL FOR INTRODUCTION OF THE TRANSITION METAL CYCLOPENTADIENYL COMPLEXES INTO HETEROCYCLES

I.A. Utepova
A.A. Musikhina
M.A. Shcherbakova
O.N. Chupakhin

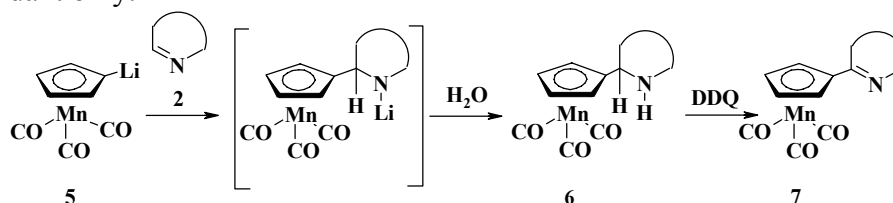
Ural Federal University, Ekaterinburg, Russia
utepova@mail.ustu.ru

At the present time C-C couplings which require neither metal catalysis nor any additional azine activation are used for modification *N*-containing heterocycles. These reactions are based on the methodology of nucleophilic aromatic substitution of hydrogen (S_N^H). This versatile approach can be applied to various azines, such as mono-, di- and triazines bearing heteroatoms in different positions in the ring, to substituted and unsubstituted azines and to benzannelated systems.

It has been shown that lithioferrocene **1** reacts with azines **2** to form ferrocenylazines according to the nucleophilic substitution of hydrogen mechanism.^{1,2} This transformation realizes in two steps. The first step is known to be the addition of lithioferrocene **1** to azine **2** to form σ^H -adducts **3**. Lithium derivatives are supposed to undergo the hydrolysis in the presence of water to dihydroazines **3**. The second step is the aromatization of dihydroazines **3** to derivatives **4** under oxidant (atmospheric oxygen or 2,3-dichloro-5,6-dicyanobenzoquinone - DDQ).



This approach could be applied for the synthesis of cymantrenylazines **7**. It should be noted that as opposed to ferrocene in the case of cymantrene the reactions proceed in the presence of DDQ as an oxidant only.³



The structures of the metallocenylazines were confirmed by NMR and IR spectroscopy, mass spectrometry, and X-ray.

References:

- ¹ Chupakhin, O. N.; Utepova, I. A.; Kovalev, I. S.; Rusinov, V. L.; Starikova, Z. A. *Eur. J. Org. Chem.* **2007**, 5, 857-862.
- ² Goldberg, A.; Kiskin, M.; Grinberg, V.; Kozyukhin, S.; Bogomyakov, A.; Utepova, I.; Sidorov, A.; Chupakhin, O.; Eremenko, I. *J. Organomet. Chem.* **2011**, 696, 2607-2610.
- ³ Utepova, I. A.; Musikhina, A. A.; Chupakhin, O. N.; Slepukhin, P. A. *Organometallics* **2011**, 30 (in press).

This study was financially supported by the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-65261.2010.3, Grant MK-1901.2011.3) and the Russian Foundation for Basic Research (Project No. 10-03-00756-a).

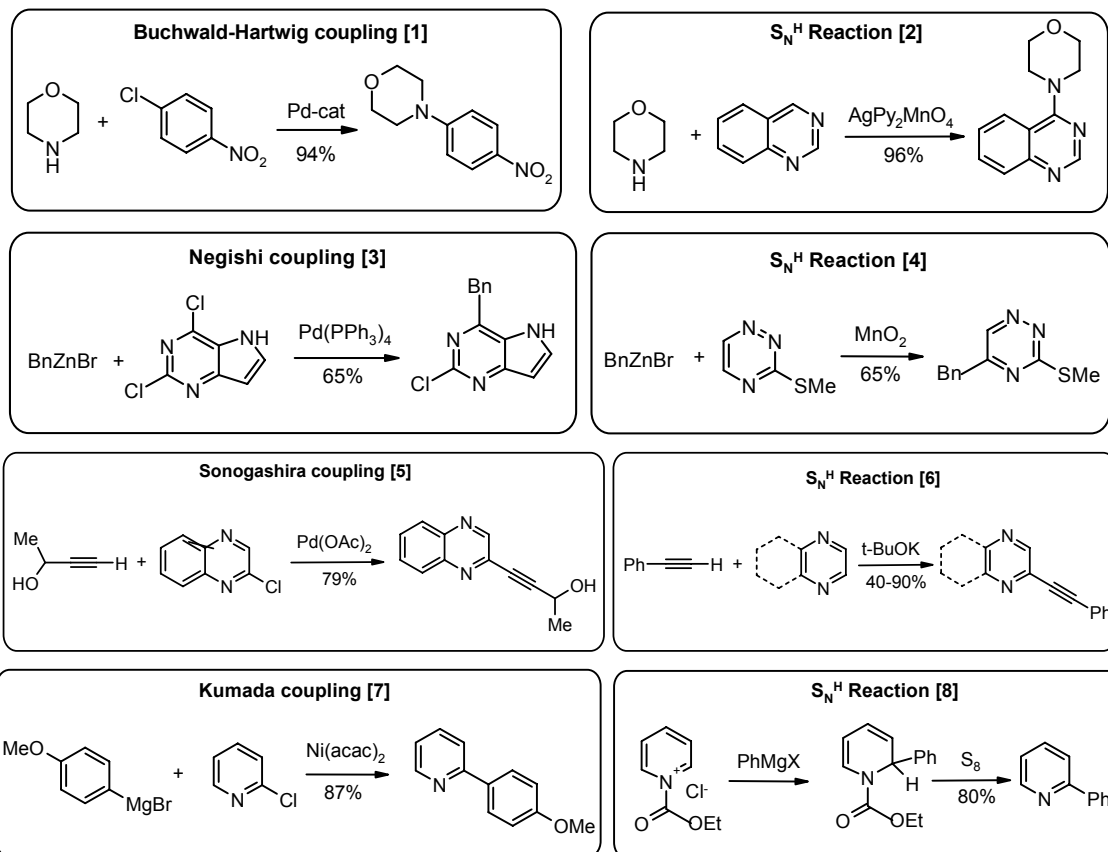
**THE METHODOLOGY OF C-C BOND FORMATION
BY NUCLEOPHILIC SUBSTITUTION OF
HYDROGEN (S_N^H) IN THE COMPETITION WITH THE
CORRESPONDING METAL CATALYZED
CROSS-COUPLING REACTIONS**

O.N. Chupakhin
V.N. Charushin

Institute of Organic Synthesis, Ekaterinburg, Russia
chupakhin@ios.uran.ru

Cross-coupling reactions are part and parcel of a modern organic synthesis. Meanwhile, the reactions of nucleophilic substitution of hydrogen (S_N^H) are an alternative method for the π -deficient arenes (heteroarenes) functionalization. These transformations are used to form a variety of C-X bonds (including C-C ones) in the synthesis and modification of nitrogen-containing these compounds. The advantages of such reactions is to use them directly, in the absence of any good leaving groups and metal complex catalysis.

Some examples illustrating the possibilities of the S_N^H reactions in comparison with cross-couplings are presented.



The comparison indicates a real competitiveness of the S_N^H reactions in the case of π -deficient arenes/heteroarenes.

Not all examples of the comparison of these reactions are presented in this communication (for more information, see references 9-12).

References:

1. Verkade J. et al., *J. Org. Chem.*, **2008**, 73, 3047; 2. Gulevskaya, A.; Maes, B. et al. *Eur. J. Org. Chem.* **2009**, 564; 3. Otmar M. et al., *Tetrahedron*, **2007**, 63, 1589; 4. Guillaumet, G. et al. *Synthesis* **2004**, 17, 2893; 5. Joule J. et al., *J. Chem. Soc., Perkin Trans.1*, **2001**, 3232; 6. Prokhorov A., Makosza M., Chupakhin O., *Tetrahedron Lett.*, **2009**, 50, 1444; 7. Ackermann L. et al., *Angew. Chem. Int. Ed.*, **2005**, 44, 7216; 8. Comins D. et al., *J. Org. Chem.*, **1982**, 47, 4315; 9. Verkade J. et al., *J. Am. Chem. Soc.*, **2004**, 126, 16433; 10. Corey E. et al., *Org. Lett.*, **2005**, 7(24), 5535; 11. Verkade J. et al., *J. Org. Chem.*, **2010**, 75, 1744; 12. Strekowski L. et al., *J. Org. Chem.*, **1993**, 58, 4476.

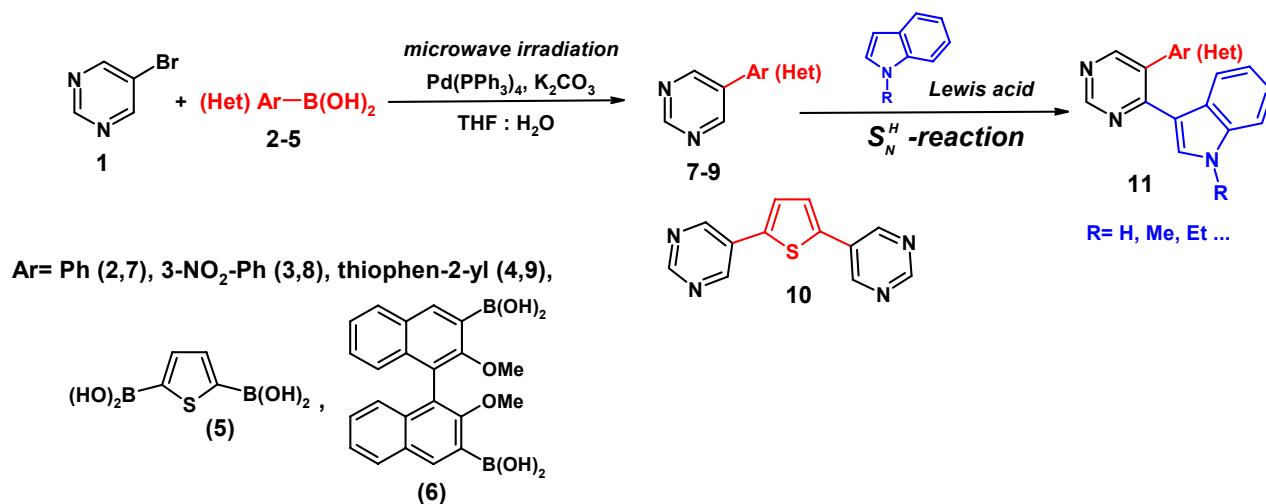
E.V. Verbitskiy
M.G. Pervova
M.A. Samorukova
G.L. Rusinov
O.N. Chupakhin
V.N. Charushin

MICROWAVE-PROMOTED SUZUKI-MIYaura CROSS-COUPLING AND S_N^H REACTIONS AS A VERSATILE PATHWAY TO SUBSTITUTED 5-(HET)ARYLPYRIMIDINES

I.Ya. Postovsky Institute of Organic Synthesis (Ural Division of the Russian Academy of Sciences), Ekaterinburg, Russia
Verbitsky@ios.uran.ru

Biaryls comprise an important class of organic compounds. Indeed, the biaryl unit is incorporated in the structure of many natural products and molecules of pharmaceutical interest. There are a variety of coupling reactions leading to biaryls which have been reviewed comprehensively in the literature. We have recently discovered a new synthetic approach to the family of 5-(het)arylpyrimidines **7-9**, when reacting Ar-B(OH)_2 with 5-bromopyrimidine **1** (the Suzuki cross-coupling reaction) under a microwave irradiation. Advantages of this method are considered to be high yields of biaryl compounds (~80-90%), short reaction times (10-15 min), and the absence of absolute inert conditions. A mixture of **9** and 2,5-(pyridine-5-yl)thiophene **10** has been obtained by using 2,5-thiophenediylbisboronic acid **5**. Yields for the cross-coupling reactions have been estimated through the GC/MS procedure.

Compounds **7-10** were used for preparation of 3-[5-(het)aryl-pyrimidin-4-yl]-1-*R*-indoles **11** by means of the S_N^H -reactions with *N*-substituted indoles.



This work was supported by the Programs of Ural Division of RAS 09-II-3-2004, 09-II-3-1015, 09-T-3-1022, State Contract № 02.740.11.0260., the Russian Foundation for Basic Research (grant no. 10-03-96078-r_ural_a) and the State Program for Supporting Leading Scientific Schools of the Russian Federation (grant no. NSh-65261.2010.3)

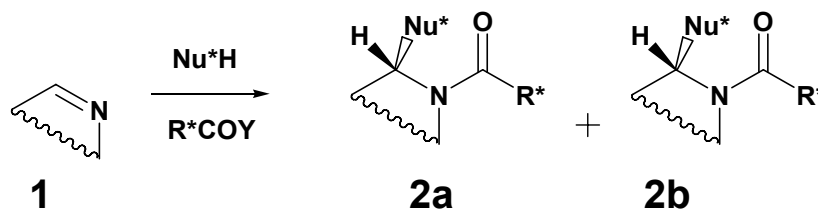
STEREOSELECTIVITY CONTROL IN
NUCLEOPHILIC ADDITION AT THE C-H BOND IN
AS-TRIAZINONES

G.V. Zyryanov¹
I.N. Egorov²
V.L. Rusinov²
O.N. Chupakhin¹

1 - Urals Federal University, Organic Chemistry Department,
I.Ya. Postovskiy Institute of Organic Synthesis, Yekaterinburg, Russia
2 - Urals Federal University, Organic Chemistry Department,
Yekaterinburg, Russia
gvzyryanov@gmail.com

The nucleophilic aromatic substitution S_N^H reactions in (het)arenes are the useful synthetic tool for the direct introductions X-centered nucleophiles into (het)aromatic core. The unsubstituted sp^2 -carbon atoms of (het)arenes **1** are prochiral, thus the σ^H -adducts formed at the nucleophilic addition step are usually exist as a mixtrure of *S*- and *R*-enantiomers (diastereoisomers) **2**. The stereoselectivity of those reactions depends on various factors.

In a current presentation a different approaches for the stereoselectivity control in reactions of isomeric *as*-triazinones with chiral and achiral nucleophiles will be discussed.



This work was supported by the Ministry of Science and Education of Russian Federation (State Contract № 14.740.11.1020).

SYNTHESIS OF 2-(1H-INDOL-3-YL)-3H-INDOL-3-ONE 1 OXIDE IN OXIDATIVE CONDITIONS

I. Kovalev¹
G.V. Zyryanov²
I.N. Egorov³
V.L. Rusinov³
O.N. Chupakhin²

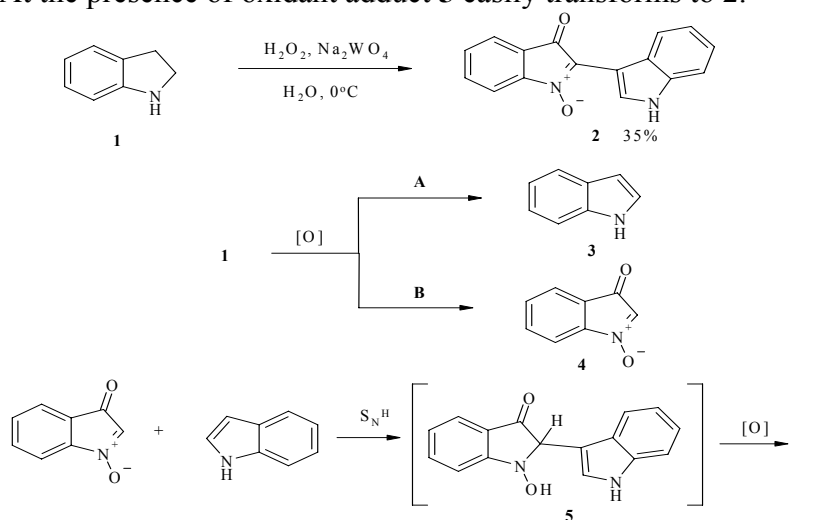
1 - Urals Federal University, Organic Chemistry Department, "Sphere" Ltd., Yekaterinburg, Russia

2 - Urals Federal University, Organic Chemistry Department, I.Ya. Postovskiy Institute of Organic Synthesis, "Sphere" Ltd., Yekaterinburg, Russia

3 - Urals Federal University, Organic Chemistry Department, Yekaterinburg, Russia
kovalev@mail.ustu.ru

The great synthetic potential of S_N^H reactions is based on the fundamental ability of C-H bond of π -deficient arenes or hetarenes to form directly new C-X bonds (where X = Csp³, Csp², Csp, O, N, S, P etc.) under the action of various nucleophiles. In some cases besides the nucleophilic addition/substitution products at C-H bond the self-coupling products of π -deficient (het)arenes or nucleophile (in rare cases) are formed. For instance, pyrimidine [1], pyridine, quinoline or isoquinoline [2] were dimerized during their lithiation by the action of superbases. Symmetrical 2,2'-indoles are the common products in reactions with strong acids [3]. 2,3'-Indoles can not be obtained directly from indoles and some modifications are required [4]. In our studies we developed easy method for 2,3'-indole derivative synthesis by direct oxidative nucleophilic dimerization of indoline in water solution.

Thus, the oxidation of indoline **1** by hydrogen peroxide in water in presence of Na₂WO₄ afforded 2-(1H-indol-3-yl)-3H-indol-3-one 1-oxide **2** as the only product in satisfactory yield. One can assume that there are two possible ways for this reaction: way (A) assumes the dehydration of indoline **1** to indole **3** (as at ref. [5]); *via* way (B) 1-oxide of 3-oxo-3H-indole **4** forms first (ref. [6]). As a last step the nucleophilic attack at azomethine carbon atom of **4** by formed *in situ* indole molecule occurs. At the presence of oxidant adduct **5** easily transforms to **2**.



References:

- N. Plé, M. Turck, K. Couture, and G. Quéguiner // *J. Org. Chem.* **1995**. vol. 60. pp. 3781-3786.
- A. J. Clarke, S. McNamara and O. Meth-Cohn // *Tetrahedron Lett.* **1974**. p. 2373.
- D.S.C. Black, N.E. Rothnie, L.C.H. Wong // *Tetrahedron Letters* **1980**. vol. 21. pp. 1883-1886.
- V. Bocchi, G. Palla // *J. Chem. Soc. Chem. Commun.* **1983**. pp. 1074-1075.
- T. Chandra S. Zou and K. L. Brown // *Tetrahedron Letters* **2004**. vol. 45. pp. 7783-7786.
- J. Slätt and J. Bergman // *Tetrahedron* **2002**. vol. 58. pp. 9187-9191.

This work was supported by the Ministry of Science and Education of Russian Federation (State Contract # 14.740.11.1020)

AUTHOR INDEX

A

Abakumov G.A.	63, 213, 405
Abashev G.G.	123
Abdrakhmanova L.M.	432
Abramov I.G.	462, 472
Adgamova D.I.	166
Ageeva T.A.	147
Ahrens V.	400
Aimakov O.A.	98, 361
Akhmedov I.M.	65
Akhmetdinova N.P.	90
Akhmetova V.R.	216
Akhmetyanova V.A.	90
Akmanov B.F.	217
Aksenov A.V.	454, 457, 460
Aksenov N.A.	457, 460
Aksenova I.V.	454, 457
Albantova A.A.	362
Albov D.V.	200
Alekseeva O.M.	362
Aleshunin P.A.	124
Alfimov M.V.	244, 231, 242, 252, 273, 291, 299, 323
Aliyev I.A.	65, 66
Allakhverdiyev M.A.	158
Allen C.	403
Almetkina L.A.	88, 93, 301, 419
Alosmanov R.M.	67
Aminova R.M.	68, 72
Amirov R.R.	253
Ananikov V.P.	94, 107, 212, 284
Andriyashin V.V.	363
Androsof D.A.	470
Anisimov A.V.	305
Anisimova N.A.	153, 320
Aniskin A.S.	69
Aniskov A.A.	125
Aniskova T.V.	125
Anokhin M.V.	223
Antipin I.S.	230, 262, 266, 271, 274, 298, 303, 308, 315, 319, 324
Antipin M.Yu.	44
Aristarkhov V.P.	244
Artamonova T.V.	67
Artemenko E.A.	193
Artemenko A.G.	386
Asadov Kh.A.	159
Atabekyan L.S.	263
Avakyan V.G.	263, 273, 299
Avdeeva E.A.	320
Averin A.D.	223

Azizov A.A.	67
Azmukhanova R.R.	257

B

Babaev E.V.	43
Bachi M.D.	82
Bachurin S.O.	340, 382
Badeeva E.K.	421,
Bagatur'yants A.A.	267, 288
Bagmanov B.T.	70
Bakhtiyarova Yu.V.	363, 420
Balakina M.Yu.	55
Balova I.A.	111, 423
Baltina L.A.	359
Balueva A.S.	86
Banik A.	383
Barabanov I.I.	121, 126
Baranov D.S.	69
Baranova T.Yu.	389
Baranovskyy V.S.	127
Barsukova T.A.	128
Bashurova V.S.	121
Basok S.S.	267
Batra V.K.	335
Batyeva E.S.	421
Bauer I.	258
Bauman M.A.	243
Bazhin D.N.	131
Bazhin N.M.	307, 310
Beard W.A.	335
Beck-Sickinger A.G.	400
Belen'kii L.I.	450
Beletskaya I.P.	30, 223, 247, 348
Belikov A.A.	373
Beljakova S.V.	234
Belostotsky D.E.	295
Belov A.S.	197, 387
Berdnikov E.A.	115, 139, 145, 150, 154
Berestovitskaya V.M.	58
Berezin M.V.	461
Beschastnova T.N.	202
Bessmertnyh-Lemeune A.	237
Bezuglov V.V.	382
Bibi A.	99
Bikmuhametova A.A.	259
Bilan M.I.	352
Bilokin Y.	82
Binyukov V.I.	362
Birin K.P.	280
Blackburn G.M.	36, 372
Bobileva A.A.	305
Bobrov M.F.	260
Bochkova O.D.	236, 262, 297
Boehnke S.	400

Boerner A.	95
Bogachenkov A.S.	129
Bogacheva A.M.	422
Bogdanchikov G.A.	121
Bogdanov A.V.	130, 313, 326, 428
Bogomyakov A.S.	453
Bogorad N.N.	243
Bohmer V.	283
Bokach N.A.	423, 430
Boldyrev I.	261
Boldyrev V.V.	377, 378
Boldyreva E.V.	327, 377, 378
Bolusheva I.Yu.	163
Bonifazi D.	109
Boyarskaya I.A.	218
Boyarskiy V.P.	218
Boyko Y.D.	214
Bredikhin A.A.	83
Bruce D.W.	103
Brunilina L.L.	354
Bubnov Y.N.	346
Budnikov H.C.	390
Budnikova Yu.G.	220, 221, 317, 431
Bukharaev A.A.	270, 259
Bukharov S.V.	128
Bukvetskii B.V.	244
Bunyad-zadeh I.A.	67
Burangulova R.N.	159
Burdzinski G.T.	126
Burgart Ya.V.	131, 185, 415
Burilov A.R.	128, 183, 195, 257, 269, 277, 279, 282, 301, 317, 331, 365
Burilov V.A.	236, 262, 266, 297, 306
Burlakova E.B.	328, 332, 362
Burnaeva L.M.	432
Buruhina O.V.	125
Buslaeva T.M.	288
Buzykin B.I.	429
Bykov R.A.	180

C

Caminade A.M.	60, 61
Carletti E.	337
Chaban I.H.	364
Chaban T.I.	364
Chachkov D.V.	58
Chamberlain B.T.	335
Chapurina Yu.S.	81

Charushin V.N.	34, 85, 192, 196, 422, 444, 452, 461, 464, 465, 467, 468, 471, 473, 474, 476, 477
Chemikosova S.	355
Cheprakova E.M.	196
Cherkasov R.A.	88, 92, 93, 168, 265, 289, 419
Cherkasov V.K.	69
Chernikova E.Yu.	233
Chernova A.V.	144
Chernysheva N.B.	351
Cheshkov D.A.	132
Chibisov A.K.	249, 263
Chirkova Zh.V.	462, 472
Chistyakov V.A.	365
Chmutova G.A.	53, 115, 150, 154
Chuchelkin I.V.	97
Chugunov A.	261
Chugunova E.A.	365
Chuklanov A.P.	259, 270
Chulakov E.N.	85, 133
Chupakhin O.N.	34, 330, 384, 392, 415, 444, 452, 453, 463, 464, 465, 468, 471, 473, 474, 475, 476, 477, 478, 479
Chupin V.	261
Churakov A.V.	407
Churakova M.V.	267
Chuvylkin N.D.	450
Chvalun S.N.	245
Collin J.	81
Collins T.J.	206
Combes S.	348, 374
Correia C.R.D.	120

D

Däbritz F.	258
Dal H.	366
aaDalkilic E.	264
Danilova L.V.	320
Dastan A.	264
Davankov V.A.	417
Davletshin R.R.	265
Davydov N.A.	266
Davydova M.P.	46
De Kimpe N.	29
Deev S.L.	384, 392
Deukeleire S.	29
Demakova M.Ya.	87
Demina O.V.	373
Denat F.	223
Deng N.	307, 310
Derevyanko N.A.	152
Dhooghe M.	29
Dil'mukhametova L.K.	408
Dilman A.D.	414
Dimukhametov M.N.	424, 425
Djilani A.D.	367
Dmitrieva G.S.	268

Dmitrieva S.N.	267, 288
Dmitrieva U.N.	167
Dobrynin A.B.	269
Dogadina A.V.	136
Drapailo A.B.	240, 286
Druzhkov N.O.	69
Dubovik S.S.	180
Dubovskii P.	261
Dubrovskiy A.V.	134, 161
Dulnev P.G.	171
Duruskari G.Sh.	66
Dyakonov V.A.	207
Dyson P.J.	50
Dzhemilev U.M.	207, 217, 219, 408, 413, 439
Dzyurkevich M.S.	176

E

Ecer K.	181
Efimova I.G.	259, 270
Efremova E.A.	219
Egorov I.N.	463, 478, 479
Egorov M.P.	37
Egorova S.N.	349, 368
Ekti Dal S.F.	135
El Sayed I.	353
Elistratova Yu.G.	236, 434
Elmali A.	371
Enakieva Yu.Yu.	237
Epifanova N.A.	271
Epishina M.A.	138
Eremenko I.L.	38
Ergun Y.	366
Erkhitueva E.B.	136
Ermolaev V.V.	50
Evtugyn G.A.	234
Ezhova A.S.	115

F

Fadeev M.A.	356
Farzaliyev S.F.	65
Fattakhov S.G.	328, 332
Fedenok L.G.	59, 121
Fedin V.P.	232, 256, 272, 275
Fedorenko E.V.	244
Fedorenko S.V.	262, 306
Fedorov A.Yu.	187, 348, 374
Fedorov B.S.	356
Fedorov Yu.V.	233, 305, 312
Fedorova O.A.	233, 255, 305, 312, 316
Fedushkin I.L.	405
Fershtat L.L.	178
Fesenko A.A.	119, 189
Filimonov S.I.	462, 472
Filimonov V.D.	137

Filippov A.P.	243
Finogenov A.O.	138
Flid V.R.	224
Florio S.	31
Fomin M.A.	373
Fomina M.V.	273, 299
Fomina O.S.	402
Fominykh O.D.	55
Frank R.	400
Freidzon A.Ya.	267, 288
Fuchs S.	61
Furer V.L.	60, 61

G

Gabbasova T.M.	282
Gabdullina G.T.	88, 419
Gabibov A.G.	360
Galimullina R.M.	220
Galjautdinova A.N.	139
Galkin V.I.	71, 72, 194, 349, 363, 368, 420, 426, 451
Galkina I.V.	194, 322, 349, 363, 368, 420, 426, 451
Galukhin A.V.	274
Galyaltinov Sh.F.	275
Ganebnykh I.N.	474
Ganushevich Y.S.	440
Garabadzhiu A.V.	345
Garazadeh Kh.A.	66
Garifzyanov A.R.	92, 265, 289
Gatiatulin A.K.	276
Gavrilov K.N.	95, 97, 417
Gavrilova E.L.	331
Gavrilova M.N.	97
Gavryushin A.E.	374
Gaynanova G.A.	322
Gazizov A.S.	277
Gerasimov A.V.	275, 278
Gerbst A.G.	352
Gevorgyan V.	445
Gibadullina E.M.	183, 257, 279, 365
Gimalova F.A.	388
Giniyatullin R.Kh.	358
Glebov E.M.	256, 316
Gnevashev S.G.	173
Gocmenturk M.	366
Goerner H.	249
Goloshapov A.N.	362
Golovanov A.	370
Golovkina M.V.	57
Golubev P.R.	172
Goncharov V.I.	454
Goodman M.F.	335
Gorak O.Ya.	63, 213
Gorbachuk V.V.	239, 259, 270, 275, 276, 278, 283, 293, 309, 329
Gorbunov Ye.B.	464

Gorbunova Yu.G.	237, 280
Görgülü A.O.	418
Gorshkova T.	355
Goryaeva M.V.	415
Grachev A.A.	352
Greckina O.T.	70
Green A.	106
Gretskaya N.M.	382
Gridnev I.D.	208
Grigoriev V.V.	340
Grishchuk B.D.	127
Grishko V.V.	141
Gritsan N.P.	52, 126
Grivin V.P.	325
Gromov S.P.	231, 242, 263, 267, 273, 288, 291, 299, 304, 323
Groshkin N.N.	417
Groza N.	370
Gruner M.	258
Gruzdev D.A.	85, 89
Gryaznova T.P.	50, 246
Gryaznova T.V.	221, 317, 431
Gubaidullin A.T.	144, 202, 331
Gubaidullin R.R.	408
Guilard R.	223, 237
Gulakova E.N.	233
Guler H.	140
Gulevskaya A.V.	448
Guliyev A.M.	160
Guliyev K.G.	160
Gulle S.	366
Guney M.	264
Guseynov F.I.	159
Gushchin P.V.	427

H

Habicher W.D.	279, 317
Hannedouche J.	81
Hayvali M.	371
Hayvali Z.	140
Hey-Hawkins E.	86, 400, 440
Hissler M.	396
Hoffmann R.W.	32
Hokelek T.	366
Howard J.A.K.	273
Hur D.	135
Hur E.	135

I

Ibragimov A.G.	217, 219
Ibrayev N.Kh.	311
Igidov N.M.	180
Ignatenko N.K.	474
Ignatyeva S.N.	86
Igosheva E.V.	141
Ildyakov A.V.	377

Ilgach D.M.	243
Ilin A.V.	130
Inokuchi T.	142, 353
Ioffe S.L.	182, 214
Ionin B.I.	129, 136
Ionova I.V.	252
Isaacs L.	233
Isachenko A.I.	387
Ishchenko A.A.	152
Ishmaeva E.A.	58
Ishmetova R.I.	474
Ismaylov V.M.	62
Ismiyec A.I.	157
Ismiyev A.I.	158
Ivanov A.A.	389
Ivanov D.A.	304
Ivanov D.V.	180
Ivanova A.A.	389
Ivanova J.V.	212
Ivanova N.A.	90
Ivanova T.A.	375
Ivantsova M.N.	143
Ivkova G.A.	432

J

Javadova S.N.	156
Jin Y.	372
Jonusauskas G.	233

K

Kadirov M.K.	56, 220, 290, 300
Kadyrova S.F.	202
Kagirov R.M.	402
Kalinichenko E.N.	391
Kalinin A.A.	144
Kalinovskaya I.V.	244
Kamarova K.A.	280
Kamneva I.E.	125
Kandalintseva N.V.	199
Karasik A.A.	86, 220
Karlov S.S.	407
Karpichev E.A.	238
Karpova E.A.	320
Kasenova N.B.	98
Kashapov R.R.	254, 281, 282,
Kashemirov B.A.	335
Kasymova E.M.	282
Kataeva O.N.	194, 246, 420, 426
Katayev V.A.	375
Katsyuba S.A.	50, 246
Kawashima T.	411
Kayupov A.R.	257, 279, 282
Kazakov D.V.	51
Kazakova E.Kh.	296
Kazakova V.V.	416
Kazimirchenko O.V.	176, 381

Khabibullin A.A.	71
Khabibullina G.R.	216
Khafizova L.O.	408
Khairullina R.R.	217
Khalikova G.M.	388
Khalilov L.M.	219, 413
Khalymbadzha I.A.	384, 392
Kharitonova N.I.	277
Kharlamov S.V.	166, 254, 271, 281
Kharlampidi Kh.E.	128
Khasiyatullina N.R.	428
Khayarov Kh.R.	283
Khaybulova T.S.	218
Khazipova G.R.	379
Khizhnyak S.D.	356
Khlebnikov A.F.	57, 148, 210, 211
Khlevin D.A.	91
Khodonov A.A.	373
Khokhlova E.A.	284
Khramchikhin A.V.	136
Khrisanforova V.V.	317
Khrizanforov M.N.	221, 431
Khusainova N.G.	145
Kim T.V.	410
Kim Yu.A.	362
Kiselev V.D.	215
Kiselyov A.V.	209
Klafki H.-W.	338
Klimenko L.S.	285
Klimochkin Yu.N.	146, 170, 222
Klimovitskii E.N.	139, 173
Knishevitsky A.V.	209
Knochel P.	374
Knöelker H.-J.	338
Knyazeva E.A.	146
Knyazeva I.R.	317
Kobelev S.M.	223
Kochetkov S.V.	84
Kodess M.I.	85
Koifman O.I.	147
Komarova O.A.	180
Komissarov G.G.	268
Komissarova N.G.	379
Konev A.S.	57, 148
König B.	229
Kononevich Y.N.	149
Konovalov A.I.	27, 215, 230, 236, 238, 254, 262, 266, 274, 279, 281, 282, 287, 296, 297, 298, 306, 308, 319, 322, 324
Konovalova I.V.	432
Konovalova N.P.	356
Konstantinovskii L.	82
Kopchuk D.	330
Korda T.M.	240
Korneev S.M.	211
Kornev A.N.	63, 213, 433
Korolev V.V.	256, 316

Korotina A.V.	474
Korotkikh N.I.	209
Korshin D.E.	254
Korshin E.E.	82
Koryagina N.N.	180
Koshevoy I.O.	321
Koskin S.A.	92
Kosolapova L.S.	150, 292
Kostin A.A.	429
Kostin G.A.	240, 286
Kostjuk S.V.	407
Kotov A.D.	446
Kotovskaya S.K.	465
Kovalenko E.A.	272
Kovalenko V.I.	60, 61, 278
Kovalev I.S.	330, 479
Kozhevnikov D.N.	85, 133, 466
Kozhukhar V.J.	151
Krasnikov A.A.	377
Krasnov S.A.	220
Krasnov V.P.	85, 89, 133
Krasova A.S.	243
Krementsova A.V.	362
Kritchenkov A.S.	430
Krivolapov D.B.	75, 93, 130, 145, 175, 176, 183, 246, 424, 428, 451
Krивonogich V.N.	155
Kryuchkova N.A.	286
Kucherenco A.S.	84
Kuchin A.V.	87, 468
Kudaibergenov S.E.	311
Kudryashova Yu.R.	287
Kudryavtsev K.V.	344
Kudyakova Yu.S.	415
Kuibida L.V.	126
Kukhar V.P.	401
Kukushkin V.Yu.	398, 423, 430
Kulagin B.P.	356
Kulak T.I.	391
Kulchin Yu.N.	244
Kulik N.V.	358
Kulikov A.S.	138
Kulinkovich O.G.	399
Kunakova R.V.	217
Kurbangalieva A.R.	115, 150, 154, 292
Kurchavov N.A.	267, 288
Kurdyukova I.V.	152
Kurnosova N.V.	289
Kuropatov V.A.	113
Kursheva L.I.	421
Kutaev N.V.	377
Kutonova K.V.	137
Kuzhaeva A.A.	153
Kuzmin V.E.	386
Kuzmina L.G.	231

Kuzmina O.M.	200, 273, 288, 291, 323
Kuznetsov A.S.	180
Kuznetsov M.A.	112
Kuznetsov V.V.	177, 178
Kvashennikova S.V.	402
Kvashnin Yu.A.	467, 468, 471
Kyselyova O.I.	410

L

Lammertsma K.	357
Laptev A.V.	373
Larock R.C.	104, 134, 161
Latypov Sh.K.	166, 254, 271, 281, 298, 308, 326, 431, 436
Latypova L.Z.	154, 292
Lebed E.G.	197, 437
Lee A.	106
Leemans E.	29
Leonova E.S.	412
Levin V.V.	414
Levinson F.S.	349, 426
Levit G.L.	85, 89, 133
Linning P.	338
Lipunova G.N.	192
Lisovenko N.Yu.	155
Litvinov A.I.	290
Litvinov I.A.	75, 93, 130, 144, 175, 176, 269, 424, 428, 451
Livantsov M.V.	179
Livantsova L.I.	179
Livshits V.A.	252
Liyasova M.	337
Lobanov A.V.	268
Lobanov C.V.	184
Lobov A.N.	381
Lobova N.A.	263, 273, 291, 323
Lockridge O.	337
Lodochnikova O.A.	75, 115, 150, 154, 175, 176, 292
Loska R.A.	469
Lu W.-J.	353
Luchai K.V.	293, 329
Lukashenko S.S.	281
Lukin A.Yu.	373
Lukovskaya E.V.	305
Lukyanova O.V.	63, 213, 433
Lushchekina S.V.	64
Lutfaliyev A.G.	66
Lutfullin M.Kh.	349
Lyakhovnenko A.S.	454
Lyapunova A.G.	470

M

Ma L.-J.	142
Madzhidov T.I.	53
Maes B.U.W.	205, 448
Magerramov M.N.	66
Maharramov A.M.	65, 66, 67, 156, 157, 158, 159
Majoral J.-P.	60, 61
Makarenko I.G.	387
Makarov M.V.	412
Makhova N.N.	138, 177, 178
Makosza M.	443, 469
Malih N.A.	192
Maltsev O.V.	84
Malysheva Yu.B.	374
Mamedli S.B.	160
Mamedov I.A.	62
Mamedov V.A.	116, 144, 166, 202
Manakov A.Yu.	377, 378
Marichev K.A.	209
Markina N.A.	161
Markitanov Yu.N.	162
Martianov Ye.M.	88, 93, 419
Martin Pendas A.	53
Martyanov T.P.	285
Martynchuk E.R.	68
Martynchuk S.L.	68
Masson P.	64, 337
Masterova Yu.Yu.	163
Matern A.I.	456
Mazalov L.N.	286
McKenna C.E.	39, 335
Medvedeva A.I.	193
Mei Z.-W.	353
Meleshko T.K.	243
Melnikova N.B.	235
Merkushev A.A.	155
Meshcheryakova S.A.	375
Meshkov I.B.	149, 416
Meshkovaya V.V.	164
Metz P.R.	342
Miagkova G.	370
Miftakhov M.S.	90, 388
Mikhailov A.S.	358
Mikhailova L.R.	359
Mikhalitsyna E.A.	247
Mikhaylov D.Y.	221, 431
Mikolajczyk M.	397
Mikshina P.	355
Milaeva E.R.	343
Milenin S.A.	165
Mill E.M.	362
Miller J.S.	45
Milyukov V.A.	50, 246, 409, 440
Minayeva Y.V.	169
Mindubaev A.Z.	295
Minkin V.I.	33

Minzanova S.T.	294, 295, 376
Mirochnik A.G.	244
Mironov M.A.	143, 191
Mironov V.F.	69, 130, 294, 295, 313, 326, 376, 395, 424, 425, 428, 429, 432, 434, 435, 436
Mironova D.A.	296
Mironova E.V.	202
Mironova L.G.	294, 295, 376
Mitani M.	96
Mochulskaya N.N.	422
Mokrushin V.S.	143
Molchanov A.P.	430
Mollet K.	29
Mori K.	79
Morozov A.G.	405
Morozova J.E.	296
Moskva V.V.	62
Mostovaya O.A.	274
Mukhametshina A.R.	297
Munasipova D.A.	375
Muravev A.A.	298
Murtazina A.M.	166
Murzakova N.N.	216
Musikhina A.A.	475
Musin L.I.	130, 313
Musina E.I.	86, 220
Mustafayev A.M.	156
Mustafina A.R.	236, 262, 266, 297, 306, 331
Muzafarov A.M.	149, 165, 416
Mysyk D.D.	152
Myz S.A.	377, 378
Myznikov L.V.	167

N

Nabiyev N.S.	67
Nachon F.	64
Nadein O.N.	457, 460
Nasibov S.S.	62
Nasibullina E.R.	180
Nastapova N.V.	144
Nasybullina G.R.	254
Naumov R.N.	86
Naveed Umar M.	99
Nawrozkiy M.B.	354
Nazarov Sh.I.	158
Nazarov V.B.	273, 299
Nefedov O.M.	37, 408
Nefedov S.E.	237
Nekrasov A.G.	227
Nemtarev A.V.	69, 395, 434
Nemukhin A.V.	64
Nenajdenko V.G.	49
Nifantiev N.E.	352
Nikipelov A.S.	405
Nikitin Ye.N.	301

Nikitina L.E.	173
Nikolaev A.E.	358
Nisanci B.	264
Nizameev I.R.	300
Nizamiev I.P.	313
Nizamov I.D.	168
Nizamov I.S.	88, 93, 168, 301, 419
Nizamova A.M.	390
Nosov R.V.	324
Nosova E.V.	192
Novakov I.A.	354
Novikov I.M.	95, 417
Novikov M.S.	57, 210, 211
Novikova O.P.	179
Nugent T.	99
Nugumanova G.N.	128
Nuriev V.N.	250
Nurmaganbetova M.T.	169

O

Odinets I.L.	412
Oertell K.	335
Ofitserov E.N.	74
Ogienko A.A.	377
Ogienko A.G.	327, 377, 378
Ognichenko L.N.	386
Ogurtsov V.V.	364
Oleynikova I.A.	391
Oleynikova J.V.	98
Olivucci M.	48
Omran O.A.	302
Onysko P.P.	184, 410
Oprunenko Y.F.	407
Orlinson B.S.	354
Orlov A.V.	379
Orlov N.V.	94
Orlov V.Yu.	446
Oshchepkov A.S.	255
Osipov D.V.	170
Ostrovskii V.A.	124
Osyenin V.A.	170
Ovcharenko V.I.	453
Ovchinnikov D.V.	345
Ovchinnikov M.M.	356

P

Padnya P.L.	303
Pakhomov P.M.	356
Palchikov V.A.	171
Palysaeva N.V.	458
Palyulin V.A.	47, 336
Panchenko A.O.	186
Panchenko P.A.	312
Pankova A.S.	112, 172
Panova J.S.	433
Panova Yu.S.	63, 213
Panteleeva E.V.	449

Paramonov S.V.	316
Parfenova L.V.	413
Pashagin A.V.	294
Pashirova T.N.	279, 281, 282
Pavelyev R.S.	173
Peng W.	353
Pervova M.G.	196, 477
Pestov A.V.	452
Peterson I.V.	174
Petrosyan V.A.	447
Petrosyan V.S.	179
Petrov M.L.	470
Petrov N.Kh.	304
Petrov P.S.	380
Petrova A.	355
Petrova G.R.	294
Petrova L.N.	340, 382
Petrova Zh.S.	305
Petrovskii P.P.	57
Petukhova V.Yu.	177, 178
Pinus M.V.	306
Platova E.V.	421
Platz M.S.	126
Plemenkov V.V.	175, 176, 381
Pleshchev M.I.	177, 178
Plyusnin V.F.	307, 310, 325
Polischuk P.G.	386
Polukhin A.V.	126
Popov A.F.	238
Popova E.V.	271
Postnikov P.S.	137
Potapova O.V.	417
Pozdeev O.K.	349, 368
Pozdnyakov I.P.	307, 310, 325
Prediger P.	120
Preobrazhenskaya M.E.	352
Prishchenko A.A.	179
Prishlyak I.S.	171
Pritchina E.A.	126
Prokashev K.A.	141
Prokhorov A.M.	406
Prokop A.	187
Prosenko A.E.	199
Proshin A.N.	340, 382
Proskurnina M.V.	91
Pudovik M.A.	195, 257, 277, 301, 317
Pulina N.A.	151, 180

R

Rakhimova E.B.	219
Ramazanov I.R.	408, 439
Ramsh S.M.	167
Rasputin N.A.	471
Rassukana Y.V.	410
Rastorguev E.A.	97
Reau R.	396

Reznik V.S.	358
Reznikov A.N.	222
Ritter S.	385
Rizvanov I.Kh.	144
Roeschenthaler G.-V.	118
Romanenko G.V.	453
Romanenko V.D.	401
Romanova E.A.	155
Romanova I.P.	313, 326
Romeo R.	341
Rostovskii N.V.	210, 211
Rovnova T.A.	308
Rozhkova Yu.S.	122
Rubailo A.I.	174
Rubtsov A.E.	151, 180, 186
Rubtsova S.A.	87
Rudiyak V.Yu.	273
Rusanov A.I.	227
Rusinov G.L.	196, 444, 461, 464, 467, 468, 471, 473, 474, 477
Rusinov V.L.	330, 384, 392, 463, 478, 479
Rybakov S.M.	145
Rybalkina E.Yu.	412

S

Sabirzyanova G.R.	301
Sadykova Yu.M.	269
Safina G.D.	293, 309, 314, 329
Safiullin T.G.	375
Saiai A.	96
Saifutdinova M.N.	331
Saigitbatalova E.Sh.	154
Saikia A.K.	117
Saikia M.D.	383
Salakhov M.S.	70
Salamci E.	181
Salin A.V.	71, 72
Salkeyeva L.K.	169
Salomatova V.A.	307, 310
Saloutin V.I.	131, 185, 415
Samigullina A.I.	144, 202
Samorukova M.A.	196, 477
Samsonenko D.G.	232, 256
Sapchenko S.A.	232, 256
Sayfutdinov Sh.U.	219
Sayfutdinova I.F.	432
Sazhnikov V.A.	244
Sazonov S.K.	323
Sazykin I.S.	365
Sazykina M.A.	365
Schegolkov E.V.	185
Scherbakov K.V.	131
Schieb H.	338
Schlick Sh.	56
Schmalz H.-G.	96, 187, 348, 385

Scholz M.	400
Schopfer L.M.	337
Schreiner P.R.	35
Schulz E.	81
Sedakova T.V.	244
Selektor S.L.	241
Seliverstova E.V.	311
Semakin A.N.	182
Semeikin A.S.	147
Semeikina C.A.	147
Semenov A.V.	380
Semenov V.E.	358
Semenov V.V.	351
Semenova A.	261
Semenova M.N.	351
Semionova V.V.	256
Senturk M.	181
Sergeeva A.N.	312
Serkov I.V.	340
Serkov I.V.	382
Shaekhov T.R.	183
Shafeeva M.V.	193
Shaikhutdinova G.R.	313
Shakhtshneider T.P.	378
Shakurov M.Sh.	349
Shalimov A.A.	184
Shamagsumova R.V.	234
Shamilov R.R.	168
Sharafutdinova D.R.	183, 195
Sharunov V.S.	462, 472
Shashkov A.S.	352
Shatalova N.I.	331
Shcherbakova M.A.	475
Shcherbina M.A.	251
Shekurov R.P.	246
Sheremetev A.B.	458
Sheremetyeva N.A.	165
Shermolevich Yu.G.	162
Shestakova T.S.	384, 392
Shestopalov A.M.	201
Shevchuk M.V.	401
Shevelev S.A.	459
Shi Y.	80
Shibayeva A.K.	169
Shibryaeva L.S.	362
Shipilovskikh S.A.	186
Shipov A.E.	412
Shiryaev A.A.	95, 417
Shklyaev Yu.V.	122
Shklyaeva E.V.	123
Shteingarts V.D.	449
Shtyrlin Yu.G.	139, 173
Shulaeva M.P.	349, 368
Shulga S.V.	437
Shurov S.N.	180
Shurpik D.N.	175
Shutalev A.D.	119, 132, 189, 200
Shvaika O.P.	209
Shvartsberg M.S.	59
Shvets V.I.	373
Sidorenko N.I.	288

Sidorov A.A.	38
Simonova Yu.A.	155
Sinelshchikova A.A.	237
Sinichkina R.I.	314
Sinita A.D.	184
Sinyashin O.G.	50, 86, 220, 221, 246, 313, 326, 331, 402, 409, 421, 431, 440
Sirotkin O.S.	73
Sirotkin R.O.	73
Sitdikov R.R.	315
Sitnikov N.S.	187, 348
Siyutkin D.E.	84
Skatova A.A.	405
Skripacheva V.V.	236, 262, 266, 297
Slavnova T.D.	249
Slepukhin P.A.	196, 330, 452, 461, 467, 473
Smetanin I.A.	210
Smirnov A.N.	460
Smolentsev A.B.	316
Sokolenko W.A.	174
Sokolov V.V.	114
Sokolova V.I.	317
Solovieva S.E.	230, 266, 271, 297, 298, 308
Solovyev P.A.	189
Solovyeva D.O.	318
Sorochinsky A.E.	401
Sosnin E.A.	123
Sosonyuk S.E.	91
Spiridonova M.P.	368
Spiridonova Yu.S.	220
Spirihin V.V.	381
Stakheev V.V.	420
Starikova Z.A.	197
Starosotnikov A.M.	459
Stass D.V.	453
Stoikov I.I.	230, 274, 303, 315, 319, 324
Stoikova E.E.	234
Stoporev A.S.	378
Stryapunina O.G.	122
Stuzhin P.A.	437
Sudarikov D.V.	87
Sukhorukov A.Yu.	182, 214
Surin N.M.	149
Sushev V.V.	63, 213, 433
Suturina E.A.	52
Suzenet F.	404
Suzuki A.	28
Svintsitskaya N.I.	98
Svirskaya N.M.	174
Syakaev V.V.	296
Synytsya A.D.	410
Syrbu C.A.	147
Syrchikova T.S.	123
Sysolyatin S.V.	190

T	
Takhautdinova G.L.	368, 451
Tamm L.A.	193, 320
Tarasova I.V.	380
Tarasova R.I.	331
Tartakovsky V.A.	182, 214, 414
Tatarinov D.A.	429, 434
Tatjanenko L.V.	356
Taylor J.G.	120
Tayshibekova E.K.	169
TePLYakov F.S.	470
Tercan B.	366
Terentyev A.O.	110
Termath A.	385
Theumer G.	258
Thomas J.	106
Tietze L.F.	108
Timofeeva T.V.	412
Timoshenko V.M.	162
Tinkov O.V.	386
Titova Yu.A.	461
Tokareva M.I.	191
Tolmacheva I.A.	141
Tolshchina S.G.	474
Tolstikov G.A.	46
Torgov V.G.	240, 286
Trafimova L.A.	119
Trashakhova T.V.	192
Tretyakov E.V.	453
Tretyakov S.V.	171
Trifonov A.A.	81
Trishin Yu.G.	193, 320
Trofimova E.A.	402
Trusova M.E.	137
Tseitler T.A.	463
Tsepaeva O.V.	294
Tsivadze A.Yu.	237, 280
Tsuboi S.	105
Tsyganov D.V.	351
Tudriy E.V.	194, 349, 368, 426, 451
Tumanov N.A.	378
Tumashov A.A.	133
Tung T.Q.	430
Tunik S.P.	321
Turin A.P.	222
Tyaglivaya I.N.	448
Tyurin V.S.	247

U

Uryadov V.G.	74
Us T.V.	240
Ushakov E.N.	231, 242, 285
Ushakova N.A.	352
Usov A.I.	352
Ustyuzhanina N.E.	352
Utepova I.A.	453, 475

V	
Vafina R.M.	139, 173
Vaganova T.A.	449
Vagapova G.I.	322
Vagapova L.I.	128, 195
Valaeva V.N.	224
Valeeva F.G.	287, 290, 322
Valiev M.F.	150
Valitov M.I.	220, 313
Valiullina Z.R.	90
Valova M.S.	192
Vandyukov A.E.	60, 61
Varaksin M.V.	453
Varaksina E.N.	435, 436
Varfolomeev S.D.	64, 373
Varol G.A.	135
Varzatskii O.A.	197, 346, 387, 437
Vasilenko I.V.	407
Vasilevsky S.F.	46, 69, 271
Vasilyev A.V.	54
Vasin V.A.	163
Vatsadze S.Z.	250
Vedernikov A.I.	231, 263, 267, 273, 288, 291, 299, 323
Velder Ja.	96, 187, 348
Veliyeva G.Kh.	156, 159
Verbeeck S.	448
Verbitskiy E.V.	196, 461, 467, 477
Veremeychik Ya.V.	175, 381
Vereshchagina Ya.A.	58
Vershinnikova T.G.	273, 299
Vinnik N.A.	218
Vitrik O.B.	244
Vokcoboynikov A.Z.	224
Volkov S.V.	437
Vologzhanina A.V.	387, 437
Voloshin Y.Z.	197, 308, 346, 387, 437
Voloshina A.D.	358
Volynsky P.	261
Voronin V.V.	112
Voronina J.K.	75, 183, 195
Voronina L.V.	252
Voronina N.V.	149, 416
Votintseva G.V.	193
Vshivkova T.S.	122
Vyshtakaliuk A.B.	376
Vysotsky M.O.	283

W

Waltho J.P.	372
Wang L.	353
Weidlich S.	338
Wilson S.H.	335

Wiltfang J.	338
Wood J.L.	339
Wu F.	307, 310
Wu Y.	335

Y

Yagarmina A.N.	324
Yaglioglu G.	371
Yagolnik E.A.	362
Yagunov S.E.	199
Yakhvarov D.G.	313, 326, 402
Yakimansky A.V.	243
Yakushev A.A.	223
Yanilkin V.V.	144, 254, 296
Yantemirova A.A.	324
Yaroslavova A.V.	408, 439
Yatluk Yu.G.	452
Yazvenko M.A.	193
Yegorov V.A.	388
Yegorova A.Yu.	125
Yilmaz H.	371
Yudashkin A.V.	164
Yunoshev A.S.	377, 378
Yunusov M.S.	379
Yurchenko S.P.	361
Yurkova M.P.	325
Yusubov N.N.	62
Yusupova G.G.	326
Yusupova L.M.	194, 349, 365, 368, 426, 451

Z

Zabelina O.N.	196, 461, 464
Zagidullin A.A.	440
Zaharova L.Y.	290
Zairov R.R.	236, 262
Zaitsev K.V.	407
Zaitsev S.Yu.	318
Zaitseva G.S.	407
Zakharov B.A.	327
Zakharova L.Ya.	238, 279, 281, 282, 287, 300, 322
Zakharova V.M.	335
Zakirova E.I.	202
Zamilatskov I.A.	200
Zavyalova V.K.	201
Zefirov N.S.	47, 91, 336, 340, 389
Zefirova O.N.	389
Zelinsky G.E.	387
Zemtsov A.A.	414
Zevatskiy Y.E.	167
Zhang Y.	142
Zhdanov R.I.	76
Zheglov S.V.	97
Zhigacheva I.V.	328, 332
Zhikhareva P.A.	244

Zhil'tsov A.	416
Zhiltsova E.P.	279, 281, 282
Zhizhchenko I.V.	244
Zhmurov P.A.	214
Zhukova N.A.	202
Zhumabaeva G.A.	465
Ziatdinova F.Kh.	294
Zibarev A.V.	52
Ziganshin M.A.	239, 259, 270, 275, 276, 278, 283, 293, 309, 314, 329
Ziganshina A.Yu.	254, 281
Ziganshina S.A.	259, 270
Ziyatdinova G.K.	390
Zlotin S.G.	84
Zobov V.V.	358, 376
Zubarev A.A.	201
Zvereva E.E.	50
Zyryanov G.V.	330, 463, 478, 479

CONTENT

Committees	2
Greeting Letters	5
Preface	7
Titles of Sessions	8
Congress Schedule	9
Scientific Programme	13
 Key-note Lectures	 25
 Section 1. Theoretical Organic Chemistry:	
Bonding, Structure and Reactivity	41
Plenary lectures (PL1 – PL4)	43
Oral reports (O1 – O12)	47
Poster presentations (P1 – P18)	59
 Section 2. “Chiral” Organic Chemistry	 77
Plenary lectures (PL42 – PL43)	79
Oral reports (O100 – O105)	81
Poster presentations (P252 – P264)	87
 Section 3. Advanced Methods of Organic Synthesis	 101
Plenary lectures (PL5 – PL10)	103
Oral reports (O13 – O26)	109
Poster presentations (P19 – P96)	123
 Section 4. Catalysis in Organic Synthesis	 203
Plenary lectures (PL39 – PL41)	205
Oral reports (O91 – O99)	208
Poster presentations (P244 – P251)	217
 Section 5. Supramolecular Organic Chemistry: VI International Symposium “Design and Synthesis of Supramolecular Architectures”	 225
Plenary lectures (PL25 – PL33)	227
Oral reports (O61 – O79)	237
Poster presentations (P149 – P223)	257
 Section 6. Bioorganic and Medicinal Chemistry	 333
Plenary lectures (PL18 – PL24)	335
Oral reports (O44 – O60)	342
Poster presentations (P118 – P148)	361

Section 7. Organometallics in Organic Synthesis	393
Plenary lectures (PL11 – PL17)	395
Oral reports (O27 – O43)	402
Poster presentations (P97 – P117)	419
 Section 8. Symposium “Modern trends in functionalization of C-H bonds in arenes and heteroarenes”	441
Plenary lectures (PL34 – PL38)	443
Oral reports (O80 – O90)	448
Poster presentations (P224 – P243)	460
 Author index	480

SPONSORS

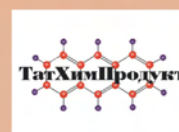
Bruker Ltd. Moscow



DIA-M



NPO «TatKhimProdukt»



Ecopharm



MEDIA SUPPORT

The monthly review journal
Uspekhi Khimii



