BOOK OF ABSTRACTS
CHEMTRENDS
2018

Институт органической химии имени Н. Д. Зелинского РАН

CHEMTRENDS-2018

Сборник тезисов докладов

Международной научной конференции
«ОРГАНИЧЕСКИЕ И ГИБРИДНЫЕ
ФУНКЦИОНАЛЬНЫЕ МАТЕРИАЛЫ
И АДДИТИВНЫЕ ТЕХНОЛОГИИ»

23–28 сентября 2018 г. Москва

МАКС ПРЕСС

МОСКВА – 2018

УДК 54
ББК 24
К35

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В настоящем сборнике представлены тезисы пленарных, устных и стендовых докладов участников Международной научной конференции ChemTrends-2018, организованной ИОХ РАН. Тематика работ охватывает актуальные направления в области гибридных и органических функциональных материалов, органическом синтезе, катализе, зеленой химии, разработке аддитивных технологий, дизайне супрамолекулярных систем и компьютерной химии.

Сборник представляет интерес для научных работников, преподавателей, аспирантов и студентов химических вузов.

УДК 54
ББК 24

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Dr. M. A. Syroeshkin

ChemTrends-2018 : Book of Abstracts of the International scientific conference, September 23rd–28th 2018, Moscow. – Moscow : MAKS Press, 2018. – 114 p.

ISBN 978-5-317-05932-3

This book contains proceedings of plenary, oral and poster presentations of participants of the International scientific conference ChemTrends-2018. The Conference program covers modern trends in the areas of hybrid and organic functional materials, advanced organic synthesis, catalysis, green chemistry, additive manufacturing technologies, supramolecular systems and computational chemistry.

The book will be useful for researchers, teachers, postgraduates and students.

Электронная версия сборника тезисов конференции доступна на веб-сайте:
http://chemtrends.org/index.php/en/

Electronic version of the book of conference abstcacts is available on the web-site:
http://chemtrends.org/index.php/en/

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WELCOME TO CHEMTRENDS-2018

Dear Participants,

On behalf of the organizers, it is our pleasure to invite you to attend the International Conference «Organic & Hybrid Functional Materials and Additive Technologies», to be held in Moscow, September 23-28, 2018.

Development of functional organic and hybrid molecular systems is currently at the peak of its relevance. It admittedly represents one of the foremost priorities in development of new technologies and applications. Recent advancements in the chemical sciences provide outstanding opportunities of obtaining the most complex molecular architectures ever possible. The remarkable advent of 3D printing and other additive technologies brings unprecendented challenges to this area.

Innovative organic and hybrid materials and their continuously increasing impact on life sciences, nanotechnology, catalysis, energy research, additive manufacturing, photonics, electrochemistry, biomass recycling, and many other modern activities are approaching a point of cost-effective commercialization. Rational application of such materials will substantially reinforce the related industries, being ultimately translated into social, economical, and environmental benefits.

Research topics dealing with organic and hybrid systems were rapidly developed in Zelinsky Institute of Organic Chemistry in recent years and were supported by Russian Science Foundation. We will be happy to discuss the results of this research project and possible areas of collaboration.

We believe that the great history and cultural heritage of Moscow, making the city an attractive venue for an exceptional scientific program, will also reward the participants with excellent social experience and sightseeing. We take pride in the Red Square and Kremlin being included in the UNESCO World Heritage List as the top historical places to visit in Russia. The monumental architecture, masterpieces of the Tretyakov Gallery and the Pushkin State Museum of Fine Arts, and many other unforgettable attractions compose the unique atmosphere of Moscow, strong and balanced even in our rapidly changing modern reality.

Looking forward to welcome you at the ChemTrends-2018,

Cordially yours,
Mikhail Egorov and Valentine Ananikov.

Mon., 24 September 2018, 10.00 – 10.40

Valery V. Fokin

Department of chemistry
the bridge@usc and loker hydrocarbon research
institute university of southern california,
Los Angeles, ca 90089

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CHEMICAL TOOL FOR DECIPHERING COMPLEXITY

Discovery and construction of new molecular architectures depend on the efficient methods for controlled and selective formation of new chemical bonds in complex environments. Chemical transformations that reliably introduce various functional groups in reaction products are required for the synthesis of materials with desired properties. Catalytic reactions offer unprecedented potential for making them useful for both laboratory and industrial preparation of new substances. Our studies of new catalytic processes, the insights into their mechanism and catalyst behavior, and the resulting applications will be highlighted in the presentation.

SHORT BIOGRAPHY

Valery Fokin is a native of Nizhny Novgorod, Russia. After completing his undergraduate studies at the N.I. Lobachevsky University of Nizhny Novgorod (1993) and Calvin College (BSc, 1993), and graduate work at University of Southern California (PhD, 1998, with Nicos Petasis), Fokin joined TSRI as a postdoctoral fellow in 1998 (with K. Barry Sharpless) and became a faculty member in 2000. After 15 years as a faculty member at Scripps, he moved his research program to his alma mater accepting a position of Professor in the Department of Chemistry and founding member at The Bridge@ USC, an Institute at the Center of the Convergent Bioscience in October of 2015.

The research in Valery Fokin's group at University of Southern California is centered on discovery of new catalytic reactions and chemical reactivity and on applying it to the studies of biological and macromolecular phenomena.

His discoveries have contributed to now widely used reactions, such as the copper and ruthenium-catalyzed azide-alkyne cycloaddition reactions (CuAAC, often called "click chemistry" and its sister, RuAAC) and catalytic transformations of 1,2,3-triazoles which proceed via the intermediacy of rhodium azavinyl carbene species. His laboratory is currently involved in using these processes in the synthesis of pharmaceutically relevant compounds, probes for cellular and tissue imaging and targeted drug delivery, and functional polymeric materials

Prof. Fokin has authored and co-authored over one hundred publications, eight book chapters, co-edited a book, and is an inventor on over twenty patents and patent applications. Several of his articles are among the most cited and accessed papers, and in 2011 Thomson-Reuters ranked him among the top ten chemists of the decade worldwide based on the impact of his published work. In 2013, the same agency named him a Citation Laureate, and placed him among "the World's Most Influential Scientific Minds" in 2015, 2016, and 2017.

2015-present	Professor, Department of Chemistry, University of Southern California Founding Member, The Bridge Institute at USC
2006-2016	Associate Professor, Department of Chemistry, The Scripps Research Institute, La Jolla, California
2000-2006	Assistant Professor, Department of Chemistry, The Scripps Research Institute, La Jolla, California

Mon., 24 September 2018, 10.40 – 11.20

Tsuyoshi Kato

Université Paul Sabatier - LHFA - UMR 5069
118, route de Narbonne, 31062 Toulouse Cedex 9

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SILICON COMPLEXES WITH TRANSITION METAL BEHAVIOR

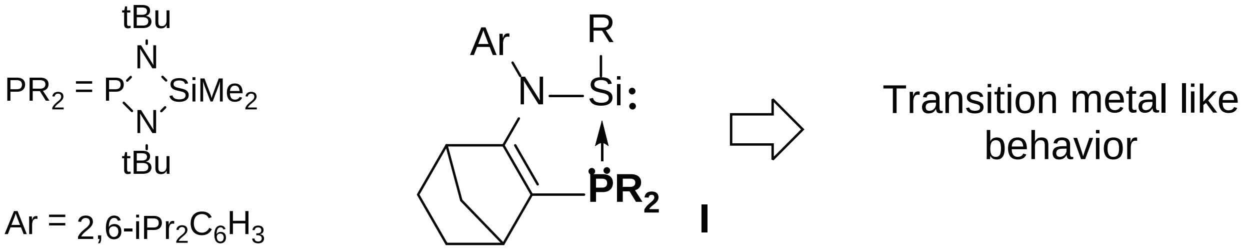
Université de Toulouse, UPS, LHFA, 118 route de Narbonne, F-31062 Toulouse, France, and CNRS, LHFA UMR 5069, F-31062 Toulouse, France.

Silylenes are neutral silicon species featuring a divalent silicon atom with only six valence electrons and they are in general highly reactive transient species with a short life time. Since the discovery of first stable silylenes, several methods to stabilize such species have been developed. Among them, the use of a donating ligand, which thermodynamically stabilizes silylenes by electron donation but also increases the steric protections, have been recognized to be an efficient methodology to synthesize various types of silylenes.

Since several years, we are developing the chemistry of silylenes complexed with a phosphine ligand I Of particular interest, they retains the silylene reactivity in spite of their high stability and presents somewhat transition metal like behavior.[1] Here we will show their chemistry and some interesting perspectives.

References:

[1] a) R. Rodriguez, D. Gau, T. Kato, N. Saffon-Merceron, A. De Cózar, F. P. Cossío, A. Baceiredo, Angew. Chem. Int. Ed. 2011, 50, 10414; b) R. Rodriguez, Y. Contie, D. Gau, N. Saffon-Merceron, K. Miqueu, J.-M. Sotiropoulos, A. Baceiredo, T. Kato, Angew. Chem. Int . Ed. 2013, 52, 8437; c) R. Rodriguez, Y. Contie, Y. Mao, N. Saffon-Merceron, A. Baceiredo, V. Branchadell, T. Kato, Angew. Chem. Int. Ed. 2015, 54, 15276; d) R. Rodriguez, Y. Contie, R. Nougué, A. Baceiredo, N. Saffon-Merceron, J.-M. Sotiropoulos, T. Kato, Angew. Chem. Int. Ed. 2016, 55, 14355.



SHORT BIOGRAPHY

Tsuyoshi Kato is Directeur de Recherche of CNRS and a member of Labaratoire d'hétérochimie Fondamentale et Appliquée (LHFA) at Université Paul Sabatier at Toulouse in France.

He obtained his PhD in Chemitry at Université Paul Sabatier (France) in 2001 for research on the application of phosphorus in cation, carbene and radical chemistry with Professor Guy Bertrand. After post-doctoral stay in the laboratory of Professor Christopher Reed at University of California Riverside (Synthesis of persistent carbocations with weakly coordinating carborane anion, 2001-2004), he began his research carrier as Chargé de Recherche of CNRS at LHFA in 2004.

2012-	Research director 2nd class.
2008-2012	Research Associate 1st class
2004- 2008	Research Associate 2nd class
2001-2004	Post-Doc, California University Riverside (Pr. C. Reed)
1998-2001	Ph.D, Université Paul Sabatier de Toulouse (Dr. Guy Bertrand)
1996-1998	Master, Okayama University – Japan (Pr. K. Uneyama)

Tue., 25 September 2018, 10.00 – 10.40

Alex Spokoyny

University of California, Los Angeles (UCLA), CA, USA

ATOMICALLY PRECISE HYBRID NANOPARTICLES WITH MULTIVALENT CAPABILITIES

Unlike proteins and small-molecules, hybrid nanoparticle assemblies are never atomically precise and therefore have non-uniform composition and size. This fundamentally limits the researcher's ability to precisely engineer recognition and binding properties of these assemblies. This is especially true of a large class of hybrid noble metal nanoparticles including gold-based systems (AuNPs). Weak metal-ligand interactions contribute to a statistical distribution of defects and positional uncertainty of ligands around the metal core, limiting their molecular precision. Consequently, inherent polydispersity features of hybrid nanoparticles leads to their diminished selectivity when they are designed to target and bind biomacromolecules. Furthermore, under relatively benign conditions, weak metal-ligand interactions in the hybrid nanoparticles can result in scrambling events and ultimately degradation. Therefore, the status quo in the field largely centers on our inability to rationally address structure-function properties of hybrid nanomaterials.

Our work can be characterized as a "nanoparticle total synthesis", where we are utilizing a bottom-up approach for the synthesis of large hybrid molecules using atomically precise 3D inorganic clusters as rigid templates. Specifically, we developed a new strategy for building robust, atomically precise hybrid nanomolecules using air-stable inorganic clusters densely decorated with perfluoroaromatic functional groups. This strategy is very appealing given its similarity to the synthesis of AuNPs; however, in this case, the resulting structures maintain full atomic precision and exhibit dramatically improved stability due to the full covalency of the resulting systems. In my presentation, I will show how this strategy can be used for facile attachment of receptor building blocks and positioning these in three-dimensions with an atomic precision. I will furthermore highlight our recent effort in improving the attachment chemistry to render the assembly of these structures more facile.

Ultimately, our work should help to promote a thorough understanding of the design rules governing interactions between hybrid nanomaterials and biomolecules and elucidate the dominant factors that enhance specific inhibition of complex biomolecular targets. For the first time, combining elements of inorganic cluster chemistry, chemical biology and materials science we will enable researchers to create well-defined programmable hybrid nanosystems with unique capabilities for binding and sensing complex biomolecules.

SHORT BIOGRAPHY

Alex Spokoyny is currently an Assistant Professor in Chemistry and Biochemistry at UCLA and a faculty member of the California NanoSystems Institute (CNSI). Prior to this he received a Ph.D. degree in 2011 from Northwestern University in inorganic and materials chemistry and conducted a post-doctoral stint at MIT in chemical biology until 2014. His group's research encompasses an interdisciplinary approach focusing on pressing problems in chemistry, biology, medicine and materials science. Specifically, Spokoyny and his co-workers are currently developing new and potentially useful solutions to problems in catalysis, energy conversion and storage and protein recognition and labeling. Alex is also a recipient of several awards including Cottrell Scholar from Research Corporation for Science Advancement (2018), Maximizing Investigator's Research Award (MIRA) from the NIH (2017), Alfred P. Sloan Research Fellowship (2017), Chemical and Engineering News (C&EN) Talented 12 (2016), 3M Non-Tenured Faculty Award (2016), Grand Poster Prize from the American Peptide Society (2013), International Union of Pure and Applied Chemistry (IUPAC) Prize for Young Chemists (2012), NIH Ruth Kirschstein Fellowship (2012-2014), and American Chemical Society Inorganic Young Investigator Award (2011).

Tue., 25 September 2018, 10.40 – 11.20

Antonio Benedetto

School of Physics and Conway Institute of Biomolecular and Biomedical Research, University College Dublin, Dublin 4, Ireland
Laboratory for Neutron Scattering, Paul Scherrer Institut, Villigen, Switzerland

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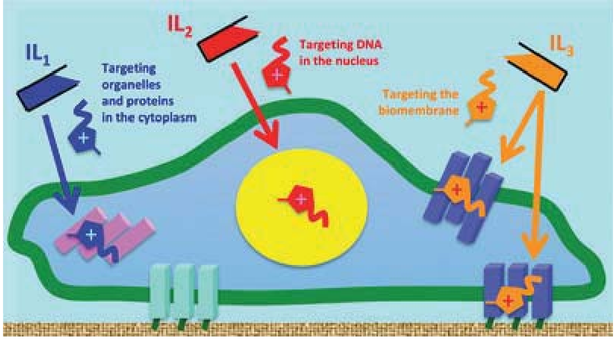
IONIC LIQUIDS AND BIOMOLECULES: FROM FUNDAMENTAL RESEARCH TO APPLICATIONS

In the past few years the interaction between a new family of ionic systems, known as ionic liquids, with biomolecules and biosystems has polarized the attention of an increasing number of research groups [1-4]. Ionic liquids are ionic compounds made by an organic cation and either and organic or inorganic anion, they are liquid around room temperature, have low-vapour pressure and other peculiar properties, e.g. some of them have a magnetic character. It has been shown, for example, that selected ionic liquids are able to (1) diffuse into biomembranes and eventually disrupt them at high dose; (2) stabilize proteins and enzymes and their biochemical function; (3) either support or prevent the aggregation of proteins in amyloids; (4) extract, purify, and even preserve DNA; (5) dissolve polysaccharides and cellulose; and (6) kill bacteria and cancer cells while leaving eukaryotic healthy cells almost unaffected. Research in this subject points to understand the microscopic characteristic of interactions behind the meso- and macro-scopic effects relevant in biomedicine, pharmacology and, more in general, in bio-nanotechnology. In my lecture I will present an overview of the subject to then focus on specific cases we are working on in our Lab [5-7].

Fig. 1 - Living cell under attack by ionic liquids (ILs). A deep knowledge of ILs-biomolecules interactions can then lead to unprecedented applications in bio-nano-technology. Figure taken from Ref. [4]

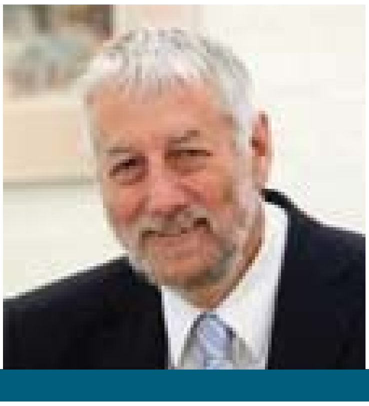


References:

[1] Benedetto A, Ballone P (2016) ACS Sustainable Chem Eng 4:392-412
[2] Benedetto A, Ballone P (2016) Phi Mag 96:870-894
[3] Benedetto A (2017) Biophys Rev 9:309-320
[4] Benedetto A, Galla HJ (2018) Biophys Rev 10:687-690
[5] Benedetto A, et al. (2014) J Phys Chem B 118:12192–12206
[6] Rotella C, Kumari P, Rodriguez B, Jarvis S, Benedetto A (2018) Biophys Rev 10:751-756
[7] Benedetto A, Ballone P (2018) Langmuir, 34:9579-9597

SHORT BIOGRAPHY

Antonio Benedetto was born in Padua, Italy, in August 1984. He is a Science Foundation Ireland PI based at the School of Physics, University College Dublin, Ireland, and an associate at the Laboratory for Neutron Scattering, Paul Scherrer Institut in Switzerland. As an invited scientist, he regularly visits several of the largest neutron facilities worldwide, i.e., Institute Laue-Langevin (FR), Rutherford Appleton Laboratory (UK), National Institute of Standards and Technology (USA), Oak Ridge National Laboratory (USA), and Heinz-Maier-Leibnitz Zentrum (DE). In 2011, he obtained his Ph.D. in physics with the mention of Doctor Europaeus (University of Messina, Italy) defending a thesis on protein dynamics with the experimental part carried out at the Institute Lau-Langevin in Grenoble, France. His Ph.D. thesis has been awarded two national prizes by the Italian Chemical Society and by the Italian Biophysical Society, respectively. In March 2012, supported by an individual Endeavour Research Fellowship of the Australian Government, he moved “down under”, joining the Bragg Institute and the University of Sydney. In September 2012, supported by a Marie Curie Individual Fellowship of the European Commission, he joined the School of Physics, University College Dublin (UCD) in Ireland. At this time, he started to work on the interaction between ionic liquids and phospholipid bilayers. In January 2015, supported by another Marie Curie Fellowship, he moved to the Paul Scherrer Institute (PSI) in Switzerland. At PSI, he extended his interest in ionic liquids towards their effect on biomolecules at large. In January 2017, he came back to UCD School of Physics supported by a Start Investigator Research Grant awarded by Science Foundation Ireland.



Wed., 26 September 2018, 10.00 – 10.40

Graham J. Hutchings

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CATALYSIS USING NANOMATERIALS

Catalysis is of crucial importance for the manufacture of the goods and infrastructure necessary for the effective wellbeing of society. Catalysis underpins the manufacture of most good as they need a catalyst for their manufacture at some point. In this way catalysis contributes towards over 25% of global domestic product. Hence designing new catalysts is a topic of intense research interest in the scientific community. For example, the identification that gold in nanoparticulate form is an exceptionally effective redox catalyst has paved the way for a new class of active catalysts. Alloying gold with other metals can enhance the activity and these catalysts are effective for the oxidation of alcohols and hydrocarbons as well as the direct synthesis of hydrogen peroxide. In this presentation the use of AuPd colloids for the selective oxidation of hydrocarbons will be used as an example of bimetallic catalysts and aspects of the latest research on topics involving new nanomaterials will also be presented

SHORT BIOGRAPHY

Special interest is in gold nanocrystals as novel active heterogeneous catalysts and their characterisation. Supporting gold on graphite or activated carbon makes catalysts that can oxidise alkenes with molecular oxygen under mild conditions. New gold palladium catalysts have been designed that can be used under inherently safe, non-explosive conditions. His group also works on environmental catalysis.

Wed., 26 September 2018, 10.40 – 11.20

Alexei R. Khokhlov

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MULTISCALE SIMULATION OF POLYMER NANOCOMPOSITES WITH CROSSLINKED MATRIX

One of the most promising organic-inorganic composite materials represents a polymer network (matrix) with incorporated filler nanoparticles (NPs), such as spherical silica NPs, surface-functionalized nanotubes, graphene, metal nanowires, etc. A common feature of this class of polymer nanocomposites (PNCs) is their structural heterogeneity, which occurs at different length scales, and the presence of a network-like architecture of the matrix with a complex topology of chemically connected and strongly entangled polymer chains. PNCs having both weakly and highly crosslinked matrix offer enormous opportunities to design novel material systems. In order to elucidate the structure–property relationships of these hybrid materials and provide the direct quantitative comparison between experiment and theory, molecular level modeling and simulation are required. Such simulations should normally use a computational strategy based on multiscale simulations. This strategy typically encompasses the following main stages: (i) coarse-gaining of atomistic structures; (ii) crosslinking the coarse-grained monomers or precursor polymers in the presence of embedded filler particles and the subsequent equilibration; (iii) reverse mapping of the coarse-grained model to an atomistic representation and its further equilibration and refinement; (iv) large-scale fully atomistic molecular dynamics simulations for predicting the materials properties. We will provide details in developing this multiscale simulation framework and illustrate its challenges and opportunities by demonstrating its applicability to the large-scale molecular simulation of bulk nanocomposite systems and randomly crosslinked networks.

SHORT BIOGRAPHY

Graduated with honors from MSU Faculty of Physics(1977); Candidate of Physics and Mathematics (1979); Doctor of Physics and Mathematics (1983), Academic Title of Professor (1988), Corresponding Member of the Russian Academy of Sciences(1990), Full Member of the Russian Academy of Sciences (2000); Member of Presidium of the Russian Academy of Sciences (2008).

Head of Laboratory of Physical Chemistry of Polymers, Nesmeyanov Institute of Organoelement Compounds, RAS (1991); Chair of Polymer Physics and Crystallophysics of MSU Faculty of Physics (1993). Head of the Polymer Council of RAS (2002), Member of the Advisory Council on Science, Education and High Technologies for the President of Russian Federation (2008). Alexei R. Khokhlov has been awarded Lomonosov Prize for Pedagogical Achievements(2005), Russian National Award in Science and High Technologies (2007) and a number of other Russian and foreign prizes.

Member of Academia Europaea (2000), Honorary Professor of a number of foreign universities.
Alexei R. Khokhlov is the head of a scientific school, the author of textbooks widely-known both in Russia and abroad. The range of his interests covers polymer science, statistical physics of macromolecules, physical chemistry of polyelectrolytes and ionomers, microphase separation in polymer systems, polymer liquid crystals, polyelectrolyte responsive gels, topological restrictions in polymer systems, dynamics of concentrated polymer solutions and melts, coil-globule transitions, associating polymers, computer simulation of polymer systems, biomimetic polymers, proton-conducting polymer membranes. His publications include works on both theoretical and experimental science, some of the former being classical in the field. Among others, he has proposed methods to synthesize “protein-like» copolymer sequences as well as macromolecules whose functional properties can be preset. The theoretical principles he developed have been successfully implemented in the field of oil extraction, in production of durable biocompatible polymers and new efficient catalysts to synthesize vitamins.

He is a member on a number of editorial boards and Editor-in-Chief of the Russian journal “Vysokomolekularnie Soedinenia” (High-molecular weight compounds).

Alexei R. Khokhlov has published over 500 scientific papers, 7 books and 25 article reviews.

Thu., 27 September 2018, 10.00 – 10.40

Richard Catlow

Department of Chemistry
University College London

MODELLING, SYNCHROTRON RADIATION AND NEUTRON SCATTERING STUDIES OF STRUCTURE, DYNAMICS AND REACTIVITY IN CATALYTIC SYSTEMS

Richard Catlow; Department of Chemistry, University College London; School of Chemistry, Cardiff University; UK Catalysis Hub, Research Complex at Harwell, UK

The concerted use of synchrotron, neutron and modelling techniques has proved to be a powerful approach in probing catalytic structures and processes at the molecular level. We will illustrate the approach by recent applications to a range of systems including:

- Hydrocarbon dynamics and reactivity in microporous catalysts, where we will describe how the concerted use of modelling with neutron spectroscopy can yield unique information on molecular transport and reactivity in hydrocarbon synthesis and auto-exhaust catalysts.
- Structural and electronic properties of nano-particulate catalysts where the focus will be on the combination of modelling with synchrotron techniques in developing detailed structural models of supported nano-particles.
- Carbon dioxide and methane activation on oxide and carbide catalysts where the focus will be on developing models for the activation mechanisms.

We will discuss how this powerful combination of techniques might be applied more widely in catalytic science.

SHORT BIOGRAPHY

Richard Catlow's scientific programme develops and applies computer models to solid state and materials chemistry - areas of chemistry that investigate the synthesis, structure and properties of functional materials. His approach applies powerful computational methods with experiment, to contribute to areas as diverse as catalysis and mineralogy. His approach has also advanced our understanding of how defects in the atomic level structure of solids can play a key role in modifying the electronic, chemical and mechanical properties of solids.

His work has offered insight into the behaviour of nuclear fuels under irradiation and to the molecular mechanisms underlying industrial catalysis, especially involving microporous materials and metal oxides, in structural chemistry and mineralogy. Simulation methods are now routinely used to predict the structures of complex solid materials.

His work has been extensively published and cited with over 1000 research articles and several books and reviews.

He has worked extensively on collaborative projects with the developing world, especially in Africa and was elected Foreign Secretary of the Royal Society- the Academy of Sciences of the UK and Commonwealth - in 2016.

Thu., 27 September 2018, 10.40 – 11.20

Alexander V. Kabanov

Director, Center for Nanotechnology in Drug Delivery Mescal S. Ferguson Distinguished Professor at UNC Eshelman School of Pharmacy Co-Director, Carolina Institute for Nanomedicine

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HYPERLOADED POLY(2-OXAZOLINE) MICELLES AS DRUG CARRIERS FOR CANCER THERAPY

Polymeric micelle (PM) drug carriers were invented a quarter of century ago.[1] Today nearly a dozen of drug formats based on PM undergo clinical trials and one product, Genexol-PM, a PM Paclitaxel, was approved for cancer therapy in South Korea.[2] The value proposition of PM drugs include increased drug solubility, passive distribution and targeting to disease sites as well as increased drug activity with respect to multidrug resistant cancers and cancer stem cells (CSC).[3] Poly(2-oxazoline) PM display unprecedented high loading with respect to insoluble drugs.[4] This PM platform has been validated across dozens of very poorly soluble active pharmaceutical ingredients (APIs) of different classes. The technology greatly enhances the solubility and stability of drugs (by a factor of 10,000 to 100,000 times), improves efficacy and safety and widens the therapeutic window. One example is a Cremophor-free Paclitaxel in poly(2-oxazoline) PM, which uses much less excipient and is safer than Abraxane, Genexol PM or any other Paclitaxel format on the market or under development.[5] Favorable in vitro and in vivo safety profiles and a higher maximum tolerated dose compared to clinically approved formulations are demonstrated along with higher exposure of the tumor the to drug and increased efficacy in animal tumor models. A pipeline of products under development includes single drugs and co-formulated drugs combination with excellent activity in treatment of both prevalent and orphan disease. A computational model for reliable selection of hydrophobic APIs with dramatically improved solubility in PM system is available to enhance the throughput and success of formulation development for new APIs. For many APIs, poly(2-oxazoline) PM represents the only possibility for a parenteral drug application. Poly(2-oxazoline) PM for concurrent delivery of multiple drugs display slowed-down drug release, improved blood pharmacokinetics, and increased tumor distribution of co-loaded drugs.[6] Superior antitumor activity of co-loaded drug PM micelles compared to single drug micelles or their combination as well as free drug combination was demonstrated using several cancer models. The drugs co-loading in PM improves the treatment outcomes of drug combination. The work has been supported by the United States National Institutes of Health (UO1 CA151806, 1U54CA198999).

SHORT BIOGRAPHY

Born March 27, 1962 in Moscow. Graduated from M. V. Lomonosov Moscow State University (MSU) in 1984, where also received Ph.D. in 1987 and D.Sc. in 1990. Scientific career has started in Soviet Union in MSU and continued in United States first, in the University of Nebraska Medical Center (UNMC), Omaha, Nebraska (1994-2012) where he founded the first academic nanomedicine center in the United States (2004-), and then in the University of North Carolina at Chapel Hill (2012-), where he is now a Mescal S. Ferguson Distinguished Professor, Director, Center for Nanotechnology in Drug Delivery, and Carolina Institute for Nanomedicine. Kabanov research has introduced polymeric micelles, DNA/polycation complexes (polyplexes), block ionomer complexes, nanogels, nanoparticle-macrophage carriers and exosomes for delivery of small drugs, nucleic acids and polypeptides to treat cancers and diseases of the central nervous system. Co-invented the first polymeric micelle drug to enter clinical trials. Published over 300 scientific papers, cited over 31,000 times (Hirsh index 94). Named the Thomson Reuters 2014 Highly Cited Researcher. Trained over 65 graduate students and postdocs. Cumulative research support has been over $115 M in grants and over $60 M in private investment and industry-sponsored R&D funding. Holds 34 US patents and co-founded several companies, most recently, SoftKemo/BendaRx, Ostrea and delAQUA. Founded the first nanomedicine symposium series in the United States, NanoDDS, chaired/co-chaired two Gordon Research Conferences. Elected member of Academia Europaea (MAE) and fellow of NAI, CRS and AIMBE, among other distinctions. A recipient of a Russian Megagrant and professor at MSU where he has established a laboratory with the megagrant support in 2010.

References:
1 H. Bader et al. Angew. Macromol. Chem. 1984, 123/124:457; A. Kabanov et al. FEBS Lett. 1989, 258:343; M. Yokoyama et al. Cancer Res. 1990, 50:1693.
2 M. Yokoyama et al. J. Exp. Clin. Med. 2011, 3:8.
3 E.V. Batrakova, A.V. Kabanov, J. Control. Release 2008, 130(2):98.
4 T. Lorson et al. Biomaterials. 2018, 178:204.
5 R. Luxenhofer et al. Biomaterials 2010, 31:4972; A. Schulz et al. ACS Nano 2014, 8 (3):2686; Z. He et al. Biomaterials 2016, 101:296
6 Y. Han et al. Mol. Pharmaceutics 2012, 9:2302; Wan et al. ACS Nano. 2018, 12(3):2426.

Thu., 27 September 2018, 11.50 – 12.30

Victor I. Ovcharenko

International Tomography Center, Novosibirsk
Director of the International Tomography Center,
Head of the Molecular Magnets Department at the moment,
Head of the Multispin Coordination Compounds Laboratory at ITC

BREATHING CRYSTALS AS MULTIFUNCTIONAL HETEROSPIN COMPOUNDS

Multifunctionality of a specific group of heterospin complexes based on transition metal complexes with stable nitroxides is under discussion. When the temperature (or/and pressure) changes, heterospin single crystals undergo structural rearrangements accompanied by magnetic effects similar to spin crossover. The observed anomalies are caused by the reversible spatial dynamics of Jahn-Teller coordination units containing heterospin exchange clusters. The high mechanical stability of the crystals, i.e., their ability of being reversibly compressed and expanded in the temperature range of phase transition, underlies the term «breathing crystals.» They are promising compounds that can serve as a new type of actuators and highly sensitive sensors to the external pressure.

SHORT BIOGRAPHY

Field of scientific interest: Coordination chemistry of free radicals, design of molecular magnets, spin transitions.

Research results: development of methods of selective synthesis of highly dimensional heterospin systems from coordination compounds of metals with stable organic radicals; investigation of magnetostructural correlations inherent in heterospin compounds, design of novel magnetic materials - molecular magnets; ‘breathing crystals’ were discovered.

Awards: Russian Federation State Prize winner (1994).
Publications: Over 280 publications.

Mon., 24 September 2018, 11.50 – 12.20

Vladimdir P. Fedin

Professor, Corresponding Member of the Russian Academy of Sciences
Director
Nikolaev Institute of Inorganic Chemistry SB RAS
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MULTIFUNCTIONAL POROUS COORDINATION POLYMERS

Lying on the crossing of fundamental inorganic/organic chemistry and development of novel materials, metal-organic frameworks (MOFs) has become one of the most attractive research fields during the past two decades. MOFs can be regarded as multifunctional materials due to a wide range of important properties. Here we describe our results on synthesis, structural characterization and investigation of multifunctional materials based on porous coordination polymers.

Substitution of ligands in $[Li_2Zn_2(piv)_6(py)_2]$ with bpy and terephthalate bridges (R-bdc^{2-}, R = H, Br, NH_2, NO_2) results in a series of isoreticular porous frameworks $[Li_2Zn_2(R\text{-}bdc)_3(bpy)]$ [1]. The introduction of different substituents R onto the terephthalate linkers affects the free volume of the porous compounds and the N_2 adsorption behavior. The CH_4 and CO_2 adsorption and relative selectivities have been investigated in detail, and interestingly, a fascinating interplay of luminescence properties with wavelength of excitation and nature of the host aromatic guest molecules has been observed. Moreover, such compounds demonstrate very high selectivity in the processes of separation of benzene and cyclohexane [2].

For the first time we report synthesis of MOFs based on Re_6 clusters. The frameworks demonstrate excellent CO_2/N_2 and CO_2/CH_4 selectivity, red luminescence, paramagnetic behavior and an ability to react with oxidizing agents due to the presence of redox-active cluster fragment. The oxidation of cluster nodes changed dramatically properties of the framework, and this process if fully reversible [3].

Our work was supported by the Russian Science Foundation (Grant No. 14-23-00013) and the Russian Foundation for Basic Research (Grant No. 18-53-77001).

References:

[1] A. A. Sapianik et al., Inorg. Chem., 56, 1599 (2017).

[2] A. A. Sapianik et al., 2018, submitted.

[3] Yu. M. Litvinova et al., Inorg. Chem., 57, 2072 (2018).

SHORT BIOGRAPHY

Vladimir P. Fedin received his M.Sc. degree in 1976, and PhD degree in 1980 from Department of Chemistry, Moscow State University. Since 1981 he holds permanent position at Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, and since 2005 he is Director. Since 1991 he worked for two years as a postdoctoral research fellow with Prof. Dr. A. Müller (AvH Fellowship, University of Bielefeld, Germany). In 1994-1995 he worked with Prof. T. Saito (JSPS Fellowship, University of Tokyo). He received several awards including Leading Scientific School Award from President of the Russian Federation in 2012 and 2016, Chugaev Prize of the Russian Academy of Sciences in 2015. He was visiting/invited professor at University of Versailles (France), University of La Laguna (Spain), University of Karlsruhe (Germany), and University of Bielefeld (Germany).

Prof. Dr. V. P. Fedin is editor of Journal of Structural Chemistry (2017). He is advisory board member of Russian Journal of Inorganic Chemistry, Journal of Cluster Science, and Russian Chemical Bulletin. He also served as a Panel member for European Research Council Advanced Grants.

Prof. Dr. V. P. Fedin's research interests include (1) Development of cluster and polyoxometalate chemistry; (2) Supramolecular chemistry of cucubiturils, (2) Synthesis and functional properties of metal-organic framework based materials.

Mon., 24 September 2018, 12.20 – 12.50

Oleg V. Ozerov

Organometallics, Catalysis, Energy
Texas A&M University, Department of Chemistry Professor

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NEW CHEMISTRY WITH BORON IN AND OUT OF PINCERS

Oleg V. Ozerov, Yihan Cao, Wei-Chun Shih, Loren P. Press, and Ming-Uei Hung
Department of Chemistry, Texas A&M University, College Station, TX 77845, USA

Pincer complexes of late transition metals have been widely used in studies of stoichiometric and catalytic activation of carbon-hydrogen and carbon-heteroatom bonds. Our group recently demonstrated the impressive potential of Ir pincer complexes in C-H bond borylation of terminal alkynes [1,2] and arenes [3]. Studies of transformations that involve metal-boryl intermediates where the boryl group originates from a reagent have led us to consider alternative approaches to bond activation that incorporate boryl donors into supporting pincer ligands [4]. We have discovered that activation C-H and other bonds of heteroatom-containing substrates is possible with unique selectivities relying on coordination of the heteroatom to the metal-bound boryl donor [5]. The current efforts are focused on optimizing this type of reactivity for catalytic applications.

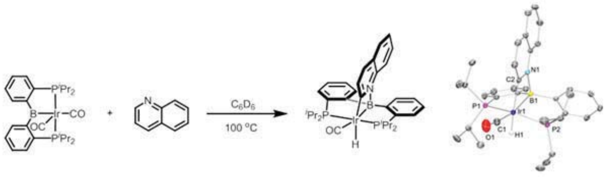

Figure 1. Selective C-H activation of quinoline.

References:

[1] Lee, C.-I; Zhou, J.; Ozerov, O. V. J. Am. Chem. Soc. 2013, 135, 3560-3566.
[2] Lee, C.-I; DeMott, J. C.; Pell, C. J.; Christopher, A.; Zhou, J.; Bhuvanesh, N.; Ozerov, O. V. Chem. Sci. 2015, 6, 6572-6582.
[3] Press, L. P.; Kosanovich, A. J.; McCulloch, B. J.; Ozerov, O. V. J. Am. Chem. Soc. 2016, 138, 9487-9497.
[4] Shih, W.-C.; Gu, W.; MacInnis, M. C.; Timpa, S. D.; Bhuvanesh, N.; Zhou, J.; Ozerov, O. V. J. Am. Chem. Soc. 2016, 138, 2086-2089.
[5] Shih, W.-C.; Ozerov, O. V. J. Am. Chem. Soc. 2017, 139, 17297-17300.

SHORT BIOGRAPHY

Oleg was born in Novosibirsk, Russia in 1976. He spent most of his early childhood there, in the district of Akademgorodok, a Siberian scientific center. In 1979-81 he and his family spent two years in Mozambique. In 1986, Oleg's family moved back to Moscow. Oleg attended School #130 in Novosibirsk, and School #79 in Moscow as well as the Moscow Chemical Lyceum (aka MCL or MHL).

In 1992, Oleg started his studies in the Higher Chemical College of the Russian Academy of Sciences (aka HCC or VHK) as part of only third entering class. During his first year in college, Oleg joined the laboratory of Professor Nikolai Ustynyuk in the Nesmeyanov Institute of Organo-Element Compounds (aka INEOS) as an undergraduate researcher. In the Ustynyuk group, Oleg gained experience working with vinylidene complexes of manganese. In 1995, Oleg spent a summer doing research on organosilicon dendrimers at the University of Kentucky in the laboratory of Professor Folami Ladipo. Oleg then returned to Russia to finish his coursework at HCC. Encouraged by the positive experience at UK and the appeal of Lexington, Oleg returned to UK in the Fall of 1996 to start his Ph.D. studies while remaining an HCC student on leave. He obtained his chemistry Diploma at HCC in 1998. Oleg's research in Kentucky focused on unusual steric effects of modified calixarene ligands in the chemistry of titanium. He defended his Ph.D. dissertation in the Spring of 2000.

Upon graduation, Oleg moved to Bloomington, Indiana to join the group of Professor Ken Caulton as a postdoctoral associate. Oleg's investigations in the Caulton group delved into the new chemistry of ruthenium and rhenium in a pincer ligand context. Among other things, Oleg was the group solvent czar during his postdoctoral spell.

In the spring of 2002, Oleg accepted an offer to join the Department of Chemistry at Brandeis University as an assistant professor of chemistry. He arrived in July of the same year to assume his new position. Oleg was promoted to the rank of associate professor with tenure in 2006. In January of 2009, Oleg relocated to Texas A&M University where he is now Professor of Chemistry. His research interests are in synthetic organometallic chemistry and its applications in catalysis and energy-related problems. Since 2011, Oleg has served as his department's Graduate Recruitment Coordinator.

- ACS Award in Pure Chemistry, 2012 (See announcement)
- Norman Hackerman Award in Chemical Research, 2012 (See announcement or tribute film)
- Camille Dreyfus Teacher-Scholar, 2007
- Alfred P. Sloan Research Fellowship, 2006
- Research Innovation Award, 2003
- Editorial Advisory Board Member, Chemical Science
- Associate Editor, Inorganic Chemistry Frontiers

Mon., 24 September 2018, 12.50 – 13.20

Nikolay E. Nifantiev

**N.D. Zelinsky Institute of Organic Chemistry RAS,
Moscow, Russia**

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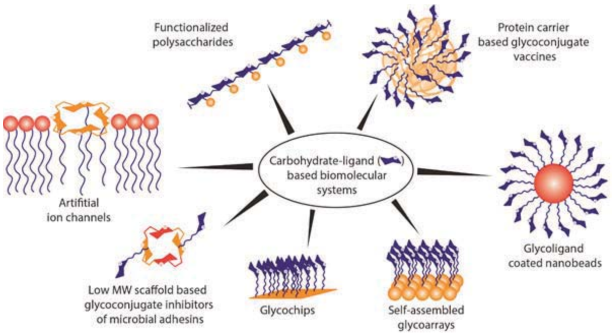
INTERDISCIPLINARY STUDIES OF CARBOHYDRATE BASED BIOMOLECULAR SYSTEMS

Marina L. Gening, Vadim B. Krylov, Dmitry V. Yashunsky, Nadezhda E. Ustyuzhanina, Elena A. Khatuntseva, Elena V. Sukhova, Maria I. Bilan, Anatolii I. Usov, Alexander S. Shashkov, Alexander O. Chizhov, Alexander A. Karelin, Yury E. Tsvetkov, Bozhena S. Komarova, Alexey G. Gerbst, Nikolay E. Nifantiev

After the tremendous impact of Genomics and Proteomics approaches in drug discovery many key directions in this field are associated with Glycomics research. In this report, an overview of our contribution to the studies of carbohydrate based biomolecular systems will be given which covers the development of innovative approaches for preparation of biologically important oligosaccharide derivatives structurally related to polysaccharide antigens of bacterial and fungal pathogens, polysaccharide engineering, design of carbohydrate vaccines of the 3rd generation, advances in glycoarray technologies in relation to infection diagnostics tools and other systems illustrated below.

The work was financially supported by the RSF grants 14-50-00126 and 14-23-00199 by using experimental infrastructure of the biochemical research unit, which was set up in Zelinsky Institute within the framework of the RSF project 14-50-00126.



SHORT BIOGRAPHY

Nikolay E. Nifantiev (born: October 12, 1958 in Krasnoyarsk, USSR) studied chemistry in M.V. Lomonosov Moscow State University and then received his Ph.D. in 1984 in academician N.K. Kochetkov's laboratory in N.D. Zelinsky Institute of organic chemistry, Russian Academy of Sciences. After certain years in the same lab and training outside the country (Germany, Denmark) he established new research unit at N.D. Zelinsky Institute - the Laboratory of glycoconjugate chemistry.

Professor Nifantiev has published 350+ papers mainly within the area of the synthesis, NMR, and conformational studies of oligo- and polysaccharides. Recent interests have focused on the development of the computer-assisted method of structural analysis of regular polysaccharides, elaboration of new materials of practical importance from natural polysaccharides (chitosan, fucoidans, fucosylated chondroitin sulfates, arabinogalactan, cyclooligosaccharides), the synthesis of complex oligosaccharides and neoglycoconjugates of medical interest, study of the topology of carbohydrate-protein binding and computer design of the inhibitors of carbohydrate binding proteins, development of glycoconjugate vaccines and diagnostic test-kits.

Professor Nifantiev was elected to be the Corresponding Member of the Russian Academy of Sciences (from 2011) and Titular Member of the International Union of Pure and Applied Chemistry (IUPAC) where he also serves as the Chair of Sub-committee on Organic Synthesis (2016-2019). He is the representative of Russia in the International Council for Science; member of Russian Chemical and Biochemical Societies. Member of the Editorial Boards of the Journal of Carbohydrate Chemistry (from 1999), Russian Journal of Bioorganic Chemistry (from 2001) and Russian Chemical Bulletin (from 2009). He is the Chairman of Scientific Council on Organic Chemistry at the N.D. Zelinsky Institute, deputy-Chair of Scientific Council on Organic Chemistry, Russian Academy of Sciences. He is also the member of Scientific Council on Chemistry, Russian Foundation for Basic Research and recipient of Russian State prize for junior researchers (1988) and M.M. Shemiakin prize of Russian Academy of Sciences (2012).

Mon., 24 September 2018, 15.35 – 16.05

Herbert W. Roesky

Professor Emeritus
University of Goettingen, Institute of Inorganic Chemistry,
Tammannstrasse 4, 37077
Goettingen, Germany

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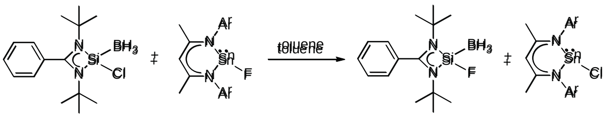
ATTRACTIVE NEW CHEMISTRY OF SILICON FLUORIDES AND ITS CONGENERS

The first preparation of SiF_2 was reported by Timms and Margrave in 1972 from SiF_4 and silicon.

$$SiF_4 + Si \rightarrow 2\ SiF_2$$

The reaction was conducted in a temperature range of 1100-1400 °C. The SiF2 is stable at high temperatures but condenses at room temperature to a polymeric material of unknown structure.

We used also SiF_4 as a precursor and reduced the cAAC•SiF_4 with two KC_8 in the presence cAAC to obtain the $(cAAC)_2$•SiF_2. This compound is stable at room temperature. The reduction of cAAC•SiF_4 with KC_8 in the ratio of 1:1 resulted in the stable radical cAAC•SiF_3. The single crystal X-ray structural analysis of both compounds will be presented. Another silicon(II)fluoride was accessible by chloride fluoride exchange, when the lone pair at the silicon was blocked by the Lewis acid BH_3.



Moreover, we prepared also the carbonyl adducts of group 6 (Cr,Mo,W) instead of using BH3. These metal complexes are exchanging chloride to fluoride without decomposition.

Finally a few soluble fluorides of low valent tin and germanium will be discussed. Especially the amidinate-tin(II)fluoride turned out to be an efficient fluorinating reagent. The cAACPLi•(thf)2 dimer reacts with fluorinated carbon compounds as well as with SiCl4 and GeCl4 under elimination of LiF and LiCl, respectively, to the corresponding phosphinidene derivatives.

SHORT BIOGRAPHY

1961 Diplom Thesis:
«Construction of a Thermo-Balance»
1963 Ph. D. Thesis:
«Fluorination Reactions under High Pressure»
1965 Postdoc with DuPont, Wilmington, Delaware, USA
«Aluminum and Coordination Chemistry»
1967 Habilitation Thesis
«Chemistry of Substituted Phosphates»
1970 Universitätsdozent
1971 - 1980 Professor of Inorganic Chemistry at the Johann-Wolfgang-Goethe-Universität,Frankfurt am Main
1973 - 1976 Director of the Institute of Inorganic Chemistry at the J.-W.-G. Universität, Frankfurt am Main
1980 - 2003 Director of the Institute of Inorganic Chemistry of the Georg-August-Universität Göttingen
1985 - 1987 Dean of the Fachbereich Chemie, GeorgAugust-Universität Göttingen
2003 Professor Emeritus

MAJOR AWARDS

1960 Wöhler - Award
1970 Dozenten - Award of the Fonds der Chemischen Industrie
1985 Centenary Lecturer, Royal Society of Chemistry
1985 Award of the Minister of Sciences in France
1986 French Alexander-von-Humboldt-Award
1987 Leibniz-Award
1990 Alfred-Stock-Memorial Award
1994 Manfred and Wolfgang Flad Award
1995 Literature Award of the Fonds der Chemischen Industrie
1998 Carus Medal of Leopoldina
1998 Carus Award of the City of Schweinfurt
1998 Grand Prix de la Fondation de la Maison de la Chimie
1998 Wilkinson Prize
1999 ACS Award for Creative Work in Fluorine Chemistry
2004 Rao Award of the Chemical Research Society of India
2004 ACS Award in Inorganic Chemistry
2004/2005 Wittig-Grignard-Award, France
2009 Prix International Henri Moissan
2012 Heinrich Rössler Preis
2013 Annual Award for Chemistry, Institute of Chemistry of Ireland
2015 Blaise Pascal Medal, European Academy

Mon., 24 September 2018, 16.05 – 16.35

Alexander Yu. Stakheev[1],
Valery I. Bukhtiyarov[2]

[1] Zelinsky Institute of Organic Chemistry RAS, Moscow, Russia
[2] Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

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METAL PARTICLE SIZE EFFECTS: AN INTERFERENCE OF ACTIVATION AND ADSORPTION FACTORS

High metal dispersion improves utilization of noble metal. On the other hand, reactivity of the surface atoms may depend significantly on the size of metal particles, since changes in the metal particle size lead to alterations of the relative ratio between edges, corners and terrace atoms, as well as changes in the electronic structures. Therefore, turnover frequency (TOF), defined as the activity per unit of exposed surface, can become dependent on the size of metal particle (particle size effect). As a result, the overall activity of the catalyst becomes a function of two major factors: (1) metal dispersion (fraction of exposed atoms) and (2) the particle size effect, which requires careful management of metal particle size for achieving optimal performance and/or minimizing noble metal loading.

The discussion of the relationship between particle size and TOF will be based on the concept proposed by Van Santen et al. [1], which rationalizes the relationship of TOF of catalytic reactions on transition-metal particle size. The concept emphasizes the dependence of the rate-limiting activation stage and the geometry of the appropriate surface active site. In this lecture particular focus will be given on the chemisorption of the reacting molecules on metal nanoparticle surface and the impact of this factor on TOF. The lecture will concentrate on the impact of chemisorption on the reactivity of metal surface atoms neglecting metal-support interface phenomena. It will be shown that in the case of small metal particles (< 3-4 nm) adsorption and/or strong structural modification of the nanoparticle surface may dominate the activation stage and the observed TOF significantly deviate from "TOF – particle size relationship" predicted by the theory [1].

References:

[1] R. A. van Santen, M. Neurock, S. G. Shetty, Chem. Rev. 110, 2005 (2010)

SHORT BIOGRAPHY

Prof. Alexander Stakheev was graduated from Moscow State University, Chemical Depertment. Now he is the Deputy Director of the N. D. Zelinsky Institute of Organic Chemistry Russian Academy of Sciences (Russia). His main field of interest is the catalysis by supported metal or oxide nanoparticles for environmental protection.

Prof. Stakheev is a member on editorial boards of "Kinetics and Catalysis" and "Russian Chemical Reviews", and a Board Member and the representative of Russia in European Federation of Catalytic Society (EFCATS). In 2016 the Russian Academy of Sciences awarded him the Balandin Prize for the outstanding research on the methods for controlling the catalytic properties of supported metal catalysts in hydrogenation and oxidation reactions.

Mon., 24 September 2018, 16.35 – 17.05

Viatcheslav V. Jouikov

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ELECTROCHEMICAL GRAFTING TO CARBONACEOUS MATERIALS: FROM MODIFIED ELECTRODES TO ARTIFICIAL GRAPHITE

The ubiquitous paradigm of grafting to carbon-based materials via diazonium salt reduction is most largely used one in surface derivatization [1]. However, it considers these materials as passive substrates only, exploiting their C_{sp2} inclusions as the sites for radical addition. Recently, nucleophilic [2] and electrophilic [3] methods of grafting to electrochemically activated polyaromatics have been introduced allowing efficient and simple ways of surface modification through the covalent attachment of various functional groups, redox or spin markers. Combining these two methods with using ambifunctional grafting agents like Me_3SiCH_2I, $Me_3SiC{\equiv}CCH_2Br$ and others [4], a layer-by-layer assemblage of a new stratified material, «artificial graphite» with on-demand interstitial distances, as well as of sponge-like carbonaceous materials based on carbon nano forms (CNT, fullerene, graphene) became possible. The principles of these methods and the examples of their application will be discussed.

References

[1] F.I. Podvorica, In: Aryl Diazonium Salts, Ed. M. Chehini, Wiley-VCH, 2012, 255.

[2] V. Jouikov, J. Simonet, Electrochem. Comm., 2014, 45, 32-36.

[3] V. Jouikov, J. Simonet, Langmuir, 2013, 29, 5556–5562.

[4] (a) V. Jouikov, J. Simonet, Electrochem. Comm. DOI.org/10.1016/j.elecom.2018.06.004. (b) A. Farhati, M. Syroeshkin, M. Dammak, V. Jouikov, Electrochem. Comm. 2018, submitted. (c) A. Farhati, PhD Thesis, University of Rennes 1, 2018.

SHORT BIOGRAPHY

Viatcheslav Jouikov was born in Russia. He received his Ph.D. and D.Sc. degrees from Kazan University and after several periods at the Universities Paris 7, Bordeaux I, Clermont-Ferrand and the University of Arizona, in 2000 he was appointed as Professor at the University of Rennes I where his work focuses on the electron transfer reactions of group 14 organometallics, molecular electrochemistry, and electrochemical functionalization of conducting interfaces.

Mon., 24 September 2018, 17.05 – 17.35

Marina Yu. Balakina

Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS
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DEVELOPMENT OF POLYMER MATERIALS WITH QUADRATIC NONLINEAR-OPTICAL ACTIVITY

Organic polymer materials, exhibiting quadratic nonlinear optical (NLO) response to the applied electric field, are at the forefront of research activities in the field of new functional materials, in particular, those for use in photonics and optoelectronics. The NLO response of such material is formed at the molecular level, its sources being organic chromophores incorporated into the material by various ways. As material should be non-centrosymmetric to exhibit quadratic NLO response, chromophore ordering in the material is performed in the applied electric field, the degree of orientation being controlled by the UV-Vis spectroscopy [1]. We consider also the alternative way of chromophores ordering via non-covalent interactions between chromophores as well as with polymer matrix, using atomistic (Monte-Carlo conformational search, molecular dynamics) and quantum chemical modeling (DFT and MP2) [2,3] and various spectroscopic techniques (IR, Raman and UV-Vis [4].

We have developed a number of polymer NLO materials on the basis of two classes of polymers, epoxy-amine and methacrylic ones, of various structure: epoxy-amine oligomers with azochromophores in the main chain (CFAO) [1] and in the side chain of different structures (OAB-DR1 [5], OAB-DF [6]), methacrylic copolymers of branched (BM-DR1) [7] and linear structure (MMA-MAZ) [8] with azochromophores in the side chain.. Our recent research consists in the design and fabrication of new classes of organic dipole chromophores containing quinoxaline π-conjugated bridge [9] and/or indolizine donor moiety [10].

NLO coefficients of the developed materials were measured by Second Harmonic Generation technique (π=1064 nm), the obtained values being rather high: 62 pm/V for CFAO, 40 pm/V for OAB-DF, 77 pm/V for BM-DR1, 60 pm/V for MMA-MAZ. Electro-optic coefficients were measured by ellipsometric Teng-Man technique (π=670 nm): 33 pm/V for BM-DR1, 27 pm/V for MMA-MAZ. Composite materials on the basis of PMMA with chromophores containing quinoxaline bridge demonstrate NLO coefficients exceeding 100 pm/V.

The financial support of Russian Scientific Foundation (grant number 16-13-10215) is gratefully acknowledged.

References

[1] T.A. Vakhonina, S.M. Sharipova, N.V. Ivanova, et al, Proceedings of SPIE, 2011, 7993, 799307(-8).
[2] M.Yu. Balakina, O.D. Fominykh, T.A. Vakhonina, IEEE Transactions on Dielectrics and Electrical Insulation, 2018, 25(3), 778-782.
[3] O.D. Fominykh, A.A. Kalinin, S.M. Sharipova, et al. Dyes and Pigments, 2018, 158, 131-141.
[4] T.I. Burganov, S.A.Katsyuba, T.A. Vakhonina, et al. J. Phys. Chem. C, 2018, 122, 1779.
[5] G.N. Nazmieva, T.A. Vakhonina, N.V. Ivanova, et al. Europ. Pol. J., 2015, 63, 207.
[6] G.N. Nazmieva, T.A. Vakhonina, N.V. Ivanova, et al. Polymer. 2018, 149, 253-265.
[7] T.A. Vakhonina, M.Yu. Balakina, G.N. Nazmieva, et al. Europ. Polym. J., 2014, 50, 158.
[8] T.A. Vakhonina, N.V. Ivanova, N.N. Smirnov, et al. Mendeleev Commun., 2014, 24, 138.
[9] A.A. Kalinin, S.M Sharipova, T.I. Burganov, et al. Dyes and Pigments. 2018. 156, 175-184.
[10] A.A. Kalinin, M.A. Smirnov, L.N. Islamova, et al. Dyes Pigm. 2017, 147, 444-454.

SHORT BIOGRAPHY

M.Yu. Balakina graduated from the Physics faculty of Kazan State University and received the Ph.D. degree from the Kazan Chemistry and Technology Institute in 1990. In 2009 she got Doctorate in chemistry (Habilitation) from A.E. Arbuzov Institute of Organic and Physical Chemistry. M.Yu. Balakina is the Head of the laboratory of Functional materials. Her research interests include development of polymer nonlinear-optical materials, design of novel chromophores and polymer electrets, analytical models for various electret properties and atomistic modeling of polymer systems and composite materials.

Mon., 24 September 2018, 17.35 – 18.05

Vladimir A. D’yakonov

**Institute of Petrochemistry and Catalysis
of Russian Academy of Sciences,
141Prospekt Oktyabrya, Ufa 450075, Russian Federation**

DyakonovVA@gmail.com

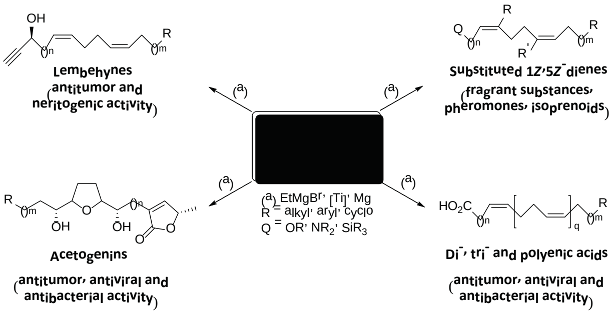
NEW METHODOLOGY FOR STEREOSELECTIVE CATALYTIC SYNTHESIS OF NATURAL ACIDS, LEMBEHYNES, AND ACETOGENINS - MODERN PREPARATIONS FOR MEDICINE

*V.A.D’yakonov, A.A. Makarov, R.A. Tuktarova, L.U. Dzhemileva, M.M. Yunusbaeva,
A.R. Salimova,S.R. Ishmukhametova, E.N. Andreev, U.M. Dzhemilev*

The report discusses the latest achievements of the authors in developing original methods for stereoselective synthesis of natural acetogenins, higher bis-methylene-separated(interrupted) di- and trienoic acids, lembehynes that are of exceptional interest as low-toxic target antitumor drugs, as well as compounds with neritogenic activity for treating neurodegenerative diseases.

The synthetic approaches to the above listed natural compounds are based on the use at the key stage of the synthesis, of new organometallic reactions, such as Ti-catalyzed homo- and cross-cyclomagnesiation of 1,2-dienes, discovered in the Laboratory of Catalytic Synthesis of the IPC RAS, involving available Grignard reagents.

The studies of the synthesized compounds for their antitumor and antibacterial activities in vitro were performed withthe use of unique equipment in “Centre for Molecular Design and Biological Screening of Candidate Substances for the Pharmaceutical Industry” at the Institute of Petrochemistry and Catalysis of RAS using modern methods such as flow cytofluorometry, fluorescence microscopy and western blotting.



In silico studies into regularities of the structural influence of the synthesized compounds on their antitumor activity were fulfilled with the use of molecular docking and molecular dynamics experiments.

For compounds that showed the greatest activity, in vivo tests were performed for linear mice with grafted malignant Lewis carcinoma.

This work was financially supported by the Russian Science Fundation(Grants 14-13-00263, 16-13-10172, 18-73-10030), Russian Foundation for Basic Research (Grants16-03-00543, 17-43-020502, 18-29-09068) and Grant of the RF President for the support of leading scientific schools(NS-5240.2018.3).

SHORT BIOGRAPHY

Vladimir A. D’yakonov was born in 1980 in Yakutia, Siberia, Russia, graduated from the Ufa State Petroleum Technical University in Ufa, Bashkortostan, Russia (2002) with an honors diploma, and obtained his Candidate, Ph.D. (2005) and Doctor of Science, Chemistry (2012) degrees from the Institute of Petrochemistry and Catalysis of Russian Academy of Sciences under the guidance of the Correspondent member of RAS, Prof. Usein M. Dzhemilev. His research interests include metal complex catalysis in organic and organometallic synthesis, the development of new catalytic synthetic methods based on transformations of strained molecules and metallacarbocycles, and the elaboration of simple “one-pot” operations for the preparation of various carbo-, hetero-, and macrocyclic compounds.

He was the facilitator of the issue ARKIVOC, 2011 (viii) and reviewer of a number of scientific journals, including Tetrahedron, Tetrahedron Letters, Organometallics, Journal of Organometallic Chemistry, Current Organic Chemistry, periodicals, and books. He is the author and co-author of 5 books, about more than 100 scientific articles and reviews. He also has more than 90 patents issued. His research interests include metal complex catalysis in the organic and organometallic synthesis, chemistry and stereochemistry of the strained and cage compounds, organic chemistry of nontrasition metals (Mg, Al, Zn, Ga, In) as well as chemistry of small, low-stable and highly strained molecules, including the development of new catalytic synthetic methods based on transformations of strained molecules and metallacarbocycles, and the elaboration of simple (“one-pot”) ways for the preparation of various carbo-, hetero- and macrocyclic compounds. Development of new synthetic methodologies for the synthesis of efficient human topoisomerase inhibitors.

Tue., 25 September 2018, 11.50 – 12.20

Igor L. Fedushkin

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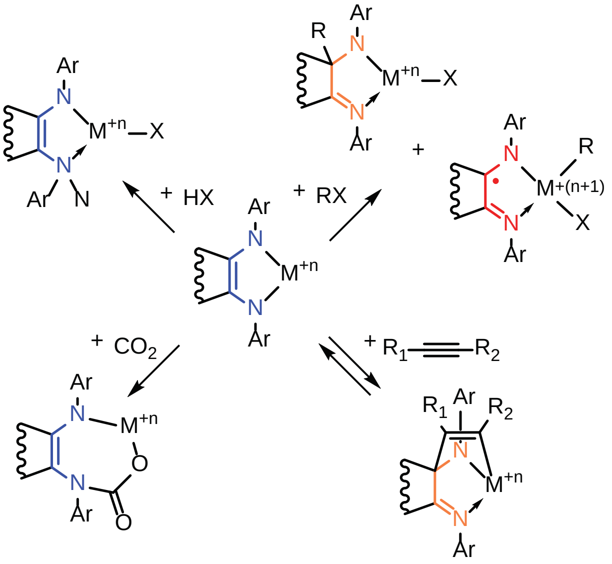
METAL COMPLEXES OF REDOX-ACTIVE LIGANDS FOR ORGANIC SYNTHESIS

Igor L. Fedushkin,a Vladimir A. Dodonov,a Alexandra A. Skatova,a Tatyana A. Koptseva,a Vladimir G. Sokolova

Redox-active ligands can substantially expand the reactivity of metal complexes, which can enable applications in catalysis. However, up to now, redox-active ligands were designed to construct complexes mainly just with transition metals, such as Ni, Co, and Fe, whose complexes with redox-active ligands may be alternatives for classical Pd, Pt, Rh, and Ru spectator ligand-based catalysts. Main-group metal complexes of redox-active ligands have also shown specific reactivity, but they have not yet been recognized as promising catalysts for organic synthesis. Here we communicate on the reactivity of group 2 and 13 metal complexes with redox-active 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian).

Acknowledgement: This work has been supported by the Russian Science Foundation (grant No. 14-13-01063).



SHORT BIOGRAPHY

Since 2016	Director of Razuvaev Institute, Chief Scientist of Razuvaev Institute
2013-2015	Vice-Director of Razuvaev Institute
2011	Elected Member of Russian Academy of Sciences
2010	Academic Title “Professor”
Since 2005	Head of laboratory at Razuvaev Institute
Since 2004	Professor of Organic Chemistry, K. Minin Nizhny Novgorod State Pedagogical University
2001	Habilitation in Organometallic Chemistry, N.I. Lobachevski University of Nizhny Novgorod
1989-2005	PhD Student, Junior/Ordinary/Senior Scientist at Razuvaev Institute
1994	PhD (M. Bochkarev), Organolanthanide Chemistry, G.A. Razuvaev Institute
1988	Diploma in Chemistry, University of Nizhny Novgorod¬

(INTER)NATIONAL FELLOWSHIPS, AWARDS, GRANTS

1998-1999	Alexander von Humboldt Fellowship
2003	Friedrich Wilhelm Bessel Prise
2004-2005	Grant “Young Doctors of Sciences” from Russian Science Support Foundation
2017-	Visiting professor North West University (Xian’, China/100 Talents Program)

PUBLICATIONS

118 scientific papers, 6 patents, over 2942 citations, h-index 33 (WoS, 08.09.2018)

RESEARCH FIELDS

Metal complexes with redox-active ligands; Main group metal based catalysts; Redox-isomerism in coordination compounds; Organometallic precursors of inorganic materials; Organolanthanides.

Tue., 25 September 2018, 12.20 – 12.50

Valentine P. Ananikov

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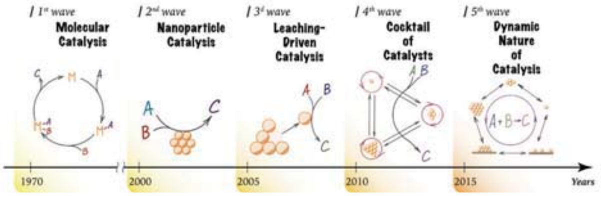
VIDEO MOVIES OF CATALYTIC PROCESSES IN SOLUTION, REACTION DYNAMICS, KNOWN AND UNKNOWN MECHANISMS

In recent decades, development of catalytic systems provided the major driving force for the paramount progress in the areas of pharmaceutical chemistry, access to new drugs, fine organic synthesis, chemical industry, fuels, biomass conversion, green and sustainable technologies, among many other directions.

Highly active molecular catalysts, involving a single metal atom surrounded by special organic ligands, have been ubiquitously utilized in synthetic procedures in the area of homogeneous catalysis. Metal nanoparticles stabilized on suitable supports were used in many industrial and research applications dealing with heterogeneous catalysis.

Attempts to understand the nature of the catalytic reactions revealed a very complicated mechanistic picture, the concept of which underwent several "waves" from the simple molecular catalysis to complex dynamic nanoparticle systems (Figure 1) [1].



In the present lecture, the complexity of catalytic cycles will be discussed with the main emphasis on the problems of reaction mechanisms, which could be solved using modern powerful analytic methods [1,2]. Understanding complex reaction mechanisms in catalysis is urgently required to develop a new generation of chemical technologies with improved efficiency, selectivity and practical utility.

SHORT BIOGRAPHY

Valentine Ananikov received his Ph.D. in 1999, Habilitation in 2003, and in 2005 he became Professor and Laboratory Head of the Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. In 2008 he was elected a Member of the Russian Academy of Sciences.

His research has been supported by grants of the President of Russia for young scientists (2004, 2007). He is recipient of the Russian State Prize for Outstanding Achievements in Science and Technology (2004), an Award of the Science Support Foundation (2005), a Medal of the Russian Academy of Sciences (2000), of the Liebig Lectureship from the German Chemical Society (2010), and the Balandin Prize for Outstanding Achievements in Catalysis (2010). In addition, he has been named Actively Cited Researcher – Russia by Thomson Reuters (2015), recipient of the Organometallics Distinguished Author Award Lectureship by the American Chemical Society (2016), and of the Hitachi High-Technologies Award in Appreciation for Novel Approaches and Outstanding Contributions to Setting New Standards for Electron Microscopy Applications in Chemistry (2016).

His educational activities include the MegaGrant research laboratory at St. Petersburg State University (since 2013) and his professorship at the Chemistry Department of Moscow State University (since 2012).

[1] Eremin D.B., Ananikov V. P., Coord. Chem. Rev., 2017, 346, 2-19; doi: 10.1016/j.ccr.2016.12.021.
[2] Kashin A. S., Degtyareva E. S., Eremin D. B., Ananikov V. P., Nature Commun., 2018, 9, 2936; doi: 10.1038/s41467-018-05350-x

Tue., 25 September 2018, 12.50 – 13.20

Andrei Malkov

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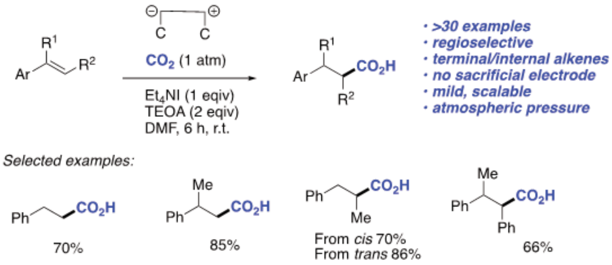
HARNESSING APPLIED POTENTIAL: THE REGIOSELECTIVE ANTI-MARKOVNIKOV HYDROCARBOXYLATION OF STYRENES

Andrei V. Malkov, Volodymyr Tabas, Benjamin R. Buckley

The construction of carboxylic acid compounds in a selective fashion, from low value materials such as alkenes remains a long-standing challenge to synthetic chemists. In particular, anti-Markovnikov addition to styrenes remains underdeveloped. Electrosynthesis has been widely studied within the electrochemical community, but represents an underused tool, with great potential for synthesis.1 As a direct result, there are currently only a few processes at the industrial or pilot-plant scale for the electrosynthesis of organic molecules.2 This presents electrosynthesis as a potential step changing technology, particularly since the use of electrons can be directly linked to many aspects associated with green chemistry.3 Herein we report a new electrosynthetic approach to the selective hydrocarboxylation of alkenes. The reported method allows direct access to carboxylic acids derived from terminal, di- and tri-substituted alkenes, in a highly regioselective manner. Plausible reaction mechanism will be discussed.



References:

1. Ritter, S. K. C&EN, Mar 13, 2017, p. 23.
2. Matthessen, R.; Fransaer, J.; Binnemans, K.; De Vos, D. E. Beil. J. Org. Chem. 2014, 10, 2484.
3. Frontana-Uribe, B. A.; Little, R. D.; Ibanez, J. G.; Palma, A.; Vasquez-Medrano, R. Green Chem. 2010, 12, 2099.

SHORT BIOGRAPHY

Andrei Malkov started his career with the award of MSs (Hons) from the Moscow State University (Russia) in 1982, which was followed by PhD studies at the Institute of Organo-Element Compounds (Moscow, Russia), successfully completed in 1986. He continued his work in the area of organometallic synthesis and catalysis, which intensified with his move to UK in 1992 where he had two postdoctoral spells at UEA (1992-1995) and the University of Leicester (1995-1999). He started his independent career in UK in the University of Glasgow in 1999 where he rose through the ranks to become Reader. In 2008 he was appointed as Professor of Organic Chemistry at Loughborough University.

- Fellow of the Royal Society of Chemistry (FRSC)
- British representative on the Management Committee of COST action ORCA (Organocatalysis, 2010-2014), budget controller for Short Term Scientific Missions
- Member of the Organising Committee of the International Symposium on Organometallic Chemistry Directed towards Organic Synthesis (OMCOS-15), Glasgow, 2009.
- Co-organiser of RSC International Symposium on Organocatalysis, Glasgow, 2006.
- Guest co-editor for the Tetrahedron Symposium-in-Print on Organocatalysis, issue 2-3, 2006.
- Referee for EPSRC, American Chemical Society Petroleum Fund and other funding agencies.
- Referee for Science, Angewandte Chemie, Journal of the American Chemical Society, Chemistry - A European Journal, Chemical Communications and others.
- External examiner for PhD examinations in UK and overseas.
- Member of the Editorial Board of the Journal of Amino Acid

Tue., 25 September 2018, 15.20 – 15.50

Charlotte K. Williams

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POLYMERIZATION CATALYSIS: POLYMERS FROM RENEWABLE RESOURCES

Catalysis plays a central role in the activation and use of renewable resources in polymer synthesis.1 Here, the renewable resources of interest include plant-derived monomers and the use of carbon dioxide as a raw material. The lecture will highlight recent work developing homogeneous metal complexes, featuring zinc/magnesium and first row transition metals for use in polymerization catalysis. In particular, discoveries that activity and selectivity are enhanced by controlling the ligand conformation and by the use of synergy in heterodinuclear catalysts will be highlighted.2-4

We have recently reported a series of catalysts that can selectively polymerize mixtures of monomers to deliver block sequence controlled copolymers.5-8 Key to the ability to selectively enchain from mixtures is the ability to switch the catalyst between different polymerization cycles/mechanisms (Fig. 1). Using this method, mixtures of epoxides/lactones/anhydrides and carbon dioxide are selectively enchained to provide multi-block copolymers. Central to the unusual performance of these catalysts is control over the inorganic chemistry of the metal-polymer chain end-group so as to switch and direct particular (block) polymer enchainment sequences. The catalyst syntheses, characterization and application data will be presented, including in situ spectroscopic and DFT studies. The catalysis allows the preparation of new block and alternating copolymers and their properties as degradable elastomers, shape memory polymers and specialty materials will be highlighted.

References

1. Zhu, Y.; Romain, C.; Williams, C. K., Nature 2016, 540 (7633), 354.
2. Thevenon, A.; Romain, C.; Bennington, M. S.; White, A. J. P.; Davidson, H. J.; Brooker, S.; Williams, C. K., Angew. Chem. Int. Ed. 2016, 55 (30), 8680.
3. Garden, J. A.; Saini, P. K.; Williams, C. K., J. Am. Chem. Soc. 2015, 137 (48), 15078.
4. Thevenon, A.; Cyriac, A.; Myers, D.; White, A. J. P.; Durr, C. B.; Williams, C. K., J. Am. Chem. Soc. 2018, 10.1021/jacs.8b01920.
5. Romain, C.; Zhu, Y.; Dingwall, P.; Paul, S.; Rzepa, H. S.; Buchard, A.; Williams, C. K., J. Am. Chem. Soc. 2016, 138 (12), 4120.
6. Zhu, Y.; Romain, C.; Williams, C. K., J. Am. Chem. Soc. 2015, 137 (38), 12179.
7. Stößer, T.; Williams, C. K., Angew. Chem. Int. Ed. 2018, 57 (21), 6337.
8. Zhu, Y.; Radlauer, M. R.; Schneiderman, D. K.; Shaffer, M. S. P.; Hillmyer, M. A.; Williams, C. K., Macromolecules 2018, 51 (7), 2466.

SHORT BIOGRAPHY

Professor of Inorganic Chemistry, Department of Chemistry, Oxford University (2016-current)

Research focuses on catalysis to make polymers, fuels and materials. In particular, we develop catalysts and processes enabling re-use/recycling of renewable resources, such as plants or carbon dioxide.

Research highlights include low pressure catalysts for carbon dioxide/epoxide copolymerization, stereocontrolled catalysts for lactide polymerization, switchable catalysis enabling selectivity from monomer mixtures, colloidal nanocatalysts for carbon dioxide reduction to methanol and discovery of the properties of polyesters/carbonates for applications spanning elastomers, coatings, medicine and electronics.

Tue., 25 September 2018, 15.50 – 16.20

Dr Laura Torrente

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A NOVEL MANUFACTURING TECHNOLOGY OF NANOMATERIALS

Department of Chemical Engineering and Biotechnology, University of Cambridge

Metal nanoparticles have stimulated the interest of the scientific and industrial community during the last decades due to their unique surface energy, reactivity and optical, electronic and magnetic properties. The field currently faces a number of challenges including the understanding of the size vs reactivity relationship, size control at large scale and their stabilisation under relevant conditions.

Our group is developing a novel manufacturing technology for the continuous synthesis of metal nanoparticles and nanostructured materials with exquisite size, shape and composition control based on microsystems. We exploit the opportunites offered by the laminar flow regime characteristic of micro-devices to prevent the agglomeration of the particles in the absence of capping ligands, while promoting transitional flows to lead to narrow size distributions. This approach constitutes a depart from previous strategies to narrow the size distribution during the continous synthesis of metal nanoparticles such as bi-phasic or Taylor flow systems in micro-reactors which require the use of stabilizing ligands.

By careful design of the reactors geometry guided by computational fluid dynamic (CFD) simulations, we have demonstrated that in curved micro-reactors, Dean vortexes are promoted on the cross section of the channels leading to the rotation of the fluid, reducing the residence times distributions. This effect is directly translated into small particles with narrow size distributions.

In addition, the absence of ligands in the surface of the particles also allows the separation of the seed formation and growth stages, allowing the production of particles with tuneable sizes and composite materials with core-shell and hollow well-defined structures.

SHORT BIOGRAPHY

Dr Laura Torrente is a Reader (Associate Professor) in the Department of Chemical Engineering and Biotechnology at the University of Cambridge. She has multi-disciplinary expertise in the areas of reaction engineering, process integration, sustainable chemical processes and energy. Her research is being supported by UK Research Council, the Royal Society, Innovate UK, international private funders and industry. She is working with a number of companies including SASOL UK, Johnson Matthey, Amyris, Synthomer, EDF Energy, Sabic and DRD Power as well as a number of SMEs.

She is a member of the UK Catalysis Hub, the UK Engineering Forums and a scientific expert of the European Commission. She has received the Future leaders in Engineering Sponsorship Award and the Rushlight Carbon Capture and Storage Award.

Tue., 25 September 2018, 16.20 – 16.50

Sergey P. Gromov

Photochemistry Center, RAS, FSRC "Crystallography and Photonics",
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Leninskie Gory 1-3, Moscow 119991, Russia

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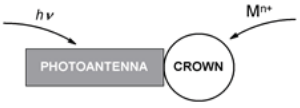
PHOTOACTIVE SUPRAMOLECULAR DEVICES AND MACHINES BASED ON MACROCYCLIC AND UNSATURATED COMPOUNDS

Currently a new trend is formed in nanotechnology "bottom-up": supramolecular engineering of supramolecular devices and machines for various purposes. The most convenient means for controlling supramolecular devices and machines is light, which can be easily adjusted both in the wavelength and in the amount.

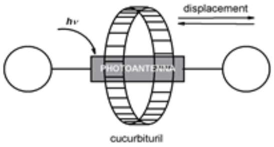
We propose a new unique class of polyfunctional photoactive compounds: unsaturated (polymethine) dyes functioning as photochromes, fluorophores and ionophores [1]. A large body of research has been performed for their synthesis, determination of their spatial structures, study of self-assembly features to give supramolecular systems, and also study of fluorescent, photochemical and complexing properties.

Resulting from the research, we elaborated for the first time universal supramolecular meccano, allowing one to accomplish building-up, with using a limited number of complementary compounds with participation of metal cations and hydrogen bonds, photoactive supramolecular systems of varied architecture with adjusted properties [2]. Within the same class of compounds one can construct in solution, solid and at the air-water interface new types of photoswitchable supramolecular devices, photocontrolled supramolecular machines, photoactive 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 supramolecular and nanophotonics, which was demonstrated, first of all, by the creation of practically important sensor [3] and photochromic materials [4,5].



supramolecular devices



supramolecular machines

ACKNOWLEDGMENT

This work was supported by the Russian Science Foundation, the RFBR, the RAS, the Ministry of Science and Education, the Moscow Government, the INTAS, the CRDF, the DFG, the Royal Society, and the ISF.

References:

[1] Sergey P. Gromov et al., Russ. Chem. Bull. 46, 611 (1997).
[2] Sergey P. Gromov, Russ. Chem. Bull. 57, 1325 (2008).
[3] Evgeny N. Ushakov et al., Russ. Chem. Rev., 77, 39 (2008).
[4] Sergey P. Gromov, Review Journal of Chemistry 1, 1 (2011).
[5] Evgeny N. Ushakov et al., Russ. Chem. Rev. 84, 787 (2015).

SHORT BIOGRAPHY

S. P. Gromov (born 1953) graduated from the Department of Chemistry of the M.V. Lomonosov Moscow State University in 1975. In 1978, he received a PhD degree from the same institution. In 1980, the results of the dissertation were recognized as a scientific discovery (USSR State committee diploma no. 205). In 1998, Dr. Gromov received his Dr. Sci. degree in chemistry from N.D. Zelinsky Institute of Organic Chemistry of the RAS. S.P. Gromov is a full professor. In 2006, Prof. Gromov won A.M. Butlerov Award of the RAS. Since 2008, Prof. Gromov is a corresponding member of the Russian Academy of Sciences. Currently he is a head of the Photochemistry Center of the RAS. In 2018 he was awarded the State Prize of the Russian Federation for Science and Technology for the development of photoactive supramolecular devices and machines. Thirteen PhD and two Doctors' dissertations were made under his supervision. He is the author of more than 1220 publications (312 scientific papers, 29 reviews in chemistry journals, 9 chapters in books, and 27 patents and inventions). His scientific interests encompass supramolecular and organic chemistry, photochemistry. Prof. Gromov is a member of three doctoral dissertational councils of the Zelinsky Institute of Organic Chemistry, chemical faculty of Lomonosov Moscow State University and the Moscow Technological University, and the editorial board of Nanotechnologies in Russia and Review Journal of Chemistry.

Prof. Gromov's research interests include (1) Synthesis and self-assembly of supramolecular systems and nano-sized architectures with specified photochemical and photophysical properties based on dyes, photochrome compounds, and organic luminophores. Design of photoactive supramolecular devices and machines., (2) Synthesis and transformation of heterocylcles: crown-ethers, pyridines, pyrimidines, triazines, indoles, indolizines, isoquinolines, quinolines, quinazolines.

Tue., 25 September 2018, 16.50 – 17.20

Sergey G. Zlotin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation

NOVEL APPROACHES TO NITROGEN-OXYGEN SYSTEMS FOR MEDICINE AND MATERIAL SCIENCE

Sergei G. Zlotin, Aleksandr M. Churakov, Igor L. Dalinger, Oleg A. Luk'yanov, Nina N. Makhova, Alexey Yu. Sukhorukov and Vladimir A. Tartakovsky

Over the past few years, a significant contribution has been made by researchers of N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences to synthesis of organic nitrogen–oxygen systems and their application as pharmaceuticals or their precursors, energetic compounds and intermediates for other useful materials (for reviews, see [1, 2]). Original syntheses of prospective hybrid molecules containing NO-releasing 1,2,5-oxadiazole 2-oxide (furoxan) and methylenebis(1-oxy-1-triazene 2-oxides) fragments decorated with suitable nitrogen heterocycles and/or functional groups have been developed. Some of the prepared compounds exhibited useful biological activities (NO-donor, anti-cancer, anti-tuberculosis, etc.) in vitro. Novel stereo- and enantioselective reactions of nitroalkane derivatives (nitronates), nitroolefins and nitroarenes have been elaborated which allowed a facile synthesis of close precursors to natural product analogues, active pharmaceutical ingredients and other useful materials to be accomplished. Promising results have been attained in an important area related to energetic nitrogen–oxygen systems. These results include the first synthesis of unique highenergy compound [1,2,3,4]tetrazino[5,6-e][1,2,3,4]tetrazine 1,3,6,8-tetraoxide (TTTO), a simple preparation of novel nitramino and nitrofuroxan derivatives with balanced elemental composition, and the development of facile green protocols for efficient syntheses of energetic N- and O-nitro (polynitro) compounds in liquid 1,1,1,2-tetrafluoroethane medium.

References:

[1] S.G. Zlotin, A.M. Churakov, O.A. Luk'yanov, N.N. Makhova, A.Yu. Sukhorukov, V.A. Tartakovsky, Mendeleev Commun., 2015, 25, 399.

[2] S. G. Zlotin, A. M. Churakov, I. L. Dalinger, O. A. Luk'yanov, N. N. Makhova, A. Yu. Sukhorukov, V. A. Tartakovsky, Mendeleev Commun., 2017, 27, 535.

SHORT BIOGRAPHY

Zelinsky Institute of Organic Chemistry RAS and the Head of N.D. Nazarov Laboratory of Fine Organic Synthesis at the same Institute. He graduated from the Volgograd Technical State University, received PhD in organic chemistry at N. D. Zelinsky Institute of Organic Chemistry in 1978 and became a full professor in 2002. He is a co-author of more than 200 papers and 16 patents on synthesis and applications of nitro compounds, nitrogen-containing heterocycles and bioactive compounds. His current research interests include chemistry of pharmacology-oriented and energetic nitrogen-oxygen systems, green chemistry, sustainable asymmetric organocatalysis, asymmetric synthesis. In 2013 he was awarded by N.D. Zelinsky prize of Russian Academy of Sciences for a significant contribution to organic chemistry and catalysis.

Wed., 26 September 2018, 11.50 – 12.20

Sergey A. Ponomarenko

Enikolopov Institute of Synthetic Polymeric Materials of Russian Academy of Sciences, Profsoyuznaya str. 70, Moscow 117393, Russian Federation
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BRANCHED AND DENDRITIC MOLECULES FOR ORGANIC PHOTONICS AND PHOTOVOLTAICS

Sergey A. Ponomarenko1,2, Oleg V. Borschev1, and Yuriy N. Luponosov1

Molecular architecture plays an important role in electronic and physical properties of conjugated organic molecules. Branching often helps to increase solubility of conjugated molecules, change their aggregation in the solution and ordering in the bulk. In this lecture recent results on design, synthesis and physical properties of branched molecules of two different classes will be considered (Fig. 1): (i) triphenylamine-based donor-acceptor star-shaped molecules for organic photovoltaics [2] and (ii) branched and dendritic nanostructured organosilicon luminophores for organic photonics and optoelectronics applications [3,4]. This work was made in the framework of leading science school NSh-5698.2018.3. Financial support from RSF (grant No. 14-13-01380) for the synthesis of star-shaped oligomers and RFBR (grant No. 16-03-01118) for the synthesis of dendritic oligoarylsilanes is acknowledged.

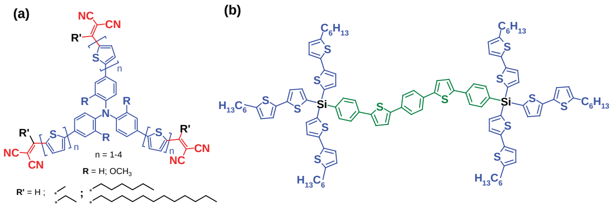


Figure 1. Examples of novel triphenylamine-based donor-acceptor star-shaped molecules (a) and nanostructured organosilicon luminophore (b).

References:

[1] Jie Min et al., Adv. Energy Mater. 7, 1700465 (2017)

[2] Oleg V. Borshchev et al., Org. Photon. Photovolt. 5, 1 (2017)

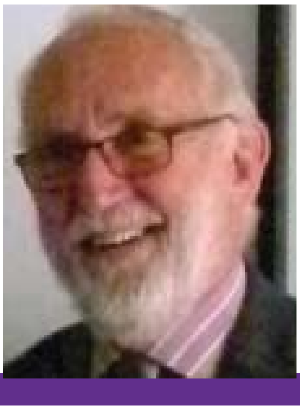
[3] Sergey A. Ponomarenko et al., Proc. SPIE 10344, 103440N (2017)

SHORT BIOGRAPHY

Sergey Ponomarenko was graduated «cum laude» from Chemistry Department of Lomonosov Moscow State University (MSU) in 1995. He made his PhD at Polymer Chemistry division of the same university and defended his PhD Thesis on Liquid Crystal Dendrimers in 1999. In 2001 - 2003 he was a PostDoc at Electronic Chemicals Research Labs of Bayer AG, Leverkusen, Germany. In 2003 he joined Enikolopov Instutute of Synthetic Polymeric Materials of Russian Academy of Sciences (ISPM RAS). In 2011 he was elected as a Corresponding member of Russian Academy of Sciences. Since

2012 he is a Professor at Chemistry Department of MSU. He is a co-funder of 3 startup companies participating at Skolkovo Innovation Center . Since 2018 he is a Director of ISPM RAS.

Wed., 26 September 2018, 12.20 – 12.50



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CATALYTIC CHEMISTRY OF METHANOL TO HYDROCARBONS: HOW ARE THE FIRST CARBON-CARBON BONDS FORMED?

The conversion of methanol to hydrocarbons over zeolite catalysts first came to prominence in the 1980s with the commercial implementation in New Zealand of Mobil's methanol to gasoline process, utilising a ZSM-5 catalyst. Variations on this technology followed, such as Lurgi's MTO process, Haldor-Topsoe's integrated TIGAS process, and UOP's MTO process utilising a silico-aluminophosphate zeolite catalyst. The declining world stocks of oil, the abundance of remote natural gas and the availability of large coal reserves in some parts of the world have revived interest in these technologies, and many plants have now been built or are under construction for producing either transport fuels or olefins from natural gas or coal using methanol as the intermediary.

The chemistry of methanol to hydrocarbons can be separated into three steps: the first formation of carbon-carbon bonds from methanol; the steady state production of hydrocarbons in a working reactor, and the eventual deactivation of the catalysts which causes loss of production. Most attention in the literature has focussed on the steady state chemistry, and there is now sound evidence for a so-called hydrocarbon pool mechanism in which a reservoir of hydrocarbon species in the pores of the ZSM-5 or SAPO-34 zeolite catalyst undergoes continuous methylation by methanol and cracking to form the observed gasoline range or olefin products. Despite much research, the mechanism of formation of the first carbon -carbon bonds from a molecule containing only carbon-oxygen bonds remains a mystery, with many different proposals in the literature. [1] This talk will describe how infrared microspectroscopy using synchrotron radiation is addressing this particular aspect of MTH chemistry.[2,3] The method is able to observe events occurring in the first few seconds after a methanol pulse enters a single crystal of a zeolite catalyst, and when coupled with on-line MS analysis of evolved products allows correlation between adsorbed species and the initial gas phase products. Formation of dimethylether from methanol is a necessary prerequisite to olefin formation; the first carbon-carbon bonds appear to be formed from reaction of dimethylether with surface methoxy groups, regenerating Bronsted acid sites. The first hydrocarbon pool species to be formed in these experiments are methylcyclopentenyl cations, which can also be generated directly by injecting propene into a fresh catalyst. Adsorbed aromatic species are formed subsequently.

References:

1. U. Olsbye et al. Chem.Soc.Rev. 44, 7155 (2015).
2. R.F.Howe et al. Topics in Catalysis 61, 199 (2018).
3. I.Minova et al. in preparation

SHORT BIOGRAPHY

APPOINTMENTS

Chair of Materials Chemistry, University of Aberdeen, 2001-present
Chair of Physical Chemistry, University of NSW, Australia, 1990-2001
Senior Lecturer and Associate Professor, University of Auckland, NZ, 1982-1990
Assistant and Associate Professor, University of Wisconsin-Milwaukee, USA, 1976-1982.
Research Scientist, CSIRO Division of Tribophysics, Australia, 1975-76
Postdoctoral Fellow, Texas A and M University, USA, 1974-75
Postdoctoral Fellow, Edinburgh University, 1971-73

CURRENT RESEARCH ACTIVITIES

Applications of neutron spectroscopy to zeolite catalysis
EPR spectroscopy of semiconductor photocatalysts.
Infrared microspectroscopy with synchrotron radiation.

PUBLICATIONS

194 refereed research and review articles in the areas of heterogeneous catalysis, surface chemistry and zeolite science. h-index = 40 (Web of Science).

RECENT EXAMPLE PUBLICATIONS

- D.W.Manley, R.T.McBurney, P.Miller, R.F.Howe, S.Rhydderch, J.C.Walton, "Unconventional Titania Photocatalysis: Direct Deployment of Carboxylic Acids in Alkylations and Annulations", J.Am.Chem.Soc. 134, 13580-13583 (2012).
- Greenaway, A.; Gonzalez-Santiago, B.; Donaldson, P. M.; Frogley, M.D.; Cinque, G.; Sotelo, J.; Moggach, S.; Shiko, E.; Brandani, S.; Howe, R.F.; Wright, P. A, " In situ Synchrotron IR Microspectroscopy of CO2 Adsorption on Single Crystals of the Functionalized MOF Sc2(BDCNH2)3", Angewandte Chemie International Edition, 53,2014, 13483-13487.
- Rhydderch S, Howe R.F., "In-situ EPR Studies of Reaction Pathways in Titania Photocatalyst-Promoted Alkylation of Alkenes", Molecules 20, 2015, 4055-4070.
- Howe R.F., McGregor, J, Parker, SF, Collier, P, Lennon, D, "Application of Inelastic Neutron Scattering to the Methanol-to-Gasoline Reaction Over a ZSM-5 Catalyst", Catalysis Letters 146, 2016, 1242-1248.
- Suwardiyanto, R.F.Howe, E.K.Gibson, C.R.A.Catlow, A.Hameed, J.McGregor, P.Collier, S.F.Parker, D.Lennon, "An Assessment of Hydrocarbon Species in the Methanol to Hydrocarbon Reaction Over a ZSM-5 Catalyst", Faraday Discuss. 197, 2017, 447- 471.
- Caux M., Fina F., Irvine J.T.S., Idriss H., Howe R.F., "Impact of the Annealing Temperature on Pt/g-C3N4 Structure, Activity and Selectivity between Photodegradation and Water Splitting", Catalysis Today 287, 2017, 182-188.

Wed., 26 September 2018, 12.50 – 13.20

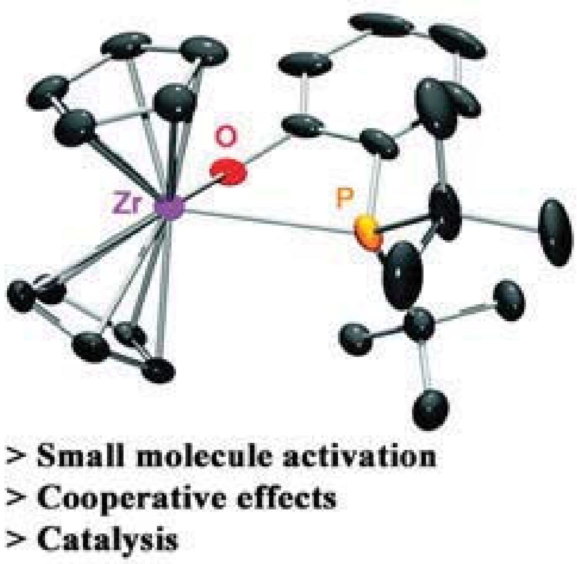
Duncan Wass

**School of Chemistry, University of Bristol,
Cantock’s Close, Bristol, BS8 1TS, U.K.**

www.wassresearchgroup.com I duncan.wass@bristol.ac.uk

COOPERATIVE CATALYSIS WITH TRANSITION METAL FRUSTRATED LEWIS PAIRS

This lecture will describe recent work in small molecule activation, and hydrogenation and dehydrogenation catalysis using combinations of electrophilic transition metal complexes and Lewis bases. These systems can be considered transition metal ‘frustrated’ or cooperative Lewis pairs. Much of our initial work has focused on cationic zirconocene aryloxide complexes in combination with intra- or inter-molecular phosphine Lewis bases. Such complexes mimic the reactivity of main group frustrated Lewis pairs, for example in hydrogen cleavage, CO_2 activation, THF ring-opening and olefin addition; as well as exhibiting new reactivity types such as C-O bond cleavage in non-cyclic ethers. Our catalytic studies to date have focused on imine hydrogenation and, in particular, amine-borane dehydrogenation or dehydrocoupling. The mechanism of this latter reaction give key insights into how the transition metal and Lewis base are working cooperatively to achieve good performance. Prospects for future opportunities in catalysis using this concept will be discussed.



References

S. R. Flynn, D. F. Wass, ACS Catal., 2013, 3, 2574–2581; A. M. Chapman, M. F. Haddow, D. F. Wass, J. Am. Chem. Soc., 2011, 133, 8826-8829; A. M. Chapman, M.F. Haddow, D. F. Wass, J. Am. Chem. Soc., 2011, 133, 18463-18478; O. J. Metters, S. J. K. Forrest, H. A. Sparkes, I. Manners, D. F. Wass, J. Am. Chem. Soc., 2016, 138, 1994–2003; S. R. Flynn, O. J. Metters, I. Manners, D. F. Wass, Organometallics, 2016, 35, 847–850; O. J. Metters, S. R. Flynn, C. K. Dowds, H. A. Sparkes, I. Manners, D. F. Wass, ACS Catal., 2016, 6, 6601–6611.

SHORT BIOGRAPHY

Duncan Wass was born in Leicestershire. He completed his undergraduate studies at the University of Durham (1992-1995). He then studied for his PhD (1995-1998) under the supervision of Professor Vernon Gibson FRS at Imperial College, London in the area of late transition metal olefin polymerisation catalysis.

In 1999, he joined BP Chemicals Ltd, working in their Sunbury-on-Thames laboratories on various olefin polymerisation and oligomerisation projects. After secondment to a commercial sales and marketing team, he moved to BP’s research site in Brussels, Belgium. Duncan joined the School of Chemistry at Bristol University in January 2004, and was promoted to Professor of Catalysis in 2012. He leads Bristol’s involvement in the Bath-Bristol-Cardiff EPSRC CDT in Catalysis, sits on the steering group for the EPSRC UK Catalysis Hub and is Research Director for The School of Chemistry at Bristol.

He lives in Bristol with his wife and two children. His interests include cooking, music, fly fishing, hill walking and supporting Leicester City.

Thu., 27 September 2018, 12.30 – 13.00

Yulia G. Gorbunova,[a,b] Alexander G. Martynov[b], Tebello Nyokong[c], Aslan Yu.Tsivadze[a,b,]

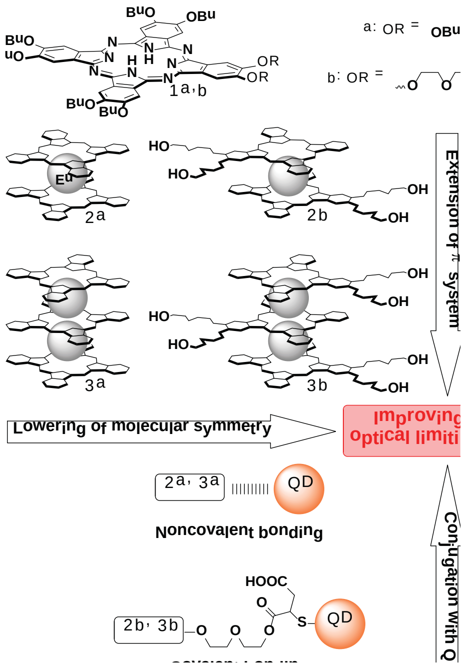
[a]N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences Leninskii pr., 31, Moscow, 119991, Russia
[b]A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences Leninskii pr., 31, bldg. 4, Moscow, 119071, Russia
[c]Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

yulia@igic.ras.ru

NEW MATERIALS BASED ON CONJUGATES OF PHTHALOCYANINES WITH QUANTUM DOTS AND NANOPARTICLES

Conjugation of phthalocyanines with different nanomaterials leads toward new functional materials with unique properties. In this talk the original strategy towards novel nonlinear optical (NLO) materials with superior optical limiting (OL) characteristics based on sandwich Eu(III) complexes with phthalocyanines will be reported (Figure). Open aperture Z-scan technique (532 nm laser and pulse rate of 10 ns) revealed that both lowering of molecular symmetry1 and extension of π-system when moving from ligands 1a,b to double and triple-decker complexes 2a,b and 3a,b significantly improve OL characteristics in terms of βeff and Im[$\chi^{(3)}$] values[2].

Altogether, these effects make the low-symmetry triple-decker complex 3b the most efficient optical limiter in the studied family of sandwich complexes which affords 50% lowering of light transmittance below 0.5 J•cm^{-2} input fluence. Two-photon reverse saturable absorption mechanism of optical limiting was deduced from the analysis of Z-scan curves. Conjugation (both covalent and non-covalent) with ternary CdSeTe/CdTeS/ZnSeS quantum dots (QD) afforded further enhancement of OL properties of both double-and triple-decker complexes likely due to heavy-atom effect and free-carrier absorption mechanism. Modification of 1b by thiol groups, leads to conjugation with TOPO-capped CdSe QD or oleylamine capped silver nanoparticles[3]. The conjugate with CdSe is the first example of Pc-based thiol conjugated with QD, revealed superior limiting characteristics with limiting threshold below 0.18 J × cm^{-2}.
Further improvement of NLO can be achieved by application of Ga(III) complex[4].



Altogether, the obtained results contribute to the development of novel nonlinear optical materials for future nanoelectronic and optical device applications.

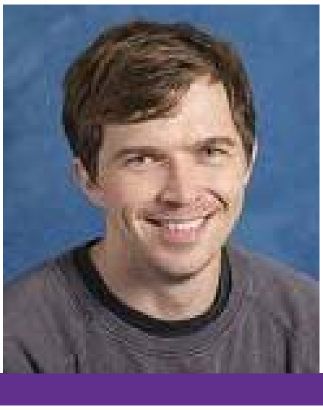
Acknowledgements: The authors thank Foundation of Russian President for support of leading scientific schools (grant No. NSh-3867.2018.3) for financial support.

SHORT BIOGRAPHY

Professor Yulia G. Gorbunova is a corresponding member of Russian Academy of Sciences (2016) and main researcher in Russian Academy of Sciences (the Kurnakov Institute of General and Inorganic Chemistry RAS (IGIC RAS) and the Frumkin Institute of Physical Chemistry and Electrochemistry RAS). She graduated in Chemistry from the Lomonosov Moscow State University in 1990 and received her PhD (1995) and habilitation (2006) from IGIC RAS. Her current research interests are the synthesis and study of new tetrapyrrolic compounds for their application for functional materials, including non-linear optics, electrochromic and single molecular magnets, sensors, hybrid organo-inorganic nanomaterials with a focus on supramolecular chemistry.

She was a recipient of the Award of European Academy of Science for young researcher (2001), the Russian Government prize in the field of science and techniques (2002) and the Chugaev Award in coordination chemistry (2010). In 2016 Prof. Gorbunova was awarded by Government of France by order "Chevalier dans l'Ordre national des Palmes Academiques".

[1] Britton, J.; Martynov, A. G.; Oluwole, D. O.; Gorbunova, Y. G.; Tsivadze, A. Y.; Nyokong, T. J. Porphyrins Phthalocyanines 2016, 20, 1296–1305.
[2] Oluwole, D. O.; Yagodin, A. V.; Mkhize, N. C.; Sekhosana, K. E.; Martynov, A. G.; Gorbunova, Y. G.; Tsivadze, A. Y.; Nyokong, T. Chem. A Eur. J. 2017, 23, 2820–2830.
[3] Oluwole, D. O.; Yagodin, A. V.; Britton, J.; Martynov, A.G.; Gorbunova, Y.G.; Tsivadze, A.Yu. and Nyokong, T. Dalton Trans. 2017, 46, 16190–16198.
[4] Managa, M.; Khene S.; Britton, J.; Martynov, A.G.; Gorbunova, Y.G.; Tsivadze, A.Yu. and Nyokong, T. J. Porphyrins Phthalocyanines 2018, 22, 137–148.



Thu., 27 September 2018, 13.00 – 13.30

Andrew J. Logsdail

University Research Fellow in the Cardiff Catalysis Institute, based at the School of Chemistry, University of Cardiff (2016-present)

1 School of Chemistry, Cardiff University, Main Building, Park Pl.,
Cardiff, CF10 3AT, UK;

LogsdailA@cardiff.ac.uk

A COMPUTATIONAL MATERIALS PERSPECTIVE ON HETEROGENEOUS CATALYSIS

As consumer desire for affordable, clean, renewable energy continues to grow, heterogeneous catalysis is vital to ensure environmental viability. In many cases, efficient heterogeneous catalysts have been produced and tested experimentally but a fundamental understanding of the reaction mechanisms and/or active catalytic properties remains elusive. Thus, computational chemistry has become a necessary tool for providing reaction insight at a molecular level, and we present our work applying computational chemistry techniques, including the embedded-cluster QM/MM methodology, [1] in the context of heterogeneous catalysis. Particular focus is towards elucidating catalytic mechanisms, understanding the effects of reaction environments, and characterizing the underlying properties of important metal oxides, such as TiO_2, at the atomic level (Figure 1). [2-4]

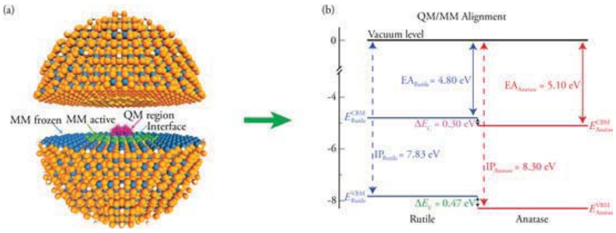


Figure 1: (a) Hybrid QM/MM embedded cluster as used for rutile TiO_2; (b) Schematic of the QM/MM band alignment of rutile and anatase TiO_2.

References:

[1] Paul Sherwood et al., J. Mol. Struct.: THEOCHEM. (2003), 632, 1
[2] David O. Scanlon et al., Nature Mater. (2013), 12 (9), 798
[3] John Buckeridge et al., Chem. Mater. (2015), 27 (11), 3844-3851
[4] Daniel Berger et al., J. Chem. Phys. (2014), 141 (2), 024105

SHORT BIOGRAPHY

Dr. Andrew Logsdail is a University Research Fellow in the Cardiff Catalysis Institute, based at the School of Chemistry, University of Cardiff (2016-present). His group focuses on harnessing modern computers to maximise the impact of predictive computational simulations, with a specific focus on material properties and applications therein towards heterogeneous catalysis.. Previously, AL was awarded his PhD in 2012, winning the Springer-Verlag PhD Thesis Prize in 2013, before then holding a postdoctoral research position (2012-2014) and Ramsay Memorial Fellowship (2014-2016) in the Department of Chemistry, UCL, where he worked extensively on implementation of novel embedding approaches for solid-state QM/MM simulations with the software package “ChemShell”.

Thu., 27 September 2018, 15.00 – 15.30

Alexander V. Navrotskiy

Volgograd State Technical University
Volgograd, Russia

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GRAFTING OF POLYMERS AS EFFECTIVE APPROACH FOR OBTAINING OF SUPERHYDROPHOBIC COATINGS

Navrotskiy A.V., Bryuzgin E.V., Klimov V.V., Novakov I.A
Volgograd State Technical University

During the last two decades, materials with superhydrophobic properties have received significant attention in terms of fundamental research and practical application. Superhydrophobic materials are characterized by a water contact angle that is greater than 150° and a low contact angle hysteresis that does not exceed 1–3°. The unique functional properties of superhydrophobic materials have potential application as anti-icing, anti-corrosion and anti-biofouling coatings for metal constructions, protective coatings for electronics, and as self-cleaning surfaces. The concept of superhydrophobic material production is based on reciprocal action of the following two factors: multidimensional roughness and low free energy of the subsurface layer. The fluorine containing polymers have many practical applications in industry for surface coating, stone preservation, in optics and microelectronics etc. because of their unique surface properties such as low surface free energy and water/oil repellency.

This work is dedicated to study of approaches for obtaining of superhydrophobic coatings on the surface of some metals and polymeric materials by grafting of random copolymers that are based on glycidyl methacrylate and a number of (fluoro)alkyl methacrylates. The chemical composition of grafted coatings was studied by X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray microanalysis.

The ways for texturing of the surfaces of some metals and polymeric materials are discussed. The formation of multimodal structure on the surfaces of materials was demonstrated by method of scanning electron microscopy (SEM).

The coatings based on copolymers of glycidyl methacrylate and fluoroalkyl methacrylates containing three to seven fluorine atoms in their monomer units on the textured surface of metals and their alloys had the water contact angle up to 170º. Besides, these coatings are capable to keep the superhydrophobic properties during the long-term contact with aqueous medium of various acidity and with salt aqueous solutions under saturated vapor conditions. Superhydrophobic coatings are stable to long-term impacts of organic solvents and detergents.

The work was supported by the Russian Foundation for Basic Research (RFBR), projects 15-03-00717, 16-29-05364.

SHORT BIOGRAPHY

Professional areas – polymer synthesis, physical chemistry of polymers

Superhifhmolecular polyelectrolytes, polyelectrolyte-surfactant complexes - methods of synthesis, solution properties, interaction with particles.

Polymer grafting to different surfaces - wettability control, morphology, adaptive surfaces, superhydrophobic surfaces.

Thu., 27 September 2018, 15.00 – 15.30

Baard H. Hoff[1] and Eirik Sundby[2]

[1] Department of Chemistry, Norwegian University of Science and
Technology, Høgskoleringen 5, NO-7491 Trondheim, Norway
[2]Department of Material Science, Norwegian University of Science and
Technology, Høgskoleringen 5, NO-7491, Norway.

Bard.helge.hoff@chem.ntnu.no

SYNTHESIS OF FUSED PYRIMIDINES AND THEIR EGFR INHIBITORY ACTIVITY

The epidermal growth factor receptor (EGFR) is an important target in molecular cancer therapy, and are also relevant for the treatment of pain. Whereas most small molecular EGFR inhibitors are based on the quinazoline scaffold, our efforts has been focused on the use of fused pyrimidines. Thus, the presentation will describe our work on developing chiral thieno- [1, 2], furo- [3] and pyrrolopyrimidine [4, 5] base EGFR inhibitors. Firstly, establishing flexible routes and scalable chemistry allowed for efficient synthesis of a library of thienopyrimidines and the generation of structure-activity relationship (SAR) data. The SAR information was then used to prepare additional furo- and pyrrolopyrimidines of which several being equipotent to the commercial drug Erlotinib. Further pre-clinical baselining with Erlotinib was then undertaken by evaluating selectivity in kinase panels, cellular activity, and key ADME properties.

References:

[1] Steffen Bugge et al., Eur. J. Med. Chem. 75, 354 (2014).

[2] Steffen Bugge et al., Eur. J. Med. Chem. 107, 255 (2016).

[3] Jin Han et al., Eur. J. Med. Chem. 119, 278 (2016).

[4] Svein J. Kaspersen et al., Eur. J. Pharm. Sci. 59, 69 (2014).

[5] Jin Han et al., Eur. J. Med. Chem. 124, 583 (2016).

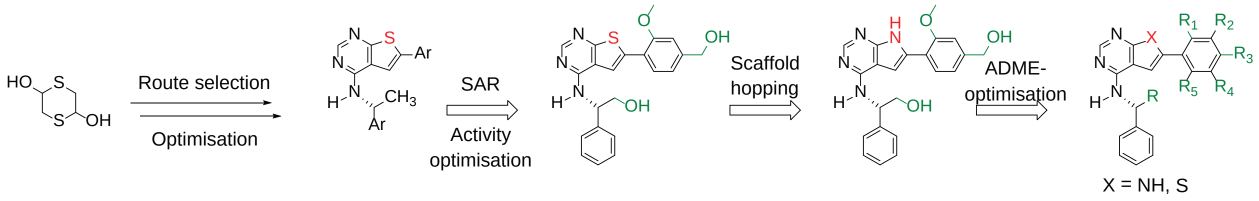

Figure 1. Synthesis and pre-clinical development of EGFR-TK inhibitors.

SHORT BIOGRAPHY

Bård Helge Hoff was born in Oslo, Norway in 1971. He received his master degree in 1995, followed by a PhD in 1999 working with Professor Thorleif Anthonsen in the field of biocatalysis. In 2000 he joined Borregaard Synthesis, Norway, where he worked as a researcher and team leader until the end of 2005. From 2006 he joined Department of Chemistry at the Norwegian University of Science and Technology, Trondheim, Norway as associate professor. He became full professor in 2016. Awards includes Outstanding OIDD collaborator: Blinded synthesis award 2016 from EliLilly, the innovation price "Gullegget" from NTNU Technology Transfer Office in 2013, and award for young organic chemists in Norway in 2011 by the Norwegian Chemical Society. His research is within applied organic chemistry with the main activity in medicinal chemistry. He has lately also entered the field of organic electronic materials. Previous research includes biocatalysis, asymmetric synthesis, fluorinated building blocks, carbohydrate chemistry, cellulose and lignin chemistry, heterocyclic chemistry and cross coupling methodology.

Thu., 27 September 2018, 15.30 – 16.00

Grigory V. Zyryanov[1,2], Oleg N. Chupakhin[1,2], and Valery N. Charushin[1,2]

[1]I. Ya. Postovskiy Institute of Organic Synthesis, Ural Division of the Russian Academy of Sciences, 22 S. Kovalevskoy Str., Yekaterinburg, 620219, Russian Federation
[2]Ural Federal University, 19 Mira Str., Yekaterinburg, K-2, 620002, RF

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SIMPLE MOLECULE-BASED ORGANIC MATERIALS: SYNTHESIS AND APPLICATIONS

Grigory V. Zyryanov[1,2], Oleg N. Chupakhin[1,2], and Valery N. Charushin[1,2]

[1]I. Ya. Postovskiy Institute of Organic Synthesis, Ural Division of the Russian Academy of Sciences, 22 S. Kovalevskoy Str., Yekaterinburg, 620219, Russian Federation
[2]Ural Federal University, 19 Mira Str., Yekaterinburg, K-2, 620002, RF

Our researches are mainly focused on the development of simple and efficient synthetic approaches (SNH/SNipso - reactions, PASE-methods, etc.) towards various classes of organic compounds, which can be used in the following areas: supramolecular materials for molecular sensing/extraction, materials for organic electronics/photonics/photovoltaics, biologically active compounds, etc. Specifically, we study some supramolecular aspects of transition metals sensing/extraction, visual detection of explosives, photochemistry, and use the produced knowledge for the preparation of simple molecule-based organic materials that can be used for preparation of fluorescence-based optical sensors, luminescent metal complexes of organic ligands, synthesis of artificial dyes and pigments, as well as synthesis of biologically active compounds/drug candidates. In current presentation some main topics of our current research will be reported.

SHORT BIOGRAPHY

Zyryanov Grigory Vasilievich, born in 1973, graduated from the Chemical Technology Department of the USTU-UPI (now UrFU), Yekaterinburg, in 1995. In 2000 he earned a degree of candidate of chemical sciences (PhD) in Organic chemistry (specialty code 02.00.03) on the topic «Isomeric 1,2,4-triazinones in reactions with nucleophiles» under the supervision of Academician of the RAS O.N. Chupakhin. From September 2001 to October 2003 and from July 2004 to September 2010, he completed a scientific internship in the United States. Since 2010, he is a research fellow (since 2018 - a leading researcher) in the I. Ya. Postovsky Institute of Organic Synthesis UrB RAS and associate professor (since 2018 – full professor) in the Department of Organic and Biomolecular Chemistry UrFU. In 2012 he earned his degree of Doctor of Chemical Sciences in Organic Chemistry (specialty code 02.00.03) on the topic «Synthesis and properties (hetero)aromatic chemosensors for nitro, nitroso compounds, as well as organic anions «, scientific adviser academician of the RAS O.N. Chupakhin. Since 2018, G.V. Zyryanov is a Professor of the Russian Academy of Sciences.

Scientific interests of Zyryanov G.V. are lie in various fields of chemistry (synthetic organic, supramolecular chemistry, green chemistry, photochemistry, coordination chemistry), as well as interdisciplinary sciences. To date, he has published over 300 scientific papers, including 1 monograph, 1 chapter in the monograph, 11 reviews, over 100 articles in Russian and foreign journals (with more than 30 articles from the Q1 quartile journals), 9 patents and 5 know-hows.

Thu., 27 September 2018, 16.00 – 16.30

Andrei V. Ivanov, Boris A. Trofimov,
Igor B. Rozentsveig, Boris G. Sukhov,
Lubov N. Sobenina

A E Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian
Academy of Sciences, Favorsky St., 1, 664033 Irkutsk, Russian Federation

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ACETYLENE-BASED SYNTHESIS OF BUILDING BLOCKS FOR VARIOUS ORGANO-ELECTRONIC APPLICATIONS

In this report, the progress in the synthesis of organic precursors and building blocks from acetylene for tailor-maid material design will be highlights. Chemistry of acetylene, a versatile building block of the organic synthesis, is continued to be rapidly developed. As compared with ethylene, highly reactive acetylene and its derivatives better match the trends in the development of chemical industry, which is more and more oriented to the production of science intensive chemicals for modern technologies, medicine and agriculture. Acetylene can be considered as an accumulator of high-density energy, i.e., the heat consumed in its formation is liberated in chemical reactions thus promoting them and providing the shortest and the least power-consuming way to the target products.

In the recent decades, systematic studies were carried out aimed at further development of classical reactions of acetylene with the use of superbasic catalysts and reagents. The concept of superbasicity was first formulated by Trofimov in 1977: `a medium consisting of a strong base and a solvent or a reagent that specifically binds cations thus `stripping' the conjugated anions is considered superbasic. Later, this concept was systematically used in the refinement of classical reactions involving triple carbon-carbon bonds.

The elaboration of a new approach to the enhancement of the reactivity of nucleophilic reagents, which is associated with the use of superbasic catalysts, have led not only to the refining of most important base-catalysed reactions of acetylene but also to the discovery of new reactions involving the triple bond and the development of synthetic methods based on them.

SHORT BIOGRAPHY

Prof. Andrey V. Ivanov graduated from the Chemistry Department of the Irkutsk State University in 2002. In 2003, he started as an engineer, and subsequently as a postgraduate student, at A.E. Favorsky Institute of Chemistry, Irkutsk. In 2007, he finished his PhD on the chemistry of 1-vinylpyrrol-2-carbaldehydes under supervision of academician B.A. Trofimov and became a full professor in 2011 with the thesis entitled “Novel aspects of the pyrrol chemistry”. In 2012-2015, he worked at A.E. Favorsky Institute as a Deputy Director for Science. From 2015 to present time he sequentially headed the Irkutsk Scientific Center of Siberian Branch of Russian Academy of Sciences and A.E. Favorsky Institute. He is currently the Director of A.E. Favorsky Institute.

Combines organizational work with productive scientific activity.

[1] B A Trofimov, N K Gusarova, Russian Chemical Reviews, 76 (6) 507-527 (2007)

Thu., 27 September 2018, 16.30 – 17.00

Mikhail Yu. Krasavin

Institute of Chemistry, Saint Petersburg State University, 26
Universitetskii Prospekt, Peterhof, Saint Petersburg 198504
Russian Federation

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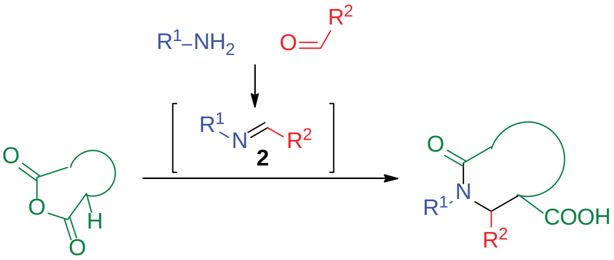
NEW FACETS AND APPLICATIONS OF THE FORMAL [2+4] CYCLOADDITION OF IMINES AND DICARBOXYLIC ACID ANHYDRIDES (THE CASTAGNOLI-CUSHMAN REACTION)

The formal [2+4] cycloaddition of imines and α-C-H dicarboxylic acid anhydrides (cyclic anhydrides) has proven itself as a remarkably efficient method of accessing polysubstituted δ- and γ-lactams. Despite the fact that the reaction has been known for over 45 years now,[1-2] certain aspects of its scope and practical format remained underdeveloped. In particular, the diversity of cyclic anhydrides[3] clearly could receive some attention in terms of expansion. Likewise, despite being a multicomponent reaction by spirit, the Castagnoli-Cushman reaction was seldom conducted by mixing all three reagents together, imine is typically pre-formed prior to addition of the cyclic anhydride component. Cyclic anhydrides themselves represent a liability due to labile hydrolytic character. Yet, approaches based on situ dehydration of a dicarboxylic acid were not explored for long time.[4]

The Castagnoli-Cushman chemistry delivers excellent, high-sp^3, stereodefined compounds that appear to be highly suitable for drug design applications. In this talk, we will present recent biomedical applications of this chemistry validated in our laboratories.



This research was supported by the Russian Science Foundation grant #14-50-00069

REFERENCES:

1 N. Castagnoli, J. Org. Chem. 1969, 34, 3187–3189.

2 M. Cushman, N. Castagnoli, J. Org. Chem. 1973, 38, 440–448.

3 M. Krasavin, D. Dar'in, Tetrahedron Lett. 2016, 57, 1635-1640.

4 A. Lepikhina, D. Dar'in, O. Bakulina, E. Chupakhin, M. Krasavin, ACS Comb. Sci. 2017, 19, 702-707.

SHORT BIOGRAPHY

Mikhail Krasavin is a Professor of synthetic organic and medicinal chemistry at Saint Petersburg State University (Russia): www.krasavin-group.org. Prior to assuming this post in 2014, he spent over 10 years in positions of increasing responsibility in pharmaceutical industry (Millennium Pharmaceuticals, Abbott Bioresearch Center, ChemDiv, Inc.) , where he was involved in multiple drug discovery programs in the areas of oncology, metabolic disease, infectious disease and CNS disorders. In 2011-2013 Prof. Krasavin led an independent research group at the Eskitis Institute for Drug Discovery (Griffith University) in Brisbane, Australia. Prof. Krasavin has authored more than 150 research articles, 8 patents, several book chapters and has consulted various drug discovery and development business entities. In 2016, he was elected a Professor of the Russian Academy of Sciences.

ZIRCONOCENE HYDRIDES AS ACTIVE INTERMEDIATES AND MECHANISTIC PROBES IN ZIEGLER-NATTA TYPE REACTIONS

Mon., 24 September 2018, 14.30 – 14.45

L.V. Parfenova, P.V. Kovyazin, T.V. Tyumkina,
L.M. Khalilov and U.M. Dzhemilev

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Catalytic systems based on metallocenes and organoaluminum compounds (OAC) are widely used in Ziegler-Natta type polymerization, di- and oligomerization, as well as hydro-, carbo- and cyclometalation of unsaturated compounds. Various intermediates were found to be the active sites of the reactions [1]. However, the literature contains scarce information on the role of transition metal hydride complexes in these processes. Our studies on the bimetallic Zr,Al-hydride intermediates formed in the systems L2ZrCl2- XAlBui2 showed that the intermediates tend to undergo intermolecular hydride exchange involving OAC molecules, which intensity defines the activity of the catalytic systems in the alkene hydroalumination [2]. Recently some new Zr,Al-hydride complexes were identified [3]. The complexes react with methylaluminoxane (MAO) and give poorly soluble heavy adducts, which is highly active in the alkene oligo- and polymerization. The adduct molecular volumes and weights were studied for the first time by DOSY NMR and MALDI TOF/TOF mass- spectrometry, correspondingly. DFT modelling demonstrated the preferable coordination of complexes with plane (MeAlO)3 unit instead of traditional bulk 3D clusters. Thus, the new hydride bimetallic clusters can function as a sort of probes for MAO, which apparently comprises a rather large proportion of linear or hexagonal fragments.

The work was supported by the Russian Foundation of Basic Research, grant 18-03-01159a.

References:
[1] Lyudmila V. Parfenova et al., In “Alkenes”, Intech, 2018, P.43-64.
[2] Lyudmila V. Parfenova et al., Organometallics, 34, 3559 (2015).
[3] Lyudmila V. Parfenova et al., J. Organomet. Chem., 851, 30 (2017).

METAL ORGANIC FRAMEWORKS: CITIUS, FORTIUS, ALTIUS

Mon., 24 September 2018, 14.30 – 14.45

L.M. Kustov, V.I. Isaeva

N.D. Zelinsky Institute of Organic Chemistry, Moscow, 119991 Russia

The concept of using hybrids based on metal organic frameworks either via the proper design of nanocomposites for mixed matrix membranes or encapsulation of macrocyclic structures, like calixarenes, crown ethers, phthalocyanines, porphyrins etc., as nano-reactors or nano-containers for specific catalytic reactions is considered from the point of view of non-covalent interactions and molecular confinement in the porous architecture of metal organic frameworks of different structural types. Tailoring of such interactions provides a key to enhancement of the efficiency of the catalysts. Design of “green” and robust metal organic frameworks is of prime importance.

A few examples of the template in situ synthesis of hybrid nanomaterials based on calixarenes as guest moieties embedded into the MOF structures are presented. Introduction of calixarenes during the synthesis results in the following beneficial features in addition to those intrinsic to the mere MOF structure:

1. Two kind of porosities arises due to the pores available in the target MOF structure and the presence of calixarene cavities acting as micropores or microporous niches;
2. The pore size distribution can be shifted towards the micropore range;
3. The stability of such a hierarchical structure can be increased because of the additional rigidity due to the presence of rigid calixarene moieties as compared to the structure of MOF itself;
4. The inclusion of the calixarene entity creates additional possibility for functionalization of the final hybrid structure due to either the presence of functional groups in the starting calixarene or the reactivity of certain calixarene sites toward the post-synthesis modification or functionalization.

ALLYL BORONATES WITH A NEW DIOL ‘HELMET’ AT BORON: IMPROVED STABILITY AND EASY ACCESS TO VARIOUS CHIRAL FUNCTIONALIZED COMPOUNDS

Mon., 24 September 2018, 14.45 – 15.00

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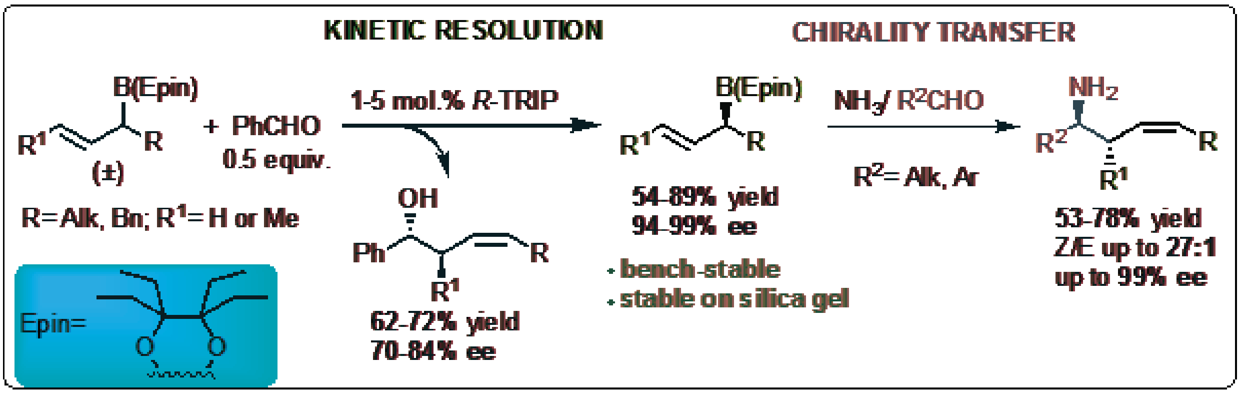
Chiral allyl boronates are valuable reagents in organic synthesis as they can be easily converted into various functionalized chiral compounds with no erosion in enantiopurity.1,2 Despite several efficient ways to prepare enantioenriched allyl boronates have been developed they are usually converted into target compounds without isolation and purification due to limited stability.3

Recently it was found that the use of tetraethylethylene glycol (Epin) group at boron atom leads to improved stereoselectivity (compared to commonly used pinacol) in the synthesis of enantioenriched Z-homoallylic alcohols upon (R)-TRIP-catalyzed kinetic resolution of racemic secondary allyl boronates.4 Moreover, these compounds were revealed to be stable upon purification on silica gel which encouraged us to investigate further the chemistry of the resolved allyl boronates.

In the present work, we have developed an efficient protocol to prepare chiral bench-stable secondary allyl boronates via (R)-TRIP catalyzed kinetic resolution of their racemic mixtures. The resolved chiral products were obtained in good yields and high enantiopurity (ee up to 99%). They were selectively converted into chiral Z-homoallylic amines upon interaction with imines (chirality transfer up to 99%). Use of Epin improved stability of boron compounds on silica and gave excellent stereoselectivity of the Z-homoallylic amines obtained (Z/E up to 27:1). The diol can the easily recovered and reused thus providing reasonable atom economy. The scope and mechanistic considerations on the stereochemical course of the reaction will be presented.



References:
1. C. Diner, K. J. Szabó, J. Am. Chem. Soc. 2017, 139, 2-14.
2. J. L.-Y. Chen, V. K. Aggarwal, Angew. Chem. Int. Ed. 2014, 53, 10992-10996.
3. A. Guzman-Martinez, A. H. Hoveyda, J. Am. Chem. Soc. 2010, 132, 10634-10637.
4. C. A. Incerti-Pradillos, M. A. Kabeshov, A. V. Malkov, Angew. Chem. Int. Ed. 2013, 52, 5338-5341.

METAL-ORGANIC FRAMEWORKS AS EFFICIENT CATALYTIC SYSTEMS FOR SYNTHESIS OF 1,5-BENZODIAZEPINE DERIVATIVES BOTH IN SOLUTION AND UNDER SOLVENT-FREE CONDITIONS

Mon., 24 September 2018, 14.45 – 15.00

M.N. Timofeeva[1,2], V.N. Panchenko[1,2], S.H. Jhung[3]

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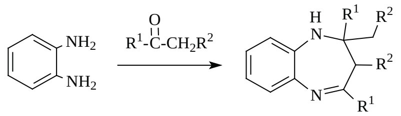
1,5-Benzadiazepines and their derivatives are a very important class of nitrogen-containing heterocyclic compounds with biological activity that are widely used in medicine. The traditional procedure for the synthesis of these compounds is a one- pot condensation between 1,2-phenylenediamine (I) and ketones.



(I) (II)

However, a large number of catalytic systems reported in the literature, suffer from several drawbacks such as the use of a large amount of catalysts, unsatisfactory product yields and problems of product isolation procedures. In recent years, the use of metal-organic frameworks (MOFs) as heterogeneous catalysts has attracted great interest in organic synthesis because their structural, textural and acidic properties can be controlled at the molecular or atomic level. Herein we report the use of MOFs as a recyclable green catalyst for the synthesis of 1,5-benzodiazepines from 1,2-phenylenediamine and ketones (acetone, acetophenone and methyl ethyl ketone). The main attention was focused on the investigation of the dependence of catalytic properties on the type of metal ions for isostructural MOFs of the families MIL-100(M) (M: V^{3+}, Al^{3+}, Fe^{3+} and Cr^{3+}) and three porous aluminium trimesates Al-BTCs (MIL-96(Al), MIL-100(Al) and MIL-110(Al)).

Reactions were carried out at 50 °C with an acetone/(I) molar ratio of 2.5 and 4.0 in different solvents (methanol, ethanol, acetonitrile, 1,2-dichloroethane) and under solvent free conditions. It was found that yield of 1,5-benzodiazepine decreases with decreasing solvent polarity. The maximal yield of 1,5-benzodiazepine was observed in methanol, a solvent with large relative polarity. A combination of catalytic, theoretical and physicochemical methods showed that reaction rates and yields of 1,5-benzodiazepines are adjusted by the type of metal ions and accessibility of active sites (Table 1). Recycling experiments point that yield of (III) does not change during at least three and six catalytic cycles for MIL-100(V) and MIL-100(Al), respectively.

Table 1

Reaction of 1,2-phenylenediamine with acetone in presence of different catalytic systems under solvent-free conditions [a]

Catalyst	pHPZC [a]	Amount of LAS [b]		Catalytic data [c]	
		M_{total} (mmol/g)	M^{3+}CUS (mmol/g)	Time (min)	Yield of (III) (%)
MIL-100(V)	3.95	5.89	0.98	180 (300)	85 (95)
MIL-100(Fe)	4.41	3.75	2.64	180 (300)	76 (88)
MIL-100(Cr)	4.11	4.34	2.28	180 (300)	72 (81)
MIL-100(Al)	3.41	3.84	2.44	180 (300)	68 (75)
HY				180	82
Heulandite				300	81
Beta Zeolite				300	39
H-ZSM-5				300	32

[a] pHPZC - zero point of charge of the surface]; [b] Amount of Lewis acid sites was determined by EPR spectroscopy using TEMPO as probe molecule; [c] 0.1 mmol of (I), 0.4 mmol of acetone, 0.02 g of catalyst, 50 °C

NEW DIRECTIONS IN THE HETARENE N-OXIDES CHEMISTRY

Mon., 24 September 2018, 15.00 – 15.15

L.L. Fershtat, D.M. Bystrov, E.S. Zhilin, A.A. Larin,
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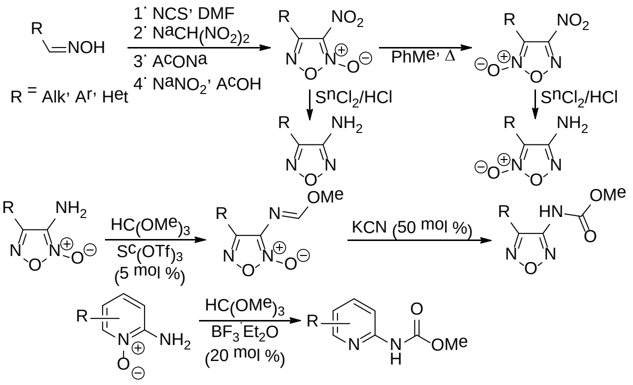
Hetarene N-oxides are a versatile class of organic compounds that are of great interest in a wide range of applications including medicine, agriculture, and materials science. In recent years, furoxans (1,2,5-oxadiazole 2-oxides) attract considerable attention due to their potential application as pharmacologically active compounds or as components of high-energy formulations [1,2]. Herein, we present our results on the regioselective construction of 3- and 4-nitrofuroxans via cascade transformations of aldoximes [3-5]. Synthesized 3- and 4-nitrofuroxans underwent N-oxide-controlled chemoselective reduction to aminofurazans and 4-aminofuroxans. In addition, we developed a new, tandem catalytic condensation/rearrangement reaction of 5- and 6-membered 2-aminohetarene N-oxides into hetaryl carbamates via an intramolecular N-oxide oxygen transfer [6].



This work was supported by the Russian Science Foundation (project 14-50-00126).

References:
[1] L. L. Fershtat, N. N. Makhova, Russ. Chem. Rev. 85, 1097 (2016).
[2] L. L. Fershtat, N. N. Makhova, ChemMedChem 12, 622 (2017).
[3] L. L. Fershtat et al., Tetrahedron Lett. 57, 4268 (2016).
[4] L. L. Fershtat et al., Tetrahedron Lett. 57, 5685 (2016).
[5] L. L. Fershtat et al., ChemPlusChem 82, 1315 (2017).
[6] D. M. Bystrov et al., Adv. Synth. Catal. 360, (2018) (DOI: 10.1002/adsc.201800407).

TOWARDS MOLECULAR MACHINES: SYNTHESIS AND SELF-ASSEMBLY OF MONOSUBSTITUTED PILLAR[5]ARENES WITH AMIDE FRAGMENT

Mon., 24 September 2018, 15.00 – 15.15

A.A. Nazarova, A.I. Gilyazeva, P.P. Padnya and I.I. Stoikov

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Nowadays supramolecular polymers attract attention of researchers working under design of a new generation of biocompatible materials with biomimetic properties able to self-healing. Monomer units are linked in supramolecular polymers by a variety of weak non-covalent interactions unlike common polymers. Due to the reversible nature of non-covalent interactions, supramolecular polymers possess a number of attractive properties, e.g., biocompatibility, self-healing, optoelectronic properties. Pillar[n]arenes are considered as a unique macrocyclic platform for the synthesis of supramolecular polymers since their first synthesis in 2008. The ability to form inclusion complexes and rotaxane-like structures is combined with easy functionalization of the macrocycle and the possibility to obtain optically active derivatives.

Thus, the main goal of the present work is study of the possibility to form different types of associates (pseudoknots and supramolecular knots) depending on the nature of solvent and the length of linear alkyl fragments in the monosubstituted macrocycles. Structure of the synthesized compounds was confirmed by physical methods (1H and 13C NMR spectroscopy, IR spectroscopy and MALDI-TOF mass-spectrometry). Self-assembly of obtained pillar[5]arenes were investigated by one and two-dimensional NMR spectroscopy, dynamic light scattering, nanoparticle trajectory analysis and diffusion-ordered NMR spectroscopy. The morphology was studied by transmission electron microscopy.

Acknowledgment

The reported study was funded by RFBR according to the research project № 18-33-00276 mol_a and the research project № 18-03-00315.

ZEOLITE BETA-BENTONITE COMPOSITE MATERIALS FOR CATALYST SHAPING

Mon., 24 September 2018, 15.15 – 15.30

Z. Vaijlova, N. Kumar, D.Yu. Murzin

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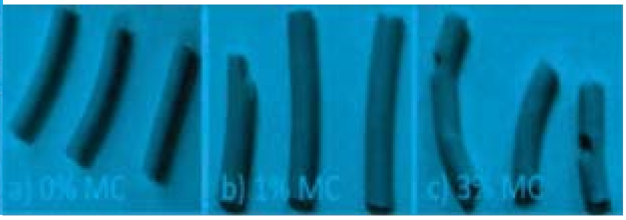
Zeolite catalysts bodies are employed on a global scale in important chemical processes, such as synthesis of many bulk chemicals as well as in crude-oil refining. If a zeolite based catalyst is to be used at an industrial level, it is shaped into bodies such as granules, spheres, and extrudates. Zeolites are pelletized with a binder to obtain larger and more resistant particles and to avoid an extremely high pressure drop in fixed-bed reactors. Shaping of the zeolite powder into pellets is commercially done using natural clays such as bentonite, attapulgite, and kaolin amounting of 15 – 20% of the zeolite pellet.

Although binders might not be catalytically active, binder-zeolite interactions can exert effects on catalytic performance through both physical and chemical means. This makes a marked influence on activity, selectivity, and stability of a zeolite. The binder presence can affect the acidic properties of a zeolite as a result of changes in the ion exchange between zeolite protons and sodium in clay. Other influence can include porosity modifications, trapping coke precursors by the binder, and/or blocking of zeolite channels during palletization.

In the current work, the composite materials for shaped catalysts were prepared by synthesis of three commercial Beta zeolites with bentonite as an aluminosilicate clay binder. All pristine materials, the synthesized powder mixtures and shaped extrudates were characterized using X-ray powder diffraction for phase purity and structure, scanning electron microscopy for morphology, transmission electron microscopy for porosity and periodicity, nitrogen physisorption for surface area, pore volume and pore size distribution, Fourier transform infrared spectroscopy using pyridine as a probe molecule to elucidate presence, strength and amount of Brønsted and Lewis acid sites. Elemental analysis was carried out using energy dispersive X-ray micro-analysis. The rheological properties of the extrusion suspensions were characterized using oscillatory tests for flow properties, while mechanical strength was elucidated for shaped catalyst bodies.

Extrusion was found to be very sensitive to composition of the suspension. Minor changes of the water content (Figure below, left) or the concentration of rheology additive (Figure below, right) can significantly change the properties of extrudates.



Through a systematic comparison of the properties of the individual components, powder zeolite−binder composites and final shaped catalysts, the study elucidated the crucial binder influence on the key properties of the catalytic supports already during synthesis of the composites in the powder form, i.e. prior to shaping. It can be concluded that the promoting effect of the bentonite binder is derived from chemical interactions with the zeolite. The resulting effect of the binder on composite properties is not a simple additive just reflecting the nominal ratio of components. The synthesis process, zeolite type (SiO_2/Al_2O_3 ratio of the framework, particle size) and binder concentration play a significant role in the resulting binder effect in composites.

SELF-ASSEMBLED HYBRID NANOPARTICLES BASED ON MACROCYCLES AND SILICA

Mon., 24 September 2018, 15.15 – 15.30

L.S. Yakimova, **I.I. Stoikov**

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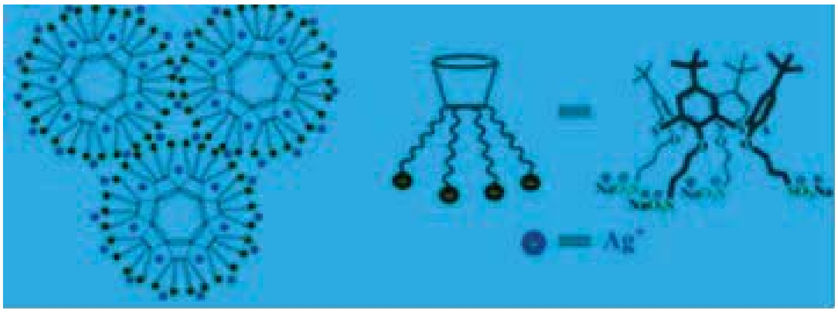
Polyionic functionalized platforms are widely used in biomedicine, catalysis, cosmetic industry, oil production, etc. The key area of their application is biotechnology, in particular polyelectrolyte encapsulation and the creation of nanocontainers for targeted delivery, protection, storage and prolonged release of biologically active compounds, genetic material. Various generations of macrocycles, such as cyclodextrins, calixarenes, cucurbiturils and pillar[n]arenes are used in the design of new delivery systems for therapeutic agents and biopolymers (DNA, RNA, proteins). Therefore, the search for new materials to create systems with controlled properties for solving the problems of biomedical diagnostics, gene therapy (nonviral vectors), address delivery systems is an actual problem.

In this paper, we propose conditions and implemented supramolecular self-assembly and synthesis of self-assembling hybrid systems based on polyfunctional (thia)calixarenes, pillar[5]arenes and chemically modified silicon dioxide by covalent or non-covalent self-assembly, capable of binding various substrates from inorganic cations to natural biopolymers (proteins and DNA).

Figure 1. Representation of the water-soluble thiacalix[4]arene and of the formation of the thiacalix[4]arene stabilized silver nanoparticles.



The work was supported by Russian Science Foundation (№18-73-10094)

NEW DIMERIC QUATERNARY PYRIDINIUM SALTS POSSESSING BIOCIDAL

Tue., 25 September 2018, 14.30 – 14.45

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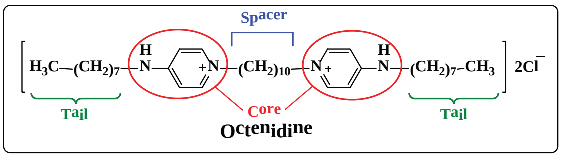
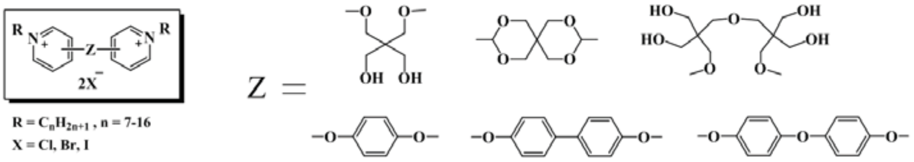
Over the world, the spread of microbes and viruses with perpetually increasing resistance to the number of known antimicrobial and antiviral drugs brings up potentially high threat to humankind. That is why it's very important to search for new chemical substances exhibiting biocidal properties against wide range of conditionally-pathogenic and pathogenic microorganisms and also viruses. In case of cancer, the development of pharmaceuticals and treatment approaches stands as important but still not accomplished scientific subject.

On contemporary Russian medical market, mono-quaternary ammonium salts are basic ingredients for superiority of disinfectants. Such disinfecting compounds are appropriate for treatment of various surfaces. However, these compounds have highly cytotoxic effect on the human cells what makes their exposure on human's skin and mucous membranes prohibited. Indeed, the quantity of skin antiseptics is rather restricted. Aforementioned chemicals are medicines diminishing the possibility of infection, sepsis and putrefaction. The most notable examples of them are clorherxidine, miramistin, octenisept. For last-mentioned enlisted drug, bis-pyridinium quaternary salt called octendihydrochloride is responsible for medical effect. Pyridinium and bis-pyridinium quaternary salts represent an important group of chemicals widely used as biocides, due to their strong antimicrobial effect even at very low concentrations, on a broad range of gram-positive and gram-negative bacteria, fungi, and some viruses. Octendihydrochloride is an active compound for various well-performing antiseptics and disinfectants.



In the present work, an original approach to the synthesis of several new types of bispiridinium salts possessing a strong antibacterial activity comparable or superior to that of octenidine is proposed. It is established that the nature of the spacer has a critical influence on anti-bacterial properties of compound [1]. New bispiridinium salts with oxygen-containing linear branched and cyclic spacers based on pentaerythritol, dipentaerythritol, 1,4-hydroquinone, biphenyl and biphenyl ether are obtained.



These compounds can become the basis for the development of new domestic medicines for the treatment of a wide range of diseases caused by pathogenic microorganisms.

The reported study was funded by Russian Science Foundation, according to the research project No. 17-73-20260.

References:
1. Y. Tsuji, M. Yamamoto, A.N. Vereshchagin, A.S. Dorofeev, T.A. Geyvandova, I.F. Agafonova, R.K. Geyvandov, Pat. Appl. WO 2014/158045.

UMPOLUNG FUNCTIONALIZATION OF NITRONATES AS A ROUTE TO BIOACTIVE MOLECULES

Tue., 25 September 2018, 14.30 – 14.45

**A. Sukhorukov, V. Dorokhov, Y. Naumovich,
P. Ushakov, S. Ioffe**

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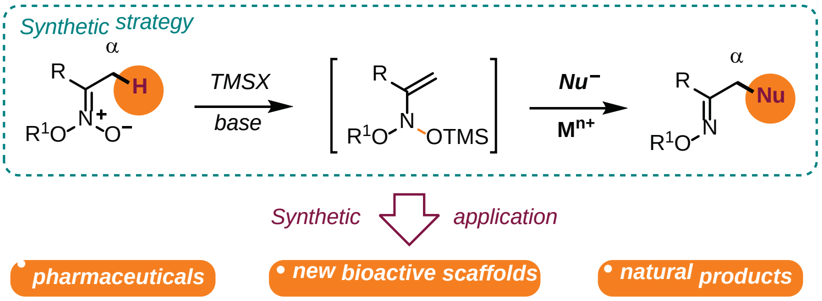
Substitution of hydrogen atoms at the α-position to functional groups (such as carbonyl or imino groups) is a classical strategy to construct new carbon-carbon and carbon-heteroatom bonds. In these transformations the initial functionalized organic substrate typically acts as an α-C-nucleophilic synthon. Recently, we developed a general approach to the umpolung functionalization of nitronates, in which the latter behave as α-C-electrophilic synthons in reactions with various C-, N- and O-nucleophiles [1]. This unusual reactivity is realized due to the presence of a weak nitrogen-oxygen linkage, which is heterolytically cleaved in the result of a metal-assisted addition of external nucleophile.

In the presentation, details of the suggested CH-functionalization strategy together with examples of its applications to the synthesis of bioactive molecules will be discussed.



This work was supported by Russian Foundation for Basic Research (grants 17-03-01079_a and 17-33-80172_ mol_ev).

References:
[1] For a representative example see: Zhmurov, P. A.; Khoroshutina, Y. A.; Novikov, R. A.; Golovanov, I. S.; Sukhorukov, A. Y.; Ioffe, S. L. Chem. Eur. J. 2017, 23, 4570-4578.

DESIGN AND PROPERTIES OF MACROCYCLIC IONIC LIQUIDS

Tue., 25 September 2018, 14.45 – 15.00

P. L. Padnya, I. I. Stoikov

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The replacement of traditional solvents is the most important practical task, one of the possible solutions of which is the use of melts of salts - ionic liquids.

The actual direction of modern organic chemistry is the synthesis of ionic liquids with given properties. Special interest is the development of approaches to the creation of new highly efficient systems based on ionic liquids and functionalized macrocycles, such as cyclodextrins, cucurbit[n]urils, calix[n]arenas, etc., for the extraction and separation of various substances from complex mixtures.

Thus, novel derivatives of thiacalix[4]arene containing simultaneously amide and imidazolium fragments at the lower rim in cone and 1,3-alternate conformation were synthesized. The structure of the obtained macrocycles was confirmed by physical methods - IR, NMR 1H, 13C spectroscopy, MALDI-TOF mass spectrometry, and composition - data of elemental analysis. Obtained ionic compounds have a melting point of less than 100 degrees Celsius, which corresponds to the definition of ionic liquid by IUPAC.

The financial support of RFBR (16-33-60141 mol_a_dk) and the Program of the President of the Russian Federation for the State support of young Russian scientists–scholarships (CP-3597.2016.4) is gratefully acknowledged.

SYNTHETIC APPROACHES TO FORMATION OF 3D-4F HETEROMETALLIC COORDINATION COMPOUNDS POSSESSING LUMINESCENCE AND MAGNETIC

Tue., 25 September 2018, 14.45 – 15.00

S. Nikolaevskii [1], **M. Kiskin** [1], **I. Ananyev** [2], **S. Kiraev** [1], **S. Melnikov** [1,2], **N. Efimov** [1],
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Search for new and original synthetic approaches for simple preparation of heterometallic coordination compounds is one of the most interesting tasks of the modern coordination chemistry. Complexes, containing two and more metals of different electronic structure are especially interesting because they can be directly used for creation of new functional materials with unique magnetic, luminescence, and/or catalytic properties, as well as they are considered as promising stoichiometric precursors for the preparation of heterometallic compounds by thermal decomposition.

In the report a wide series of tri- and tetranuclear 3d-4f-complexes based on various carboxylate anions and N-donor ancillary ligands were synthesized and structurally characterized. Capabilities of the several synthetic routes for obtaining such type compounds were evaluated. The correlation of molecular and crystal structures, luminescence [1, 2] and SMM properties of obtained heterometallic complexes are analyzed in detail.

This work was financially supported by the Russian Science Foundation (project 16-13-105-37).

References
[1] A. Goldberg, M. Kiskin, O. Shalygina et al., Chem. Asian J. 2016. V.11. P.604–612.
[2] S. Kiraev, S. Nikolaevskii, M. Kiskin et al., Inorg. Chim. Acta. 2018.V.477. P.15–23.

CHEMICAL SYNTHESIS OF COMPLEX OLIGOSACCHARIDES WITH A HELP OF STEREOELECTRONIC FACTORS TO CONTROL STEREOSELECTIVITY OF GLYCOSYLATIONS

Tue., 25 September 2018, 15.00 – 15.15

**B.S. Komarova, M.V. Orekhova, V.S. Dorokhova,
A.M. Finogenova, Y.E. Tsvetkov and N.E. Nifantiev**

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Combination of factors that control selectivity of glucosylations (Fig. 1) allowed preparation of oligosaccharides representing molecules of cell walls of Aspergillus fumigatus.[1-4] Their biotinylated derivatives were attached to microtiter plates via biotin-streptavidin pair to simulate cell surface of pathogen and to define their ability to induce production of cytokines and efficiency of their recognition with serum of aspergillosis patients.

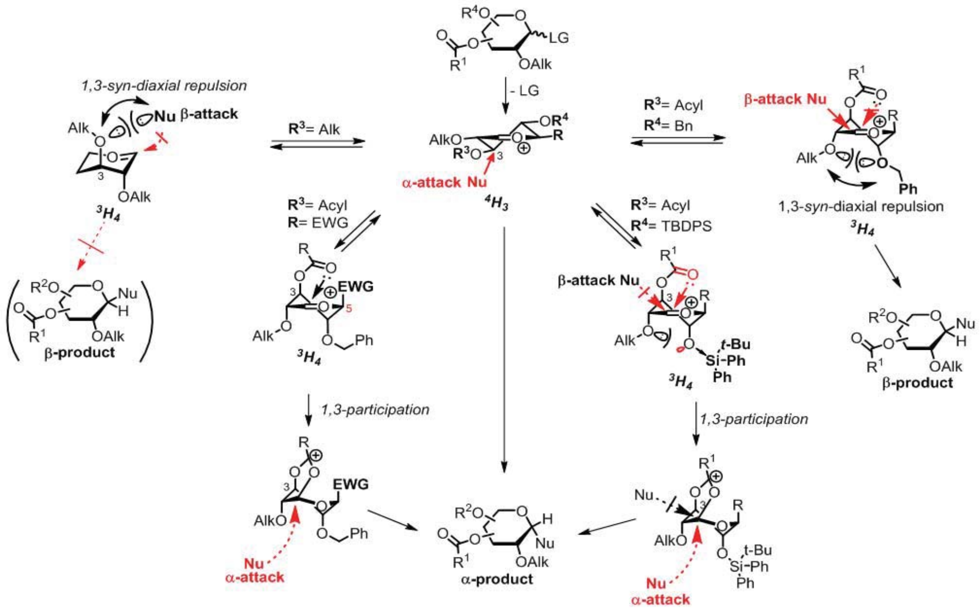

Figure 1. Impact of stereoelectronic effects and repulsive interactions of protecting groups on stereochemistry of glucosylation.

This work was supported by RSF grant 14-50-00126

References:
[1] Bozhena S. Komarova et. al., Chem. Rec. 16 488 (2016)
[2] Bozhena S. Komarova et. al., Org. Chem. Front. 5 909 (2018)
[3] Bozhena S. Komarova et. al., J. Org. Chem. 82 8897 (2017)
[4] Bozhena S. Komarova et. al., Chem. Eur. J. 21 1029 (2015)

ELECTROCATALYTIC SYNTHESIS OF DIMETALLATRANES OF THE GROUP 14

Tue., 25 September 2018, 15.00 – 15.15

D.M. Vakhrusheva[1,2,3], **E.N. Nikolaevskaya**[1], **V.K. Sablukova**[1,3,4], **I.V. Krylova**[1],
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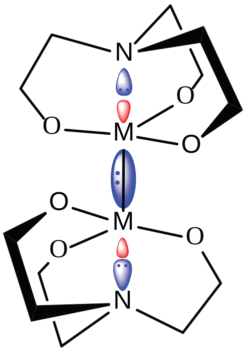

M = Si (**1**), Ge (**2**)
N:M:M:N - 4c, 6e

The development of a new class of multicenter polyelectronic chemical bonds attracts a lot of attention not only for the sake of fundamental knowledge, but in view of practical applications as well. With a specifically designed organic environment of such systems, they can be considered as analogues of a coaxial cable whwre electrons run through a conjugate system. However, synthesis of such systems is often synonymous to a great challenge. Using the possibilities provided by electrochemistry, we developed a new synthetic approach to 4c-6e dimeric metallatrane structures based on sila- and germatrane units that might serve as promising building blocks for molecular wires and molecular electronics (Scheme 1).

Electrochemical reduction of 1-halometallatranes (X = Cl, Br, I), studied in THF and MeCN on non-catalytic (glassy carbon) and catalytically active electrodes (Cu, Pt, Cd, Nb, Cu, Ag, Au, Ni), was shown to lead to metallatranyl anions or metallatranyl radicals, respectively. In the last case, the formation of the radical species was demonstrated by ex-cell EPR spectroscopy of their stable spin adducts with ⍰-phenyl-t-butyl-nitron (PBN) spin trap.

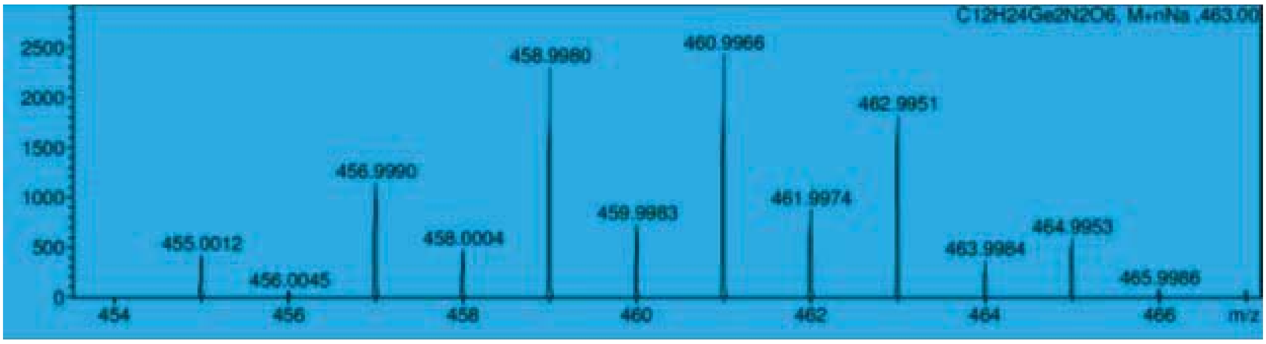

Figure 1. Mass spectrum of digermatran 2.

Formed through the reductive one-electron cleavage of Ge-X and Si-X bonds in starting halometallatranes, germatranyl- and silatranyl radicals dimerize to give the corresponding dimetallatranes 1 and 2. The structure of these new products was confirmed by NMR, IR, Raman spectroscopy, HRMS and elemental analysis.

Acknowledgements - This work was supported by Russian Scientific Foundation (grant № 18-73-10180). High resolution mass spectra were recorded in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

POSTER SESSION

DONOR-ACCEPTOR CYCLOPROPANE RING-OPENING WITH AZIDE ION IN PROTIC IONIC LIQUID MEDIA

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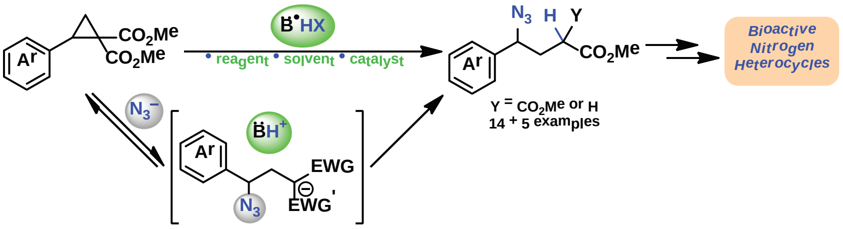
The development of effective synthetic methodologies that meet the concepts of atom economy, sustainable and green chemistry, is directly associated with the search for suitable tools – new reagents, catalysts, and solvents.

The ring-opening reactions of donor-acceptor (D–A) cyclopropanes by nitrogen-containing nucleophiles represent key stages in the synthesis of a variety of polycyclic N-heterocycles. Moreover, most of such transformations involving classical inorganic metal salts, for example, cyanides, thiocyanates, selenocyanates and several other anions, are not described in the literature primarily due to the reversible nature of these reactions.



To overcome the issue of reversibility we employed protic ionic liquids (PILs, as well as other salts formed by organic bases (B¨) and Brønsted acids, HNu), which act as multipurpose regenerable reagents (sources of nucleophilic and electrophilic components), catalysts and solvents (green media). Thorough optimization of the conditions for the ring-opening of D–A cyclopropanes by organic-soluble azide-based reagent led to (2-azido-2-arylethyl)malonates or the corresponding 4-azido-4-arylbutyrates depending on the judicious choice of PIL media. Due to the presence of several functional groups suitable for further modification, the compounds obtained can find numerous applications in the synthesis of bioactive nitrogen-containing heterocyclic compounds [1-3].

This work was supported by the President of the Russian Federation scholarship for young scientists, working on R&D in top-priority areas vital to the modernization of the Russian economy (medical technologies area, № СП-4317.2018.4)

References:
[1] Konstantin L. Ivanov, Elena V. Villemson, Ekaterina M. Budynina, Olga A. Ivanova, Igor V. Trushkov, Mikhail Ya. Melnikov, Chem. – Eur. J. 21, 4975 (2015).
[2] Anna S. Pavlova, Olga A. Ivanova, Alexey O. Chagarovskiy, Nikolay S. Stebunov, Nikolay V. Orlov, Alexey N. Shumsky, Ekaterina M. Budynina, Victor B. Rybakov, Igor V. Trushkov.
Chem. – Eur. J. 22, 17967 (2016).
[3] Maksim A. Boichenko, Olga A. Ivanova, Ivan A. Andreev, Alexey O. Chagarovskiy, Irina I. Levina, Victor B. Rybakov, Dmitriy A. Skvortsov, Igor V. Trushkov, Org. Chem. Front. accepted for publication (2018).

FACILE AND EFFICIENT MULTICOMPONENT APPROACH TO 5-[5-HYDROXY-3-(TRIFLUOROMETHYL)-1H-PYRAZOL-4-YL]-5H-CHROMENO[2,3-B]PYRIDINES

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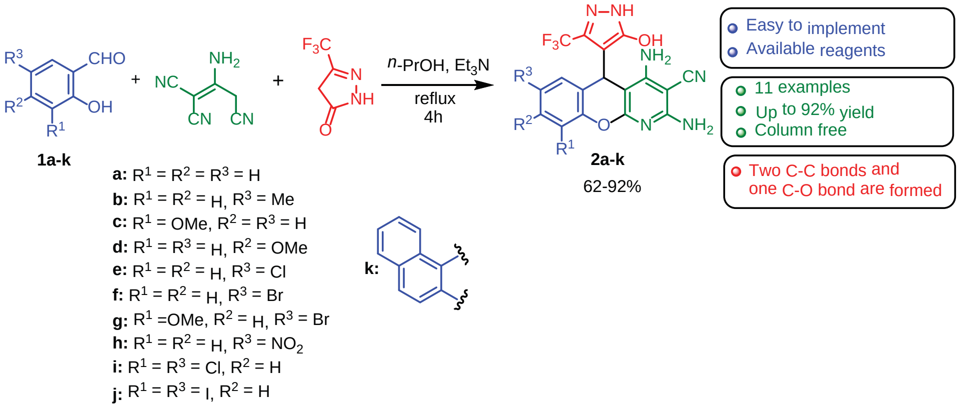
Cyano-functionalized chromeno[2,3-b]pyridines inhibit mitogen-activated protein kinase-activated protein kinase 2 (MK-2) and suppress the expression of TNFα in U937 cells [1], and also increase the level of phosphorylated cofilin in HCA2 cells, making chromeno[2,3-b]pyridines possible therapeutic option in the treatment of Werner syndrome [2]. In addition to bio-applications, 5-S substituted chromeno[2,3-b]pyridines inhibit corrosion of mild steel by adsorption on metallic surface [3]. The trifluoromethyl group is one of the most important structural fragments, because of its considerable role in modulating chemical, physical, and biochemical properties of organic molecules [4]. The trifluoromethyl fragment containing molecules have enhanced lipophilicity, membrane permeability, and resistanse to different oxidation processes [5].
It is well known that multicomponent reactions (MCRs) have extensively been used and applied for the rapid construction of important and complex molecules [6].



In the present study we found multicomponent synthesis of 5-C substituted chromeno[2,3-b]pyridines from salicylaldehydes 1a-k, 2-aminoprop-1-ene-1,1,3-tricarbonitrile and 5-(trifluoromethyl)-2,4-dihydro-3H-pyrazol-3-one. In the presence of 10 mol % of Et3N as catalyst and n-PrOH as solvent chromeno[2,3-b] pyridines 2a-k was obtained in 62-92% yields (4h, reflux):

It should be noted that two C-C and one C-O bonds are formed in this multicomponent process in a one-pot manner. The procedure found by us utilizes simple equipment; it is easily carried out, final compounds were isolated without any chromatography, through simple filtration and washing with a small amount of methanol.

This work was supported by the Russian Foundation for Basic Research (grant № 18-03-00212).

References:
[1] D. R. Anderson et al. Bioorg. Med. Chem. Lett., 15, 1587-1590 (2005).
[2] T. Davis et al. Bioorg. Med. Chem. Lett., 17, 6832-6835 (2007).
[3] C. Verma et al. RSC Adv., 6, 53933–53948 (2016).
[4] X. Liu et al. Chem. Rev., 115, 683-730 (2015).
[5] I. Ojima. J. Org. Chem., 78, 6358-6383 (2013).
[6] L. F. Tietze, Domino Reactions: Concepts for Efficient Organic Synthesis, Wiley VCH: Weinheim, Germany (2014).

1,3-DIPOLAR CYCLOADDITION REACTIONS OF 4-NITROBENZOFUROXANS WITH N-BENZYL AZOMETHINE YLIDE

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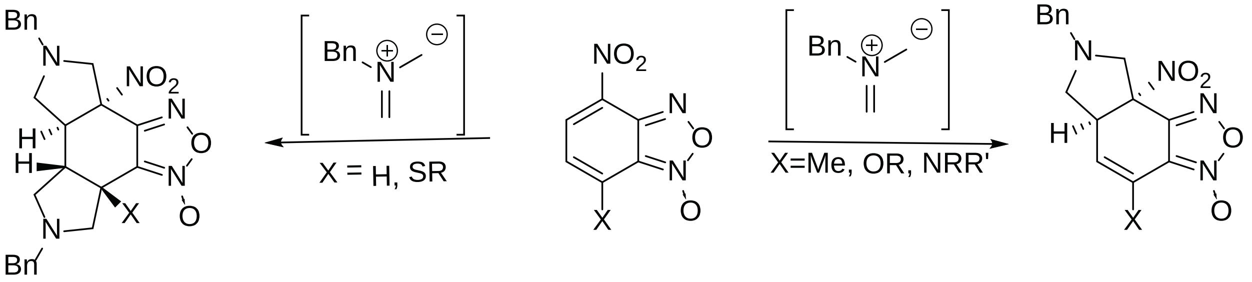
1,3-Dipolar cycloaddition reactions are the characteristic example of the multiple bond-forming transformations strategy (MBFTs) [1] and represent a powerful method of transforming simple substrates into complex heterocyclic compounds containing five-membered heterocyclic skeletons. In particular, [3+2]-cycloaddition of azomethine ylides to multiple C-C-bonds leads to formation of pyrrolidines, pyrrolines and related heterocycles. This approach was found to be exceptionally useful and convenient for the synthesis of pharmacology-oriented hybrid molecules since it allows combining a variety of pharmacophoric fragments in same molecule thus providing the structures with potential bioactivity.

Here we report a method for the synthesis of mono- and bis-pyrrolidine fused benzofuroxan derivatives on the basis of 1,3-dipolar cycloaddition of N-benzyl azomethine ylide to 7-R-4-nitrobenzofuroxans. Depending on the nature of substituent 7-R, these reactions resulted in addition of one or two equivalents of the dipole to nitrobenzene ring with formation of two or four C-C bonds respectively. It should be noted that we found a first example of double 1,3-dipolar cycloaddition of azomethine ylide to mononitro benzoazole moiety. The results obtained fit the multiple bond-forming transformations (MBFTs) concept that create new complex compounds in a single step and are of great importance for the synthesis of pharmacologically-oriented hybrid polycyclic molecular scaffolds useful for design of pharmaceuticals and drug discovery [2].



This work was supported by the Russian Science Foundation (grant no. 14-50-00126).

References:
[1] Jean Rodriguez, et al., Stereoselective Multiple Bond-Forming Transformations in Organic Synthesis, John Wiley and Sons Inc., 2015, p. 1.
[2] Alexey M. Starosotnikov et al, ChemistrySelect, 3, 2018, DOI: 10.1002/slct.201802117

(3+3)-ANNULATION OF DONOR-ACCEPTOR CYCLOPROPANES WITH DIAZIRIDINES

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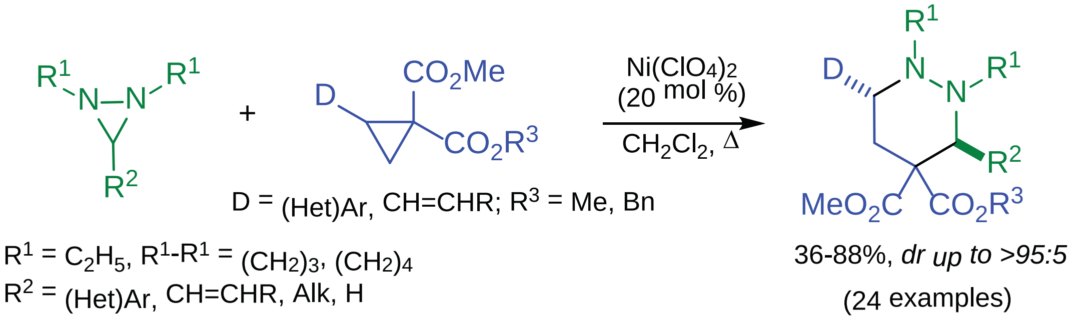
Donor-acceptor (DA) cyclopropanes are convenient building blocks for the preparation of various polyfunctionalized compounds, including carbo- and heterocycles, in reactions with various nucleophilic, electrophilic and ambiphilic agents.[1] DA cyclopropanes as well readily enter various dimerization reactions affording a broad scope of cyclic and acyclic compounds. However, until recently, there have been no examples of DA cyclopropanes interactions with other three-membered rings leading to (3+3)-annulation products.



In the course of the present investigation we have studied the reaction of DA cyclopropanes with a series of substituted diaziridines and disclosed that in the presence of nickel perchlorate, functionalized derivatives of perhydropyridazine are formed with high yields and diastereoselectivity. This reaction proceeds as formal (3+3)-annulation and can be realized for DA cyclopropanes with aryl, hetaryl and alkenyl donor substituents. It is noteworthy that the reactions of 1,5-diazabicyclo[3.1.0]heptane (R^1-R^1 = $(CH_2)_3$) derivatives predominantly afford products with trans-arrangement of groups in perhydropyridazine ring, while in the case of 1,6-diazabicyclo[4.1.0]heptane derivatives (R^1-R^1 = $(CH_2)_4$) and monocyclic diaziridines (R^1 = C_2H_5), cis-isomers are formed prevalently or exclusively. At that optically pure DA cyclopropanes afforded in this reaction optically pure annulation products. On the contrary, a reaction of diastereomerically pure cyclopropanes with two different acceptor groups resulted in the formation of mixtures of isomers. Based on the obtained results, a reaction mechanism was proposed, which includes a nucleophilic attack of diaziridine on the DA cyclopropanes, electrocyclic ring opening of the obtained derivatives, followed by the cyclization of the resulting 1,6-zwitterion ion.

The study was supported by the Russian Science Foundation (Grant No. 17-73-10404).

References:
[1] T. F. Schneider, J. Kaschel, D. B. Werz, Angew. Chem. Int. Ed., 2014, 53, 5504.

C-S BOND CONSTRUCTION OVER METAL-ORGANIC FRAMEWORKS HETEROGENEOUS CATALYSIS

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In terms of green and sustainable chemistry catalytic reactions development is accompanied with replacement of homogeneous catalyst with heterogeneous. Accordingly, creation of new support materials is highly important area of catalysis. Nowadays mineral silica materials (zeolites) find wide application in industry; nevertheless, they are continuously replaced with the synthetic structured mesoporous silica materials such as MCM-41 and SBA-15, because of their higher surface area, higher thermal and mechanical stability during reaction processes. At the edge of search of the best material to play the role of heterogeneous catalyst or catalytic support metal-organic frameworks (MOFs) were invented. They are promising hybrid materials with crystalline structure. MOFs consist of metal centers or clusters coordinated to organic linkers, what leads to indeed limitless opportunity to adjust the MOF structure and properties.

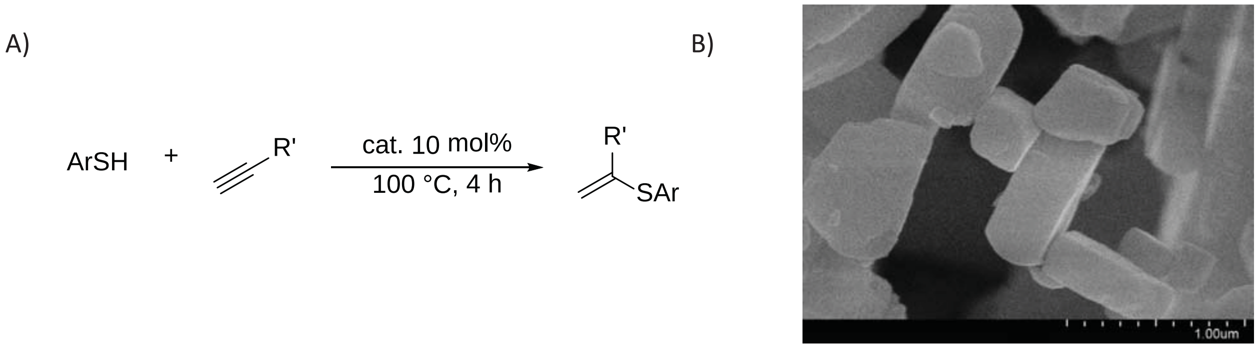

Figure 1. Reaction of thiols addition to alkynes (A). SEM image of Ni-based MOF structure utilized as catalyst.

The current research focus is development of the new heterogeneous catalytic systems efficient in construction of C-S bonds. Between the other known ways, selective atom-economic reactions are most profit and perspective, therefore catalytic thiols addition to alkynes was chosen as the process of interest. Despite the variety of catalysts efficient in hydrothiolation reaction, there is no any heterogeneous and recyclable. Unique properties of MOFs make them ideal candidates on that role. Number of earlier described MOF structures from [Ni], [Cu] and [Co] inorganic salts with various dicarbonic acids were synthesized and their catalytic activity was examined in the hydrothiolation reaction (Fig. 1). Among the varied MOF catalyst only [Ni]-based demonstrated moderate catalytic activity.

Acknowledgment. The Russian Foundation for Basic Research supported this work (Project No 18-33-01075 mol_a).

A STUDY OF DYNAMIC EQUILIBRIUM INVOLVING R-NHC COUPLING IN PALLADIUM CATALYTIC SYSTEMS

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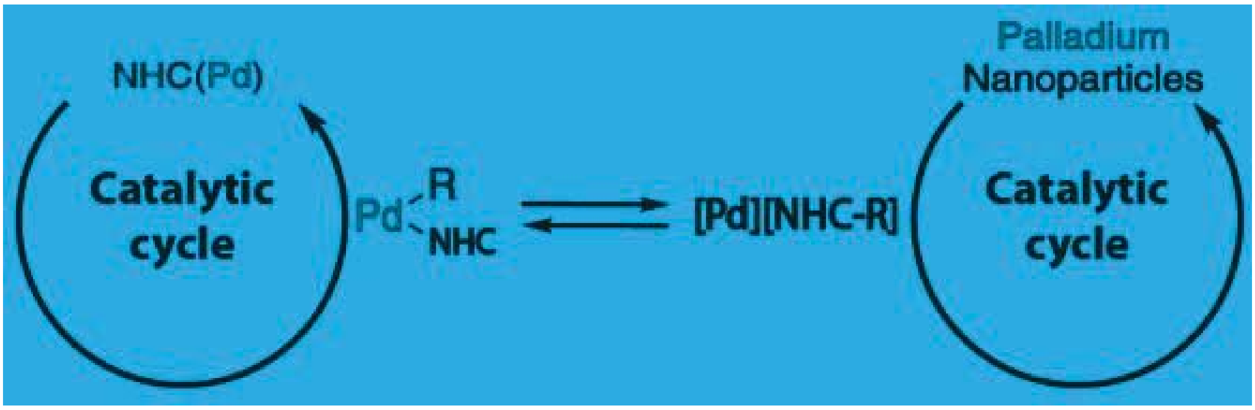
Catalytic applications of nanomaterials are highly relevant to currecnt synthetic applications. Nanocatalysts are widely used to activate substances with low reactivity, such as saturated hydrocarbons in reforming reactions. Nanocatalysts effectively promote oxygen reduction in fuel cells, lignocellulose biomass hydrolysis, hydrodeoxygenations, biomass conversion, and many other useful reactions.

Catalytic systems with nanosized particles show a variety of dynamic behaviors in solution [1-3]. These include leaching of catalytically active metal species, dissociation of soluble metal complexes, changes in morphology and size of insoluble of metal species and their further interconversions.

Dynamic equilibrium of R-NHC coupling is the subject of this work. In cross-coupling reactions, the oxidative addition step of an organic halide to a Pd(0) species is reversible, and equilibrium between the nanoparticles and the molecular complex of palladium takes place in solution (Figure 1).

Figure 1. Dynamic equilibrium of R-NHC coupling in solution.



Understanding the dynamic nature of catalytic systems plays a key role in the development of a new generation of efficient, selective and recyclable catalysts.

The study was supported by Russian Science Foundation 14-50-00126 grant.

References:
[1] Dmitry B. Eremin et al., Coord. Chem. Rev. 346, 2-19 (2017).
[2] Alexey S. Kashin et al., J. Org. Chem. 78, 1428-1433 (2013).
[3] Alexey S. Kashin et al., Nat. Commun. 9, 2936 (2018).

IONIC LIQUID TAGS FOR INVESTIGATING DRUGS AT THE LEVEL OF INDIVIDUAL CELLS

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High heterogeneity of various cell populations, especially malignant ones, has recently attracted a significant attention to the drug studies at the level of individual cells. However, successful identification of foreign chemical substances in the living cells requires overcoming two limitations: insufficient signal intensity and masking of target signals by signals of inherent cellular compounds. We propose alleviating these issues by employing ionic liquid tags. Ionic liquids with their huge fine-tuning potential have recently been suggested as important players in modern pharmacy [1,2]. In our study, we demonstrated that the conjugation of the antineoplastic drug mitoxantrone with four imidazolium tags did not lead to significant disturbance of cytotoxic activity of the drug. At the same time, sensitivity of electrospray ionization mass spectrometry (ESI-MS) to the mitoxantrone conjugate was by an order of magnitude higher than that to the original mitoxantrone dihydrochloride. Together with the shift of the observed ESI-MS signals to a clearer lower-mass region of the spectrum, it allowed us investigating the drug at the level of individual cells. The novel mitoxantrone conjugate was oil at physiological temperatures and demonstrated high aqueous solubility (Figure 1).

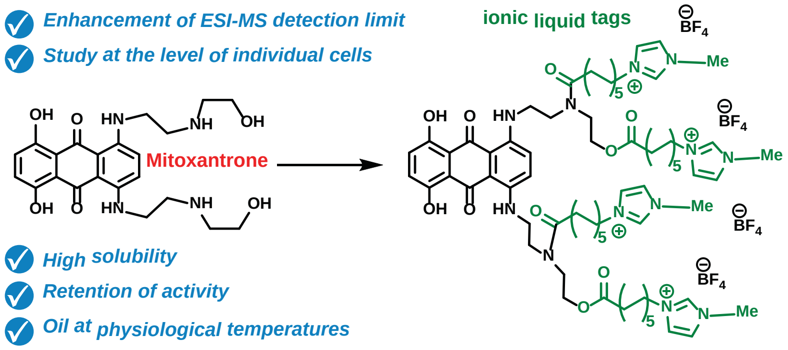

Figure 1. Ionic liquid mitoxantrone conjugate demonstrates high water solubility and biological activity, together with the improved ESI-MS detection limit that allows studying the drug behavior at the level of individual cells.

This research was supported by the Russian Science Foundation (grant 18-13-00116).

References:
[1] K.S. Egorova, E.G. Gordeev and V.P. Ananikov. Chem. Rev. 117, 7132 (2017).
[2] K.S. Egorova, M.M. Seitkalieva, A.V. Posvyatenko, V.N. Khrustalev and V.P. Ananikov. ACS Med. Chem. Lett. 6, 1099 (2015).

USAGE OF 3D PRINTING FOR DESIGN OF CHEMICAL REACTORS FOR CATALYTIC PROCESSES WITH ACETYLENE

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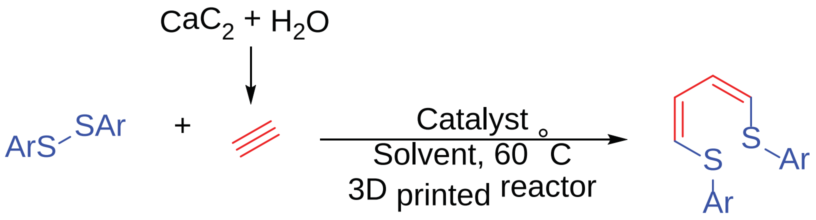
Additive manufacturing technologies (AMT) find application in various fields of science and technology. Use of AMT gives opportunity of rapid prototyping complemented to manufacturing of devices of any complexity. For the most cases required time and costs are reduced in comparison with traditional subtractive techniques (e.g. milling). Nowadays 3D printing enters to the chemical science. Reason for rapid evolution of 3D printing is high efficiency of the software for 3D models development and price reduction and improvement of 3D printers.

One of the most popular 3D printing methods is Fused Deposition Modelling (FDM) that consists in extrusion of thermoplastic polymer via the heated nozzle to realize digital model in layer by layer manner. Popularity of FDM is caused by a large variety of thermoplastics and low prices of personal FDM printers. In chemistry, FDM facilitates design of the reactors for organic reactions with improved performances in terms of time and yield[1,2,3,4]. It's efficiency is proven by creating of reactors for multi-step organic synthesis of pharmaceuticals[5].

C-S functionalization of organic molecules is an important area of organic chemistry research. For the moment, a number of catalytic systems for addition of thiols and disulfides to alkynes are developed[6]. However, unsubstituted acetylene remains aside that's caused by complicated work with it. It's gaseous, explosive and highly reactive.

Herein, 3D printed reactor for aryl disulfides addition to acetylene leading to 1,4-bis(arilthio)butadienes-1,3 is developed. Calcium carbide was used as precursor of acetylene. Use of the reactor allows affording the dienes with high efficiency.



References:
[1] Dragone, V.; Sans, V.; Rosnes, M. H.; Kitson, P. J.; Cronin, L. Beilstein J. Org. Chem., 2013, 9, 951–959.
[2] Gordeev E.G.; Galushko A.S.; Ananikov V.P. PLoS ONE, 2018, 13, e0198370.
[3] Rossi, S.; Porta, R.; Brenna, D.; Puglisi, A.; Benaglia, M. Angew. Chem. Int. Ed., 2017, 56, 4290–4294.
[4] Zalesskiy S.S.; Shlapakov N.S.; Ananikov V. P. Chem. Sci., 2016, 7, 6740-6745.
[5] Kitson, P. J.; Marie, G.; Francoia, J. P.; Zalesskiy, S. S.; Sigerson, R. C.; Mathieson, J. S.; Cronin, L. Science 2018, 359, 314-319.
[6] Eremin, D. B.; Boiko, D. A.; Borkovskaya, E. V.; Khrustalev, V. N.; Chernyshev, V. M.; Ananikov, V. P. Catal. Sci. Technol., 2018,8, 3073-3080.

CATALYTIC DEHYDRATION OF MODIFIED CARBOHYDRATES AS A NEW APPROACH TO EFFICIENT PLANT BIOMASS UTILIZATION IN ORGANIC SYNTHESIS

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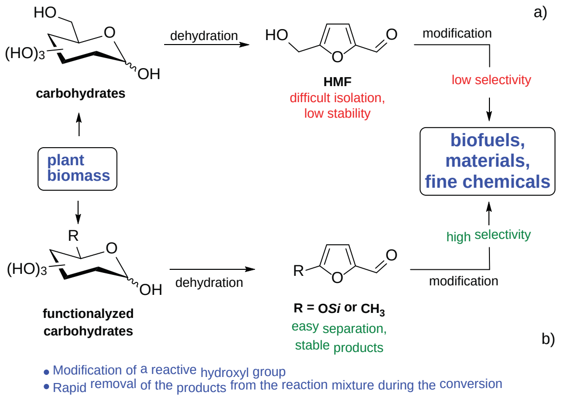
Integration of renewable bioresources for sustainable applications is one of the key challenges of modern chemical science and technology. The most perspective approach to synthetic utilization of plant biomass involves the catalytic conversion of carbohydrates to low-molecular-weight building blocks, which are defined as bio-based platform chemicals. 5-(Hydroxymethyl)furfural (HMF) is one of the key platform chemical[1] that was defined as «sleeping giant» of sustainable chemistry due to enormous synthetic and market potential. However, low chemical stability and difficult isolation process limits utilization of HMF as a reagent in organic synthesis (Figure 1, a). An efficient approach to preparation of stable HMF analogues by direct conversion of modified carbohydrates was developed (Figure 1, b). A highly efficient biomass conversion process based on introduction of a silyl protecting group to glucose allowed to increase the selectivity of furan formation and facilitated its isolation from the reaction mixture.[2] New aspects of synthesis and utilization of HMF and derivatives for biofuels, materials and pharmaceuticals production was also studied. We have shown that the aldehyde group in HMF can be easily modified into an alkyne moiety using the Ochir-Bestman reaction. A number of polyunsaturated products from obtained alkynylfurans were prepared in presence of rhodium catalysts.[3] The first example of the Diels-Alder reaction of unsubstituted 2,5-bis(hydroxymethyl)furan with maleimide was carried out under green conditions with high diastereoselectivity.[4] The implementation of described synthetic approaches opens new opportunities for the synthesis of demanded functional derivatives from bio-based furans.

Figure 1. a) general route to plant biomass utilization in organic synthesis; b) our approach based on conversion of modified carbohydrates.



This work was supported by the Russian Science Foundation (RSF grant № 17-13-01176).

References:
[1] a) F. A. Kucherov, L. V. Romashov, K. I. Galkin, V. P. Ananikov, ACS Sustainable Chem. Eng. 2018, 6, 8064-8092; b) A. S. Kashin, K. I. Galkin, E. A. Khokhlova, V. P. Ananikov, Angew. Chem. Int. Ed. 2016, 55, 2161-2166.
[2] K. I. Galkin, E. A. Krivodaeva, L. V. Romashov, S. S. Zalesskiy, V. V. Kachala, J. V. Burykina, V. P. Ananikov, Angew. Chem. Int. Ed. 2016, 55, 8338-8342.
[3] L. V. Romashov, V. P. Ananikov, Chem. - Asian J. 2017, 12, 2652-2655.
[4] F. A. Kucherov, K. I. Galkin, E. G. Gordeev, V. P. Ananikov, Green Chem. 2017, 19, 4858-4864.

APPLICATION OF 3D-PRINTED WARES FOR CATALYTIC TRANSFORMATIONS

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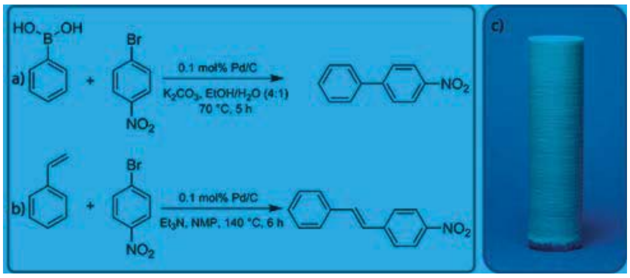
Three-dimensional printing finds more and more applications in a wide variety of activities. Equipment for 3D printing is easily available today, which allows one to appreciate all the simplicity and dignity of the method of creating new objects from digital models. A common technology of three-dimensional printing of materials is the method of fused deposition modeling (FDM). In our project the influence of FDM parameters on the possibility of using printed products in a chemical laboratory was investigated. For the best quality of 3D printing products, it is necessary to optimize a number of parameters. A defined set of options, including nozzle diameter, wall thickness, and the number of internal and external perimeters, determines the features of internal filling of the wall in the course of 3D printing.

In addition to the printing parameters per se, the influence of shape and material of a printed product on its mechanical strength and thermal resistance was also investigated. The polymer materials used in the study included PETG, PP, PLA, ABS, nylon and carbon-filled nylon; the shapes included a pyramid, a sphere, a cone, a cylinder, and a cube. To be applicable in laboratory practice, a finished 3D-printed product should be sufficiently strong and resistant to high reaction temperatures. The number of pores in its walls should be kept to a minimum in order to avoid leakage, evaporation of the solvent, and to prevent accumulation of heterogeneous catalysts within the pores.

Polypropylene wares printed at the optimized conditions (Fig. 1c) were impermeable and resistant to the stringent conditions necessary for Suzuki-Miyaura (Fig. 1a) and Heck (Fig. 1b) reactions. The reactions carried out in the printed wares proceeded with the same conversions as in the glass vials [1].

Figure 1. Studied catalytic reactions (a-b) and example of 3D-printed polypropylene glass vial (c).



In the nearest future, 3D printing can become a valuable tool in catalysis. FDM technology allows one to design unique laboratory equipment and reactor components, which would be extremely difficult to access with the same speed and cost by rational methods.

The study was supported by Russian Science Foundation 14-13-01030 grant.

[1] Evgeniy G. Gordeev et al., PLoS ONE 13, 6 (2018). DOI: 10.1371/journal.pone.0198370

NITROREDUCTASE-SENSITIVE FLUORESCENT PROBES BASED ON A FLUOROGENIC BIS-PHENOLIC BODIPY DYE

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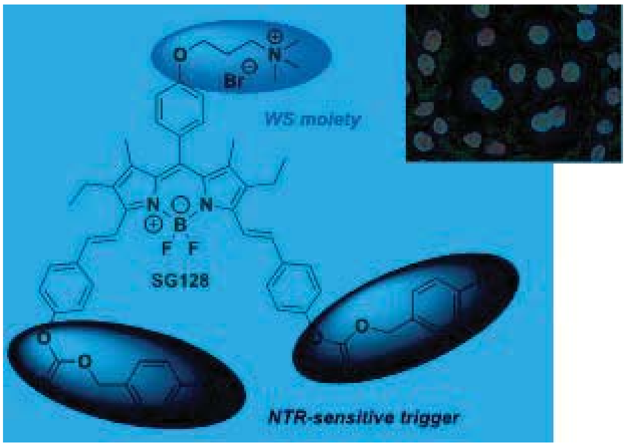
Hypoxia is a pathological condition in which tissues lack the oxygen required for cells for normal metabolization processes [1]. In some solid tumors, for example, the median oxygen concentration has been reported to be around 4%, and locally it may even decrease to 0 % [2]. Therefore, it is of considerable clinical significance to develop contrast agents for imaging the hypoxic status of tumor cells. It is known that hypoxia can induce accelerated bioreductive reactions and result in greater expression of intracellular reductases, such as azoreductase (AzoR), cytochrome P450 reductase, quinone reductase (e.g., DT-diaphorase), and nitroreductase (NTR). Consequently, one of the preferred approaches for the detection and localization of hypoxia is based on the use of «turn-on» reactive probes selectively activated by one of these redox enzyme classes [3]. Here we report novel fluorogenic bis-phenolic Bodipy dye promising for nitroreductase detection.



We designed and synthesized the dual-reactable fluorescent NTR probe based on a mono-cationic Bodipy dye. The three phenol moieties of fluorophore were derivatized to introduce an alkyltrimethylammonium group for water solubility and two para-nitrobenzyloxycarbonyl groups acting as self-immolative NTR-sensitive QRUs. This compound is promising for the allowing in theory the rapid access to effective bioreductive fluorescent imaging in cancer cells.

The reported study was supported by RFBR, research project № 17-53-16012 НЦНИЛ_а.

References
1. Sun, X.; Niu, G.; Chan, N.; Shen, B.; Chen, X., Tumor Hypoxia Imaging. Mol Imaging Biol 2011, 13, 399-410 and references cited therein.
2. Vaupel, P.; Schlenger, K.; Knoop, C.; Hockel, M., Oxygenation of human tumors: evaluation of tissue oxygen distribution in breast cancers by computerized O2 tension measurements. Cancer research 1991, 51, 3316-3322.
3. Apte, S.; Chin, F. T.; Graves, E. E., Molecular Imaging of Hypoxia: Strategies for Probes Design and Application. Curr. Org. Synth. 2011, 8, 593-603.

ADDITIVE TECHNOLOGIES IN ORGANIC CHEMISTRY AND CATALYSIS

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In recent years, additive technologies have become widespread not only in the professional community of engineers, but also among specialists from other fields. Today, 3D printing is used in medicine, scientific research, industrial and artistic design, and even in jewelry and confectionery production. 3D printing gradually permeates into all areas of manufacturing, which is due to user-friendliness of modern 3D printers. The majority of 3D printing applications do not require professional engineering skills, unless printing a critical item.

Additive technologies open awesome prospects in chemistry, chemical technology and biotechnology. With the right choice of 3D printing material, it is possible to create complex chemical reactors and equipment in a chemical laboratory by using a 3D printer without additional processing equipment [1]. Rapid manufacturing of complex parts by additive methods provides an access to fine optimization and assembling of reactors for various experimental conditions. An important issue, which is limiting the usage of additive technologies in chemistry, is the questionable resistance of 3D printing materials to organic solvents. Another important practical issue is the intrinsically high porosity of 3D printed parts, which is directly related to sealing properties of 3D printed labware and equipment, as opposed to their permeability. [1].

Another important challenge for the application of additive technologies in chemistry is the development of new catalytically active units for heterogeneous catalysis. The development of such units (cartridges) includes not only the invention or selection of a catalytically active 3D printing material, but also the design of organized and 3D-printable channel system for optimal implementation of the catalytic process.

Among the materials relevant in biotechnology, medicine and tissue engineering, a very special place is occupied by biodegradable materials that can be used to create implants. There are several successful examples of using 3D bioprinting to create biodegradable bone implants, which are gradually replaced by the natural bone tissue within the body. Accordingly, tuning of the existing biodegradable materials and their further adaptation for additive technologies, as well as the design of new materials for bioprinting, represent very important trends [2].

One of the 3D printing technolgoies, which is considered very promising for applications in chemistry, is called ’’fused deposition modeling’’ (FDM). 3D printing by FDM consists in layer-by-layer fusion of thermoplastic material extruded from a nozzle of a small diameter. Such an approach is compatible with a wide range of thermoplastics, including those of high chemical and thermal resistance: PEEK, PEKK, PPSU, PEI, PVDF, PP, PA. Without exceeding the limitations of the technology, these materials can be easily modified by adding catalytically active metal particles or their compounds to the polymer matrix. For example, it has been shown that 3D printed catalytic systems based on ABS plastics and TiO2 composites exhibit high activity in some photochemical reactions.

The present study was supported by the Russian Science Foundation (RSF) Grant 14-50-00126.

References
[1] Gordeev E.G.; Galushko A.S.; Ananikov V.P. PLoS ONE, 2018, 13(6): e0198370.
[2] Kucherov F.A.; Gordeev E.G.; Kashin A.S., Ananikov V.P. Angew. Chem. Int. Ed., 2017, 56(50), 15931.

SELECTIVE CONVERSION OF GLYCEROL TO MONO–ALCOHOLS

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A key field in the development of renewable fuels is the production of biodiesel fuel via the transesterification of vegetable oils with the participation of methanol. Along with methyl esters of oleic and other acids, the reaction products include stoichiometric amounts of glycerol. The problem of glycerol utilization is therefore of great concern.

A promising solution to this problem is the catalytic hydrodehydroxylation of glycerol to form simple alcohols – ethanol and propanols that are used as a feedstock for the production of a wide range of high value-added chemicals. In addition, these simple alcohols or ethers produced from them can be used as additives for motor fuels to increase their octane number.

Typical glycerol hydrodehydroxylation catalysts are either platinum group metals (Pt, Rh, Ru, Ir) supported on an appropriate material or Raney Co or Ni [1–3]. Most of these catalysts have been studied in the production of 1,2-propanediol, 1,3-propanediol, and the process occurs at a relatively slow rate and with a low selectivity. From this point of view, the search for new active catalysts based on non-precious metals is of considerable interest.

In this work, we explore the possibility of glycerol conversion to 1-propanol and 2-propanol in a flow system in the presence of a 16%Ni/20%WO_3-TiO_2 catalyst that combines both the acid function to accelerate dehydration of glycerol and the metal function required for hydrogenation of C–O bonds formed after dehydroxylation stages. The Ni/WO_3-TiO_2 catalyst was prepared by incipient wetness impregnation of WO_3-TiO_2 with a nickel nitrate solution followed by drying and calcination. In turn, the WO_3-TiO_2 support was produced by co-precipitation of titanium and tungsten hydroxides followed by appropriate drying and calcination. Nickel was reduced in hydrogen atmosphere in the reactor just before the catalytic experiment.

The process was carried out in a flow stainless-steel tube reactor with i.d = 7 mm. The catalyst with a weight of 3 g and particle sizes of 0.25–0.5 mm was charged into the central part of the reactor. The free space of the reactor was filled with ground quartz with particle sizes of 0.5–1 mm. An aqueous solution of glycerol (30%) was fed into the reactor by a syringe pump at LHSV of 0.5–0.7 h-1. Glycerol dehydroxylation in the presence of the 16%Ni/20%WO_3-TiO_2 catalyst was studied in the temperature range of 245–255°C and hydrogen pressures of 30–32 atm.

When using the 16%Ni/20%WO3-TiO2 catalyst we obtained the total yield of 1-propanol and 2-propanol in the range of 84.7–94.2% and the glycerol conversion reached 100%, herewith the process occurring in rather mild conditions. The mechanism of glycerol hydrodehydroxylation in the presence of this catalyst is apparently as follows: at the first stage, glycerol undergoes dehydration to form acetol and 3-hydroxypropionic aldehyde, which upon addition of hydrogen are converted to 1,2-propylene glycol and 1,3-propylene glycol, respectively, and at the second stage, dehydroxylation of these diols leads to formation of 1-propanol and 2-propanol.

Thus the data suggest that the catalyst 16%Ni/20%WO_3-TiO_2 can be used to effectively convert glycerol to simple alcohols such as 1-propanol and 2-propanol with a total yield more over 85%.

References:
[1] M. Pagliaro et al., Angew. Chem., Int. Ed. Engl. 46, 4434 (2007).
[2] A. Perosa and P. Tundo, Ing. Eng. Chem. Res. 44, 8535 (2005).
[3] I. Gandarias et al., Appl. Catal. B 97, 248 (2010).

NOVEL PH-SENSITIVE MODELS OF TWIN PRODRUGS: FRET-BISFLUOROPHORE AND AZIDOTHYMIDINE-ALBUTOIN THIOUREA-BASED CONJUGATES

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O.A. Fedorova[2,3], J. Gediminas[4], D. A. Skvortcov[1],
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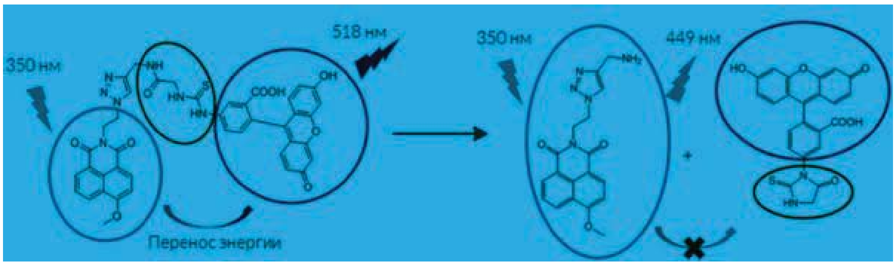
Currently used in clinical practice cytotoxic drugs are effective agents of chemotherapy for malignant neoplasms, but they have a number of serious deficiencies, the main one of which is low selectivity. The optimal way to increase selectivity is to use prodrags. Particularly prodrugs are the derivatives of the drug that are not active in the body's environment, but under the influence of specific metabolic processes, transforming into an active form.

Despite the fact that the difference in the extracellular pH of healthy and tumor cells may seem insignificant, the presence of an increased number of protons near the tumor tissues opens the possibility of the development of pH-selective prodrugs. Thus, we have synthesized new tiourea-based model compounds to study the ability of pH-sensitive cyclization of sterically hampered molecular conjugates, structurally similar to cytotoxic drugs.

To explore the cyclization ability of thiourea derivatives in a weakly acid medium, we have proposed to synthesize a sterically hindered fluorescent derivative of 2-thiohydantoic acid containing the donor naphthalimide and acceptor fluorescein fragments (FRET-pair). Theoretical calculations and study of the change in the fluorescence spectrum of a conjugate during a slow acidification of the medium provides a clear demonstration of the acid-catalyzed cyclization reaction of the thiourea derivative with the release of the amide fragment and the formation of the 2-thiogidantoin derivative. Thus, the FRET-pair can already be used as a marker of tumor cells.

Additional evidence of the effectiveness of thiourea as the basis of the pH-sensitive prodrug was the experiment on the release of a therapeutic agent in an acid medium from 3'-amino-3'-deoxythymidine conjugate with an albutoin precursor with LS-MS monitoring.

The method for the synthesis of new pH-sensitive twin prodrug based on thiourea was proposed. Prodrug structures were confirmed by NMR and HRMS. The ability of the resulting prodrugs to release therapeutic and supplementary components in a weakly acidic medium was confirmed by LC-MS, stationary and time-resolved fluorescence spectroscopy.



The study was supported by Russian Foundation for Basic Research 18-33-01038.

SYNTHESIS OF 8- AND 8,10-SUBSTITUTED BARBITURILS AND THEIR THIOANALOGS

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The methods of syntheses annelated bicyclic bisureas and their thio-analogues are constantly being developed and their properties are studied in detail. In the series of bicyclic bisureas, two main groups of compounds can be distinguished: glycolurils and propandiureas. However, spirocyclic bisureas and especially their thioanalogues are less studied, although no less attractive. The substituted 2,4,8,10-tetraazaspiro[5.5] undecane-1,3,5,9-tetraones (barbiturils) and their thioanalogues are particularly interesting, since in them the urea fragment is part of the known pharmacophore-barbituric acid. At present, a number of 2,4-disubstituted 7,11-diarylbarbiturils and their thioanalogues have been synthesized. In this work, the synthesis of previously inaccessible 8-substituted and 8,10-disubstituted barbiturils and their thioanalogues on the basis of the first studied condensation of 1-mono- and 1,3-disubstituted ureas or thioureas with paraform and barbituric or thiobarbituric acids was developed (Figure 1).

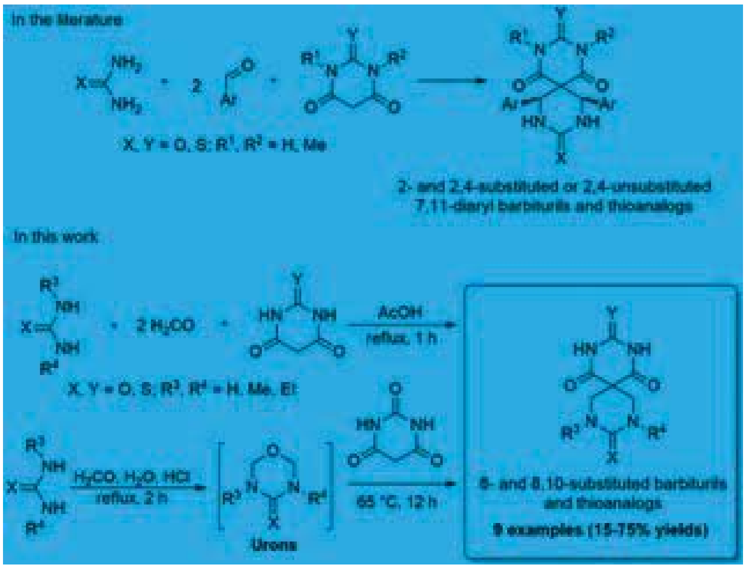

Figure 1. Synthesis of barbiturils and thiobarbiturils.

SYNTHESIS AND STUDY OF THE INFLUENCE OF SUBSTITUENTS ON THE CYTOTOXICITY OF OXINDOLYLIDENE DERIVATIVES OF IMIDAZOTHIAZOLOTRIAZINONES

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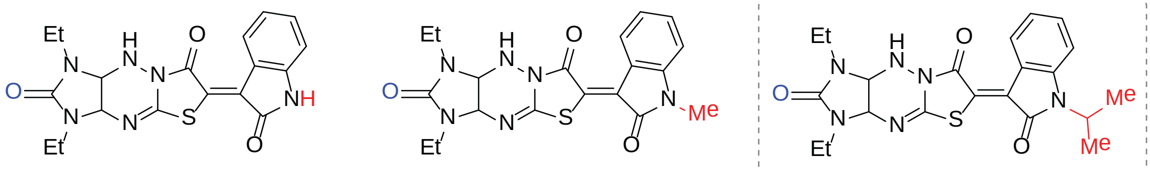
In the present work, we studied the influence of substituents at different positions of oxindolylidene derivatives of imidazo[4,5-e]thiazolo[3,2-b]-1,2,4-triazines [1,2] on their antiproliferative activity against four human tumor cell lines: rhabdomyosarcoma (RD), lung carcinoma (A549), colon carcinoma (HCT116) and breast cancer (MCF7). A series of imidazo[4,5-e]thiazolo[3,2-b]-1,2,4-triazine-2,7(1H,6H)-dione (more than 60 examples) was synthesized by the reaction of imidazotriazinetions and bromoacetic acid followed by condensation with isatines [1,2]. In general, cytotoxic effect increased with the increase in substituent size at the isatin nitrogen atom (Fig. 1).



1
RD 129˙12±3˙79
A549 239˙03±4˙82
HCT116 123˙70±1˙13
MCF7 300˙17±4˙11

2
RD 10˙21±0˙48
A549 >500
HCT116 10˙09±0˙30
MCF7 >500

3
RD 2˙20±0˙03
A549 2˙29±0˙03
HCT116 0˙47±0˙00
MCF7 3˙11±0˙01

Figure 1. Cytotoxic activities of some tested compounds [IC50, µM] after treatment for 72 h.

The most active compounds were tested against normal human embryonic kidney cells (HEK293) and against Jurkat cells (acute leukemia) to detect the effect of apoptosis-induction. The IC50 value of compound 3 against normal human embryonic kidney cells HEK293 was to 6–41-fold higher than IC50 values of 3 against human cancer cells.

This work was supported by the Russian Foundation for Basic Research (grant № 18-33-01035).

References:
[1] Gazieva G.A. et al., RSC Adv. 5, 43990 (2015).
[2] Izmest'ev A.N. et al., Russ. J. Org. Chem. 53, 753 (2018).

GERMANIUM DIOXIDE AND THE ANTIOXIDANT PROPERTIES OF CATECHOLS

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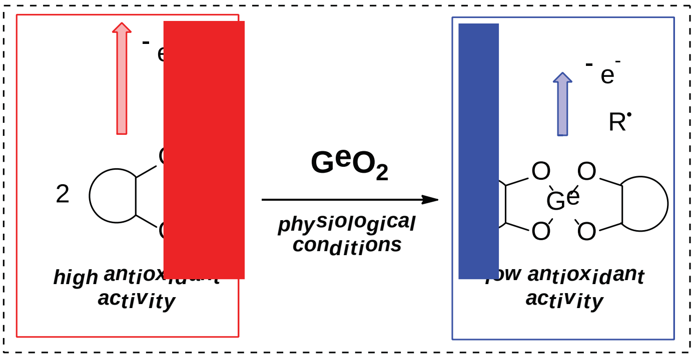
Antioxidants are a large group of physiologically active enzymes of low molecular weight easily releasing an electron and quenching the reactions of free radicals in the body. As a rule, the antioxidants are produced in the organism (internal antioxidants) or being brought with food (dietary antioxidants). The antioxidants of the former type, e.g. adrenaline (epinephrine), noradrenaline, dophamine etc., as well as of the latter (dihydroquercetin and others) are aromatic 1,2-diols (catechols), which accounts for their easy oxidation.

The present work aims to consider the previously undiscussed effect of germanium dioxide on the antioxidant properties of catechols of high biological relevance from both thermodynamic and kinetic points of view. First assessment was realized using cyclic voltammetry, a standard method for evaluation of the ease of electron release through the shift of the redox potential E. Another, kinetic, method for assessing the antioxidant properties estimates the reaction rate of a given antioxidant with 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical.



It was found that adrenaline and 3,4-dihydroxybenzaldehyde in aqueous solutions in presence of GeO2 form complexes of tetra- and hexa-coordinated germanium. The structure of the prepared complexes was confirmed by ^{1}H and ^{13}C NMR and IR spectroscopy, HRMS and elemental analysis. Cyclic voltammetry in phosphate buffer solutions (pH = 6.86) has shown the oxidation potentials Ep of these complexes to be shifted by ca. 300 mV to more positive potentials compared to the parent aromatic diols, meaning their ca. 7 kcal mol-1 hampered electron releasing properties. Kinetics of the reaction of these complexes with DPPH in the presence of 5% acetonitrile reveals an approximately one order of magnitude decrease in the radical scavenging activity of adrenaline and of the model 3,4-dihydroxybenzaldehyde upon their complexation with Ge.

Keeping in mind that 1,2-diols are widespread in the living nature and often have important biological functions, these results will contribute to understanding of the role of germanium dioxide in metabolic mechanisms and to alert against unreasonable use of Ge preparations.

This work was supported by Grant MK-755.2017.3. High resolution mass spectra were recorded in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

ASSESSMENT OF CARBOHYDRATE SPECIFICITY OF ANTI-CANDIDA IMMUNOGLOBULINS USING THEMATIC MANNAN GLYCOARRAY

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The most common fungal species caused the invasive mycosis in hospital units belong to Candida genus (particularly C. albicans). Despite the importance of early treatment of invasive candidiasis (IC), no clear methods have been developed for the early diagnosis of this infection. Identification of C. albicans by blood culture is still the gold standard, however, blood cultures are only positive in 50% of cases and may take 24-72 hours before results become available. All this encourage the development of sensitive, highly specific and rapid diagnosticum for detection of Candida pathogens in biological fluids.
The development of novel diagnosticums is based on understanding fine structure of specific antigen. To reveal it the glycoarray comprising of synthetic mannooligosaccharides related to main antigenic factors of Candida (factors 1, 4, 6, 9, 13b, 34) was applied for the investigation of carbohydrate specificity of antibody rose against different fungal species including C. albicans, Candida krusei, Saccharomyces cerevisiae, Aspergillus fumigatus and others. The obtained data are necessary for the design of the required serological EIA diagnosticums for detection and species characteristics of fungi.

This work was supported by RSF grant 14-50-00126.

References:
[1] A.A. Karelin, Y.E. Tsvetkov, N.E. Nifantiev, Russ. Chem. Rev., 86, 1073 (2017).
[2] V.B. Krylov et al., Appl. Biochem. Microbiol., 54, 522 (2018).
[3] V.B. Krylov et al., Appl. Biochem. Microbiol., 54, №6 (in press) (2018).

A RAPID AND EFFICIENT ACCESS TO NEW CHEMICALS AND MATERIALS FROM THE RENEWABLE 5 HMF BY USING A CLICK CHEMISTRY APPROACH

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Production and conversion of bio-derived platform chemicals and building blocks have received much attention in connection with the sustainable development and green chemistry concepts. Recently, 5-(hydroxymethyl) furfural (HMF), produced by catalytic dehydration of hexose carbohydrates, has been identified as a key renewable platform chemical for various synthetic applications (see, for example, [1,2]), as well as for the production of biofuels, polymers and fine chemicals [3,4]. However, just a few azide derivatives of biomass-derived furans are described to-date. Especially questionable is the applicability of biomass-derived furans to easy and rapid click chemistry synthesis of triazoles, which are reported to have interesting biological activity. Huisgen dipolar cycloaddition of azides and alkynes in CuAAC-manner (Cu (I)-catalyzed azide/alkyne cycloaddition) has proved to be one of the most important linking reactions. This reaction usually proceeds in regular conditions, with high yields and regioselectivity. It has numerous advantages in drug development, materials science, and other fields of organic, bioorganic, and medicinal chemistry.

In this work, we report synthesis and modification of a new promising bio-based monomer, 2-(azidomethyl)-5-ethynylfuran. Its ambivalent reactivity is related to the presence of both azide and alkyne moieties, which allows to carry out click polycondensation under mild conditions to afford different types of heterocyclic furan-triazole polymers. We also studied the reactivity of azide group in the AEF precursor, 5 (azidomethyl) furfural. It was tested in reactions with other alkynes following the classical CuAAC-methodology.

Possible ways for joining biomass-based approach and click chemistry will be presented and discussed. Undoubtedly, further studies on the subject will promote many applications of click chemistry approach for construction of bio-based heterocyclic frameworks.

The study was supported by Russian Science Foundation 17-13-01176 grant.

Literature

1. K. I. Galkin, E. A. Krivodaeva, L. V. Romashov, S. S. Zalesskiy, V. V. Kachala, J. V. Burykina and V. P. Ananikov, Angew. Chem. Int. Ed., 2016, 55, 8338-8342.
2. L. V. Romashov and V. P. Ananikov, Chem. Asian J., 2017, 12, 2652 –2655.
3. V. M. Chernyshev, O. A. Kravchenko and V. P. Ananikov, Russ. Chem. Rev., 2017, 86, 357-387.
4. F. A. Kucherov, L. V. Romashov, K. I. Galkin and V. P. Ananikov, ACS Sustainable Chem. Eng., 2018, 6, 8064-8092.

ASSOCIATES OF OLIGOPHRENOTIAZINE AND POLYANILINE: SELF-ASSEMBLY AND ELECTROPHYSICAL PROPERTIES

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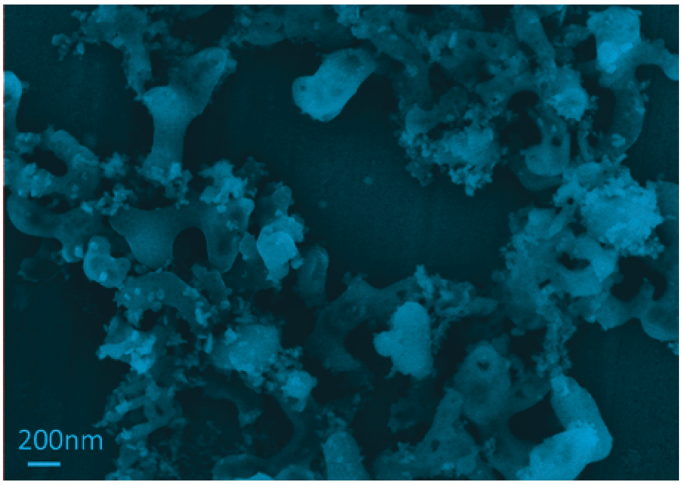
Nowadays photoactive and electrochemically active organic materials based on aromatic oligomers and polymers attract significant interest. While their efficiency and stability are often inferior to inorganic analogues', they have important advantages: due to simple coating technique, synthetic availability and environmental safety, such materials call for demand in the production of new generation solar cells, batteries, OLED and PLED devices, electrochemical sensors.

Oxidative polymerization is an accessible and easily scalable method for synthesizing oligo- and polyaromatic structures. This approach has been already successfully applied for the synthesis of polyaniline and polymers based on thiophene derivatives. Nevertheless, oxidative polymerization can lead to by-product formation, and therefore modern methods of metal-catalyzed copolycondensation and electrochemical oxidative polymerization of aromatic derivatives are widely used for most aromatic monomers.

Image 1. SEM image of oligophenothiazine.



We have proposed and implemented a simple (non-template) one-step method for obtaining nanostructures from the polyaniline complex with oligophenothiazine. UV-spectroscopy confirmed that the complex of oligophenotiazine and polyaniline exerted new absorption band in an acid medium due to donor-acceptor interaction with charge transfer. Complex structures were confirmed by scanning electron microscopy. Such a material can be used in the manufacture of new generation OLEDs, photodetectors, and organic field-effect transistors. We have investigated the influence of complex formation with oligophenothiazine on electrophysical properties such as: electrical conductivity, capacitance, dielectric permittivity.

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

PHOTOCHROMIC LABELS
AS A NEW CHALLENGE FOR THE NANOPHOTONICS

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A promising way for the new hybrid photoactive/photocontrollable systems and materials design consists in the covalent binding of the photochromic probes via their covalent "immobilization" on various substrates, e.g. polymers, lipids, proteins and quantum dots. Developing the new generation of photochromic probes containing substituents with appropriate functional group type will be required for the implementation of this procedure. Indoline spirobenzopyrans are one of the most studied photochromic compound classes. The structure of possible target substrates defines the nature of the reactive anchor group. Spectral properties and photochemical parameters of spirobenzopyrans depend significantly on the nature of the substituent present in the defined part of the molecule, hence, the targeted variation of substituents' nature allows to search directly for new photochromes with given photochemical properties and various stimulus-responsive structural elements.

Previously we have studied the spirobenzopyran formylation process under the Duff reaction conditions and the influence of different substituents in the pyran cycle on its regioselectivity. The Duff formylation of photochromic spiropyrans having electron-acceptor substituents in the pyran part of molecule (R: 6-NO_2; 8-NO_2; 6-CHO; 6-CO_2Et; 6-CO_2H) was found to mainly proceed to C5'-position of indoline fragment. As the result we developed a new synthetic method for the key carbonyl precursor - 5'-formyl-6-nitrospiropyran derivative by direct formylation of 6-nitrospiropyran, in one step with 86% yield under the Duff reaction conditions. The synthetic application potential of these precursors for targeted modification of the photochrome molecule at 5'-position has been significantly broadened by the application of well-known synthetic procedures (Wittig and Horner-Emmons olefination; nucleophilic addition to the carbonyl group with a family of reagents, possessing an active methyl or methylene groups; reductive amination; [3+2]cycloaddition reaction and others) [1-3].

We developed a number of new photochromic probes and labels on the 5'-substituted spirobenzopyran scaffold. All the types of labels were prepared by the effective synthetic approach which included the direct modification of spiropyran molecule. The choice of the target reactive group or "molecular address" was determined by type and nature of the target structure. The following conjugation procedure variants were used: a) covalent binding of the probe molecule with target binding site by self-recognition principle (bacteriorhodopsin); b) noncovalent binding of the probe molecule with target by the recognition of "molecular address" part, which was introduced in label (TxA2 receptor inhibitors); c) covalent binding of the probe molecule with target by terminal selectively reactive group (HS-group for CdSe Quantum Dots); d) covalent binding of the probe molecule with target by terminal reactive group.

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References:
1. Zvezdin K.V., Belikov N.E., Laptev A.V., Lukin A.Yu., Demina O.V., Levin P.P., Brichkin S.B., Spirin M.G., Razumov V.F., Shvets V.I., Khodonov A.A., Nanotechnologies in Russia, 2012, 7 (5), 308.
2. Laptev A.V., Lukin A.Yu., Belikov N.E., Zvezdin K.V., Demina O.V., Barachevsky V.A., Varfolomeev S.D., Khodonov A.A., Shvets V.I., Rus. Chem. Bull., 2014, 63 (9), 2026.
3. Laptev A.V., Lukin A.Yu., Belikov N.E., Barachevskii V.A., Demina O.V., Khodonov A.A., Varfolomeev S.D., Shvets V.I., Mendeleev Commun., 2013, 23 (3), 145.

SYNTHESIS OF POLYNUCLEAR DISPIROHETEROCYCLIC STRUCTURES CONTAINING Β,Β'-SPIROPYRROLIDINOOXINDOLE AND IMIDAZOTHIAZOLOTRIAZINE MOIETIES

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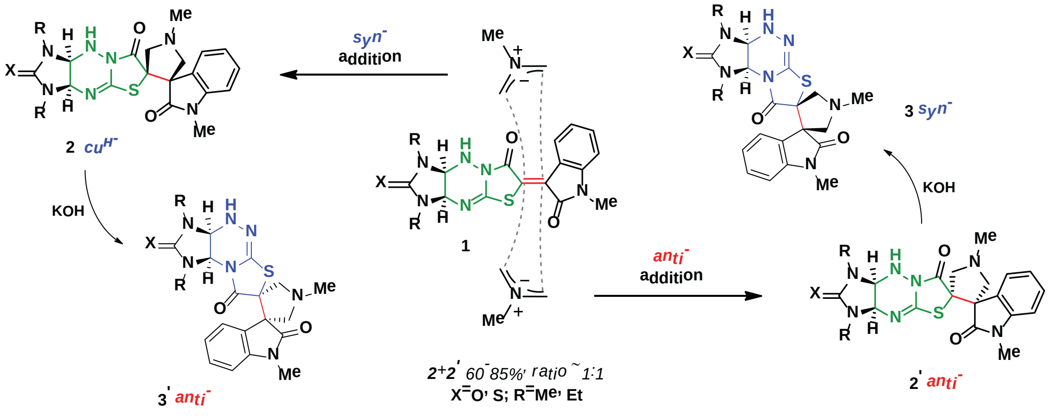
1,3-Dipolar cycloaddition of azomethine ylide generated from formaldehyde and sarcosine to the double bond is a efficient one-pot synthesis of compounds containing β,β'-spiro[pyrrolidin-oxindole] moieties [1]. We developed a method of the synthesis of diverse polynuclear heterocycles with bis-spiro junction using as dipolarophiles condensation products of isatins with the methylene-active imidazothiazolotriazines 1. Compounds 2, 2' formed as mixture of two diastereomers 2 and 2' resulting from the addition of azomethine ylide from above and from below of the plane of isatylidenes 1 (Scheme 1).



Scheme 1.

Chromatographic separation of a mixture of compounds 2 and 2' with subsequent rearrangement [2] of the individual components in methanol under the action of KOH leads to regioisomeric structures 3 and 3' with high or quantitative yields.

This work was supported by the Russian Foundation for Basic Research (grant № 18-33-01035).

References:
[1] Chris V. et al., Angew. Chem. Int. Ed., 46, 8748 (2007).
[2] Gazieva G.A. et al., RSC Adv., 5, 43990 (2015).

NOVEL HIGH NITROGEN-OXYGEN SYSTEMS

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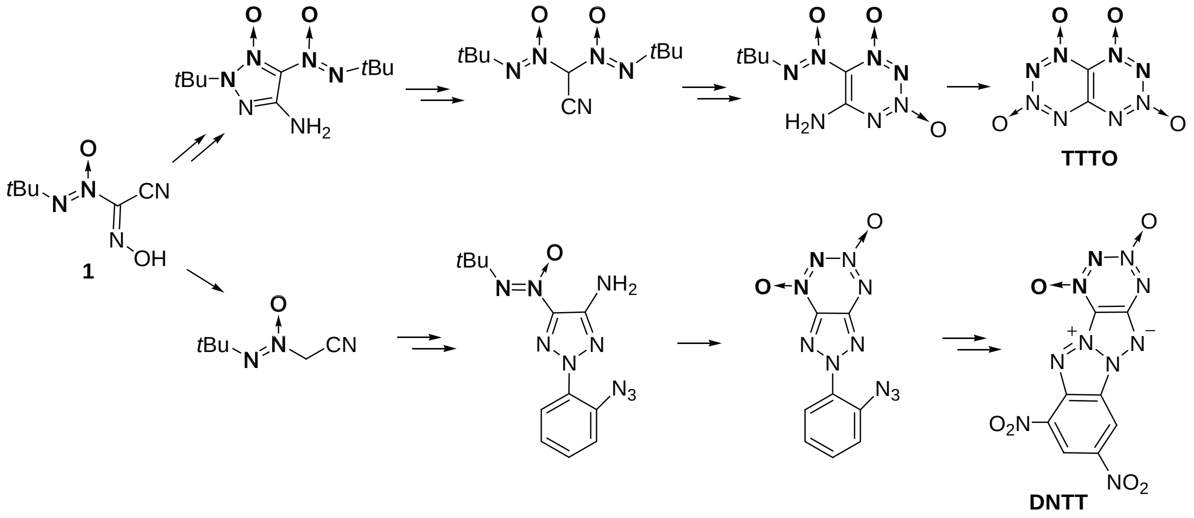
Cyclic high-nitrogen systems with N-oxide oxygen atoms are of significant interest as a new generation of high energy density materials (HEDM). One of the most promising class of compounds are 1,2,3,4-tetrazine 1,3-dioxides, [1,2,3,4]tetrazino[5,6-e][1,2,3,4]tetrazine 1,3,6,8-tetraoxide (TTTO) among them. This molecule has gained much attention in the scientific community due to its high energetic characteristics which puts it on a par with the most powerful explosives known. TTTO was synthesized from oxime 1 [1,2]. The synthetic strategy was based on the sequential closure of two 1,2,3,4-tetrazine 1,3-dioxide rings. The TTTO structure was confirmed by single-crystal X-ray.

Further encouraging example of novel energetic compounds are 1,2,3,4-tetrazine 1,3-dioxides directly fused with 1,3a,4,6a-tetraazapentalene moiety, DNTT among them. A synthesis of this compound started from oxime 1 and involved the closure of the 1,2,3,4-tetrazine 1,3-dioxide ring first and then formation of the tetraazapentalene ring [3,4]. DNTT displays high thermal stability and shows considerable promise as a new HEDM.



Scheme 1. Synthesis of TTTO and DNTT.

A number of novel synthetic methods have been elaborated in the course of the synthesis of TTTO and DNTT including the method for the synthesis of bis-(azoxy)methanes, reduction of oxime group to methylene unit and synthesis of 1,2,3,4-tetrazine 1,3-dioxide ring starting from aliphatic precursors.

This work was financially supported by the Russian Science Foundation (Project No. 14-50-00126).

References:
[1] Michael S. Klenov et al., Eur. J. Org. Chem. 6170 (2015).
[2] Michael S. Klenov et al., Angew. Chem. Int. Ed. 55, 11472 (2016).
[3] Michael S. Klenov et al., Eur. J. Org. Chem. 3845 (2016).
[4] Alexey A. Voronin et al., Eur. J. Org. Chem. 4963 (2017).

2,5-FURANDICARBOXYLIC ACID SYNTHESIS USING BASE-FREE AEROBIC OXIDATION OF 5-HYDROXYMETHYLFURFURAL OVER PT/C CATALYSTS PREPARED VIA ELECTROCHEMICAL PULSE ALTERNATING CURRENT TECHNIQUE

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5-Hydroxymethylfurfural (5-HMF) and its derivative 2,5-furandicarboxylic acid (FDCA) are regarded as a platform chemical for synthesis of various valuable compounds including polymers [1]. FDCA is one of the important monomers, which can replace terephthalic and isophthalic acids in polymers production in future. FDCA is prepared by the oxidation of HMF with the formation of various intermediates and by-products, which depend on the reaction conditions. The aerobic oxidation of HMF to FDCA in base-free conditions would be a better fitted and an environmentally friendly industrial application.

The purpose of this study was to investigate the possibility of base-free aerobic oxidation of concentrated (0.1 M) aqueous HMF solutions to FDCA by increasing of the platinum concentration in Pt/C catalysts [2]. The Pt/C (C = Vulcan XC-72) with different Pt loadings (5-30%) catalysts were prepared via electrochemical dispersion of Pt electrodes under pulse alternating current [3]. The particle size along the [111] direction (D111) calculated from the Scherrer equation on the base of XRD data is 9±1 nm. The Pt particles are uniformly distributed over the surface of carbon support according to the TEM images of all Pt/C samples. The HMF oxidation was performed in a batch-type autoclave. In a typical catalytic experiment 0.1 M aqueous solution of HMF, constant molar ratio HMF/Pt = 20, oxygen pressure 0.1-1 MPa and temperature of 105 °C were used. The reaction mixture was analyzed using high-performance liquid chromatography (HPLC).

For the multi-stage HMF oxidation process the dependence of the overall efficiency of the process on the time is extreme and complicated. Full conversion of HMF and acceleration of the target reaction are achieved by increasing the O_2 pressure that leads to increase in the available dissolved oxygen concentration. Nevertheless, high pressure increases not only oxidation of HMF to FDCA but side reactions too. The higher Pt loading on the catalyst was the faster FDCA yield of up to 60-65% was obtained. The effect of increasing the platinum loading, and hence, decreasing the carbon content in the catalyst, is positive and should be considered from two points of view. On the one hand, increasing the content of the active component in the catalyst causes increasing the rate of HMF oxidation and the formation of FDCA due to extended available platinum surface for the heterogeneous reactions. On the other hand, the carbon support, which has high adsorption ability, catalyzes the formation of humins even in the absence of platinum. Thus, the more carbon is in the reaction medium, the higher the losses are.

Hereby, the optimal conditions for the base-free aerobic oxidation of HMF to FDCA which makes possible to use reagent concentration several times higher than usually used in described techniques (0.1 M HMF) are 105 °C, 6 hours, 0.25 MPa of O2, Pt/C with 30% of Pt.

Enhancing Pt loadings to 15-30 wt% allow selective base-free aerobic oxidation of concentrated (0.1 M) aqueous HMF solutions with FDCA yields up to 65%. To the best of our knowledge, the present article represents the first example of application of heterogeneous Pt/C catalyst obtained by PAC technique in organic synthesis.

This work was supported by the Russian Science Foundation [project no. 16-13-10 444].

References

1. V. M. Chernyshev, O. A. Kravchenko and V. P. Ananikov, Russ. Chem. Rev., 2017, 86(5), 357.
2. Igor Leontyev et al, Appl.Catal. A:General 431-432 (2012)120.
3. Daria V.Chernysheva et al, Mend. Commun., 28 (2018) 431.

DIRECTIONAL SYNTHESIS OF ALKALI-MODIFIED TRANSITION METAL SULFIDE CATALYSTS FOR SYNGAS CONVERSION INTO HIGHER ALCOHOLS AND OVER OXYGENATES

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The design of molybdenum sulfide based catalysts for alcohol production from syngas attracts interest both of academic and industrial research because of several reasons. Alcohols have extensive applications as precursors of surfactants, fragrance compounds, plasticizers, extragents, etc. in various industries. Synthesis gas produced from coal, associated gas or biomass contains up to several dozen ppm of sulfuric compounds such as hydrogen sulfide, carbon disulfide, mercaptanes and thiophenes. Commercial oxide catalysts rapidly lose their activity in the presence of very small concentrations of sulfur containing compounds. Catalysts based on transition metal sulfides are not sensitive to such poisoning. Alkali-modified CoMoS is a promising catalytic system for the synthesis of higher alcohols from synthesis gas [1, 2]. The overall objective of the study was to clarify the role of potassium as a modifier of Mo sulfide catalysts for synthesis gas conversion into alcohols and other oxygenates.

Catalysts of common KCoMoS/(C)/Al_2O_3 composition were synthesized, characterized and examined in the synthesis of alcohols from CO and H2. Potassium addition to CoMoS//(C)/Al_2O_3 could affect both the morphology of molybdenum disulfide crystallites and catalyst activity in the synthesis of alcohols. Quantum chemical calculations using the density functional theory (DFT) approach, evidence the potassium influence on CoMoS phase active sites manifested in the electron density transfer from the potassium atom onto transition metal atoms (predominantly to Co) and in the decrease of the Co atom's electron deficiency. The consequence is Lewis acidity reduction, which, in turn, leads to the decrease of adsorption energies of CO and H_2. Moreover, potassium promotes dissociative adsorption of molecular hydrogen (Fig. 1).

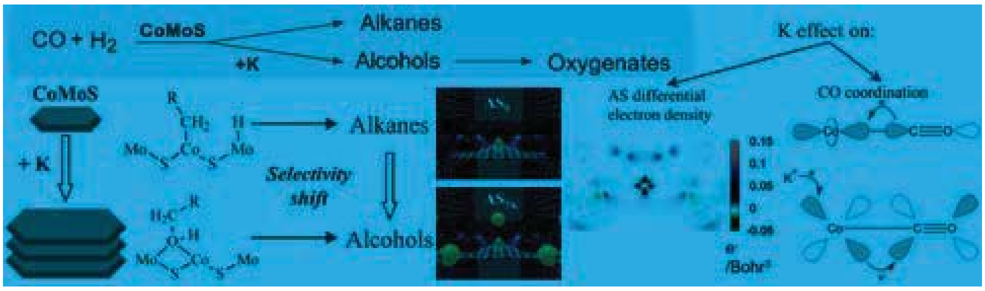

Figure 1. Effect of potassium addition on morphology, electron density of the AS and on the reaction pathways of alcohol formation.

The edge-rim and interlayer dynamic models can be applied for the explanation of KCoMoS catalyst activity in the alcohol synthesis. The active sites responsible for the alcohol formation were attributed to be alkali-modified hydrodesulphurization AS [3, 4]. The influence of ethanol addition to synthesis gas on its conversion and the product composition was examined. A sharp increase of CO conversion in the presence of ethanol was detected. A reaction network of CO conversion on KCoMoS catalyst active sites depending on the catalyst composition and reaction conditions was suggested. These data have been used to design the mechanism of the synthesis gas conversion over the K-modified CoMoS catalyst. The KCoMoS-based catalysts are expected to be suitable for large scale production of alcohols from synthesis gas.

References
1. G. Weber, R. Rauch, H. Hofbauer, Biomass Convers. Biorefin. 5 (2015) 85.
2. V.S. Dorokhov et al., C. R. Chimie 19 (2016) 1184.
3. V.S. Dorokhov et al., J. Catal. 344 (2016) 841.
4. E.A. Permyakov et al., Catal. Today 305 (2018) 19.

INVESTIGATION ON THE REACTIVITY OF OXAMIC ACID THIOHYDRAZIDES TOWARDS HALO CARBONYL COMPOUNDS: DEVELOPMENTS AND NEW PERSPECTIVES

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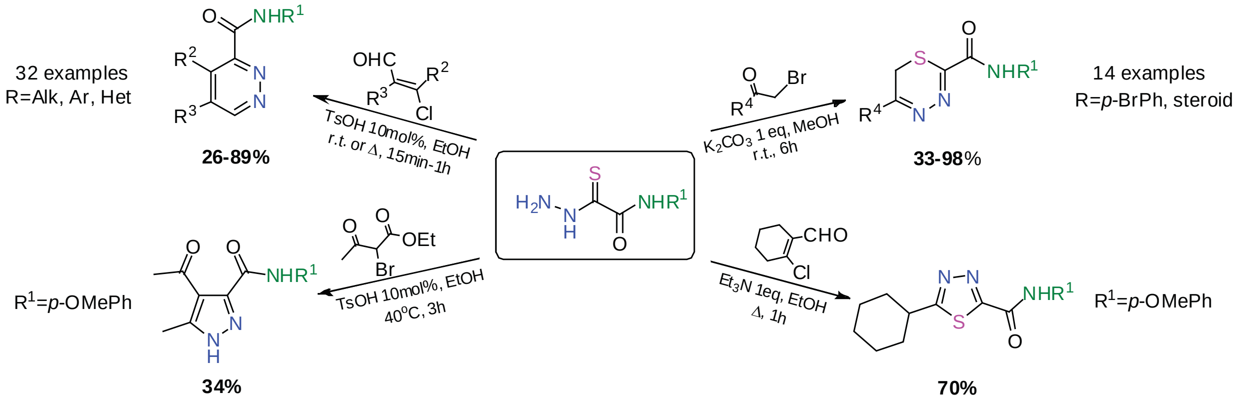
Development of new methods for synthesis of N-heterocyclic compounds is one of the main challenges in organic synthesis. Particular interest present carbamide-substituted heterocycles due to limited ways of their synthesis and promising properties, such compounds may have applications in medicinal chemistry or material science [1].

Herein, we report a convenient and highly reactive oxamic acid thiohydrazides reagent for the concise synthesis of medium–ring N-heterocyclic systems. Based on our previous results [2] and the chemistry of hydrazones, we have elaborated flexible synthetic approaches towards carbamide-substituted pyridazines, 6H-1,3,4-thiadiazines, pyrazoles, and 1,3,4-thiadiazoles with chemoselective control of heterocyclization patterns.



3-Carbamide-substituted pyridazines were exclusively synthesized via condensation of β-chlorovinilaldehydes with 3-carbamide-substituted pyridazines under acid catalysis. The method was found quite general since aliphatic, aromatic aldehydes and steroidal derivatives reacted smoothly providing diverse pyridazines. Starting from 2-bromoacetophenone derivatives we synthesized 6H-1,3,4-thiadiazine-2-carboxamides bearing aromatic moieties. Developed protocol was efficient primarily for compounds with electron-withdrawing groups. Finally, the condensation of ethyl 2-bromo-3-oxobutanoate with oxamic acid thiohydrazide resulted in pyrazole as the major product. Using non-functionalized aldehydes as a substrate in one-pot oxidation protocol, 2-carbamide substituted 1,3,4-thiodiazole was obtained in high yield and minimum synthetic steps. Thus, the development of novel methods for the synthesis of N-heterocycles based on oxamic acid thiohydrazides is high perspective.

The experiments of the research were supported by RFBR projects 18-33-00913.

[1] Filák, L., Rokob, T. A., Vaskó, G. Á., Egyed, O., Gömöry, A., Riedl, Z., Hajós, G. // J. Org. Chem., 2008, 73, p 3900.

[2] (a) Komkov A.V., Komendantova A.S., Menchikov L.G., Chernoburova E.I., Volkova Y.A., Zavarzin I.V. // Org. Lett., 2015, 17(15), pp 3734–3737. (b) Volkova Y.A., Antonov Y.S., Komkov A.V., Sherbakov A.M., Shashkov A.S., Menchikov L.G., Chernoburova E.I., Zavarzin I.V. // RSC Adv., 2016, 6, pp 42863-42868.

SYNTHESIS OF POLY-FUNCTIONALIZED PYRIDAZINES FROM THIOHYDRAZIDES

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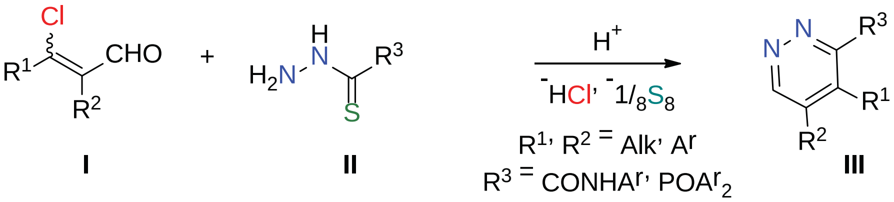
Pyridazines comprise an important class of six-membered nitrogen-containing heterocycles with a broad spectrum of biological activities [1]. Highly functionalized pyridazines are used as antihypertensive drugs (hydralazine, dihydralazine, endralazine) and antidepressants (pipofezine, minaprine). The frequent presence of the pyridazine moiety in medicinally relevant compounds, dyes and ligands for metal catalysts and its wide use in crystal engineering have inspired the development of many novel methods for their preparation [2]. Recently, we have contributed to this endeavor by developing a general synthesis of 3-carbamide-substituted pyridazines III via tandem imination/heterocyclization of β-chlorovinyl aldehydes I with oxamic acid thiohydrazides II [3].

Here, we report the results of extensive experimental investigation on the discovered reaction and elucidation of the reaction scope. The special focus was made on reactivity of functionalized thiohydrazides, which is believed to be the main source of heterocyclization. It was shown that the reaction proceeds at room temperature and is accompanied by extrusion of elemental sulfur and acidification. Thiohydrazone proved to be the first-step intermediate that undergoes isomerization in solution mediated by thione–thiol tautomerism and cis–trans isomerization at N=C-SH and N=C-H double bonds. The additives of acids were found to accelerate the reaction, while the additives of bases inhibit the formation of pyridazine and switch the reaction pathway to 1,3,4-thiadiazole. The autocatalytic character of cyclization accelerated by the formation of acid was demonstrated by means of ^{1}H NMR monitoring.



Screening of thiohydrazide component of reaction reviled hydrazides of phosphorylthioformic acid as highly reactive comopounds. Phosphamideand phosphine oxide derivatives of pyridazines were exclusively synthesized via condensation of β-chlorovinilaldehydes with hydrazides of phosphorylthioformic acid. The method was found quite general since both aliphatic and aromatic aldehydes and steroid derivatives reacted smoothly providing diversepyridazines.

The experiments of the research were supported by RFBR projects 18-33-00913.

References:
[1] (a) M. Y. Jaballah, R. T. Serya, K. Abouzid, Drug. Res. 2017, 67, 138-148. (b) M. Asif, Curr. Med. Chem. 2012, 19, 2984-2991. (c) G. Heinisch, H. Frank, Prog. Med. Chem. 1990, 27, 1-49. (d) G. Heinisch, H. Kopelent-Frank, Prog. Med. Chem. 1992, 29, 141-183.
[2] (a) B. Eftekhari-Sis, V. Zirak, A. Akbari, Chem. Rev. 2013, 113, 2958-3043. (b) P. Majumdar, A. Pati, M. Patra, R. Behera, A. K. Behera, Chem. Rev. 2014, 114, 2942-2977. (c) A. V. Gulevich, A. S. Dudnik, N. Chernyak, V. Gevorgyan, Chem. Rev. 2013, 113, 3084-3213.
[3] (a) Orglett 2015. (b) Y.A. Volkova et al., RSC Adv., 2016, 6, 42863–42868

HYDROXYL-CONTAINING IONIC LIQUIDS

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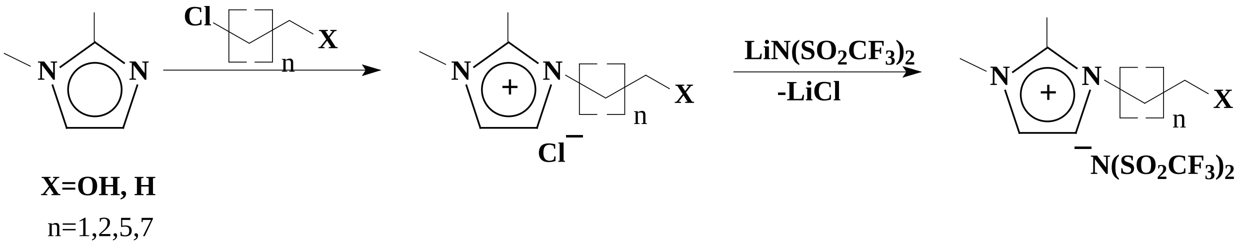
Ionic liquids (IR), which are melts of organic salts with bulky cations and anions, are characterized by two main specific properties – high polarity and low volatility. The high polarity is due to the ion character of the IL, and the low volatility is due to the Coulomb interaction of charged cations and anions. For a long time it was believed that the ionic liquids, as well as inorganic salts, almost do not evaporate. However, studies have shown that at high temperatures (~200°C), the pressure of saturated vapors of ILs is about 0.01-0.05 PA, depending on the structure, and the evaporation process is characterized by enthalpy 130-190 kJ/mol at 25°C. Earlier it was shown the volatility of ILs depends on the nitrogen atom charge in the cation [1-3]. To reduce the volatility due to the increase in the intermolecular interaction, it is possible, by introducing into the structure of the ionic liquids polar groups, capable to form hydrogen bonds in the interaction with ions. This report is devoted to the synthesis of ILs containing OH-group in the cation structure and to the study of the influence of OH-groups on ILs properties.



Scheme of synthesis of ILs.

Two rows of bis(trifluoromethylsulfonyl)imidic ionic liquids with hydroxyl group in ω-position of alkyl substituent (C$_1$-C$_8$) in imidazole cation and without it were synthesized. Physical and chemical properties of the obtained ILs such as density, viscosity, volatility are studied and the temperature range of the liquid state of the ILs (t$_{mp}$, t$_{decomp}$) is determined. The obtained data on the influence of OH groups in the cation structure on the properties of ionic liquids are analyzed. The influence of the length of the alkyl substituent in the cation on the specified parameters of the IL is estimated. The presence of hydroxyl groups in the cation structure changes the all the complex of properties of ionic liquids compared to the analogues alkylimidazolium ILs, i.e. thermal stability at 30-40 º C , tg reduces to -60 - -70 ° C, viscosity increases and volatility decreases in 2 times.

The authors thank the Russian science Foundation for supporting the work (grant RGNF № 14-19-00503).

References:
[1]. V. Krasovskiy et al. // Mend. Com. 2017. V.27. P.605.
[2] V.G. Krasovskiy et al. // Rus. J. Org. Chem. 2018. T. 54. C.143.
[3] V.G. Krasovskiy et al. // Rus. Chem. Bull., Int. Ed. 2018. №9.

FREE-RADICAL OXIDATIVE METHODS IN THE SYNTHESIS OF NEW FUNGICIDAL COMPOUNDS

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The chemical plant protection (> 90% of the world pesticide market) plays an important role in crop production and has no alternatives in the coming decades, despite the development of biopesticides. An acute problem for plant protection is the development of resistance to existing active compounds in phytopathogenic microorganisms, in particular, phytopathogenic fungi. Preservation of a stable crop yield and its quality requires the development of fundamentally new fungicidal active substances with a low risk of developing cross-resistance with existing compounds. An important requirement for agro-products is the simplicity of their synthesis, since this directly affects their cost and competitiveness. In this project, oxidative functionalization methods have been developed that allow efficient assembly of new potential fungicidal substances ia a small number of steps using simple and cheap oxidizing agents, such as the simplest and industrially produced organic peroxides. The starting substrates are carbonyl compounds, CH-acids and C-nucleophiles, including heterocyclic ones. The fundamental methodological novelty of the project lies in the development synthetic approaches in which new bonds between the starting molecules are formed via a radical pathway involving N-oxyl radicals.

The developed methods made it possible to easily obtain previously hard-to-reach structures, among which compounds with high fungicidal activity were found. Leading substances of the current research are comparable or superior to modern commercial fungicidal active substances, such as triadimefon, fluconazole, clotrimazole, kresoxim-methyl.

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DEVELOPMENT OF AN ENZYME IMMUNOASSAYS FOR DIAGNOSIS OF FUNGAL INFECTIONS CAUSED BY ASPERGILLUS PATHOGENS

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Aspergillus spp. are the causative agents of a wide range of infections, including the most dangers invasive aspergilloses (IA). In recent years, IA has been a leading cause of infection-related deaths among immunocompromised patients. The detection of circulating galactomannan (GM) has been a recognized criterion for the diagnosis of IA. However, the existing commercial assays for detection of GM have significant shortcomings: high price, lack of specificity and cross-reactivity with polysaccharides from bacteria of the normal gastrointestinal microflora.

Herein we report the development of new «sandwich»-type immunological diagnostic kits based on highly specific anti-GM monoclonal antibodies [1] obtained by using of newly synthesized oligosaccharide ligands [2-3]. This included the synthesis of GM-related oligosaccharides and glycoconjugate thereof, generation of monoclonal antibodies (mAbs) and study of their carbohydrate specificity as well as different strategies for antibodies immobilization to manage efficient «sandwich»-assembling. The developed diagnosticum is now undergoing clinical trials for subsequent introduction into medical practice.

Synthesis of oligosaccharids and glycoconjugates thereof, assaying of mAbs on glycoarray and the design of «sandwich»-kits were supported by RSF grant 14-23-00199; development of mAbs was supported by RSF grant 16-14-00083.

References:
[1] A.L. Matveev, V.B. Krylov, L.A. Emelyanova et al., PLoS ONE 13, e0193938 (2018).
[2] D.A. Argunov, V.B. Krylov, N.E. Nifantiev, Org. Biomol. Chem., 13, 3255 (2015).
[3] D.A. Argunov, V.B. Krylov, N.E. Nifantiev, Org. Lett., 18, 5504 (2016).

ZINC AND PHOSPHOROUS REAGENTS FOR THE SYNTHESIS OF COMPOUNDS CONTAINING CF2-MOIETY DERIVED FROM DIFLUOROCARBENE

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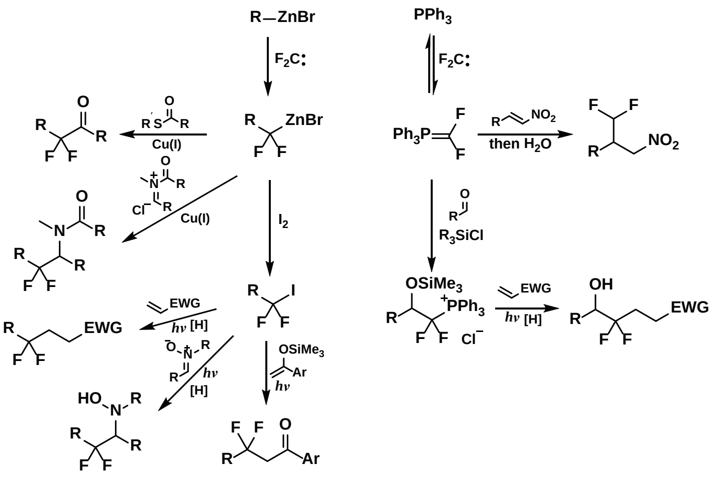
Classic methods for the synthesis of compounds containing a difluoromethylene moiety usually rely on either harsh deoxofluorination reactions or long-sequence functional group transformations. Our concept is based on stepwise coupling of difluorocarbene with a nucleophile and an electrophile[1]. As a source of difluorocarbene, silane Me_3SiCF_2Br or salt $BrCF_2CO_2K$ can be used. Reaction of organozinc halides as nucleophiles with difluorocarbene provides fluorinated zinc regents RCF_2ZnBr[2] , which further can be coupled with different electrophiles such as acyl dithiocarbamates[3] or acyliminium cations[4]. Iodination of these zinc reagents furnishes iodides RCF_2I. Under irradiation with visible light these iodides participate in radical couplings with silylenolates[5] and with electron-deficient double bonds or nitrones[6] in the presence of reductants.

Triphenylphosphine reversibly reacts with difluorocarbene with formation of nucleophilic phosphorane, which reacts with electrophiles (e. g. nitroalkenes) and after protodephosphorylation affords a product of formal difluoromethylation. One-electron reduction of the C–P-bond under photoredox conditions provides difluorinated radical, which can be trapped by C=C double bonds[7].



References:

[1] Dilman, A. D.; Levin, V. V.; Acc. Chem. Res. 2018, 51 , 1272–1280.

[2] Levin, V. V.; Zemtsov, A. A.; Struchkova, M. I.; Dilman, A. D. Org. Lett.2013, 15, 917–919.

[3] Ashirbaev, S.S.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. J. Org. Chem. 2018, 83, 478–483

[4] Levin, V. V.; Struchkova, M. I.; Dilman, A. D. Mendeleev Commun. 2017, 27, 139–140.

[5] Chernov, G. N.; Levin, V. V.; Kokorekin, V. A.; Struchkova, M. I.; Dilman, A. D. Adv. Synth. Catal. 2017, 359, 3063–3067.

[6] Supranovich, V. I.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. Org. Lett. 2018, 20, 840–843.

[7] Panferova, L. I.; Tsymbal, A. V.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. Org. Lett. 2016, 18, 996–999.

PD$_2$IN$_3$ INTERMETALLIC NANOPARTICLES AS AN EFFICIENT CATALYTIC SYSTEM FOR THE ONE-POT SYNTHESIS OF TRANS-STILBENE VIA HYDROGENATION OF DIPHENYLACETYLENE

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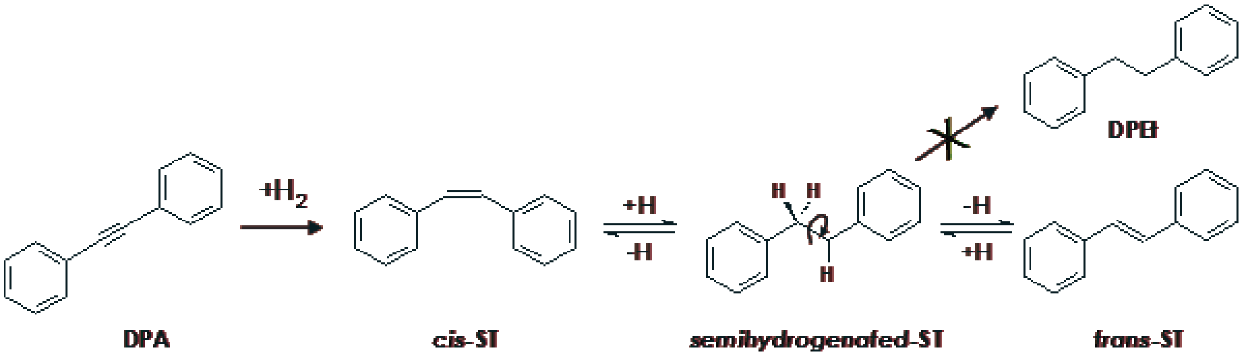
Trans-stilbene (trans-ST) is an important chemical compound serving as a valuable building block in fine organic synthesis. A several procedures are used nowadays for trans-ST synthesis including alkene metathesis and cross coupling. Selective hydrogenation of substituted alkynes remains a very attractive alternative to these methods. However in this case the geometry of triple bond must be considered since for internal alkynes cis-alkenes are formed as a primary product. Only few catalytic systems are known which are capable to provide direct trans-alkene formation from the parent alkyne [1]. Therefore the development of the efficient catalytic composition for trans-ST synthesis remains a challenge. Furukawa et al. proposed a promising approach for trans-ST formation via the tandem selective diphenylacetylene (DPA) semihydrogenation followed by isomerization of cis-ST to trans-ST (see Scheme) [2].



In our research PdIn and Pd$_2$In$_3$ intermetallic compounds (IMCs) were found to be capable to perform this concept. Catalytic tests highlighted Pd$_2$In$_3$/Al$_2$O$_3$ as the most promising catalytic composition. This sample demonstrates ~ 92% selectivity to trans-ST formation at 100% conversion of DPA and can be used for the following up-scaling.

The authors are grateful to the Russian Science Foundation (Grant RSF no. 16-13-10530) for financial support of this study.

References
[1] I. N. Michaelides, D. J. Dixon, Angew. Chem. Int. Ed. 52 (2013) 806.
[2] S. Furukawa, A. Yokoyama, T. Komatsu, ACS Catal. 4 (2014) 3581.

EFFICIENCY OF SUPPORTED INTERMETALLIC NANOPARTICLES IN LIQUID-PHASE HYDROGENATION OF C≡C BONDS

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In recent years intermetallic compounds (IMCs) have attracted attention in catalysis [1]. Important advantage of IMCs is the control of the electronic structure, specific and highly-ordered atomic-level structure and homogeneity of electronic and geometric structures [2]. By selecting IMCs with suitable structures, the properties of active sites can be fitted to the reaction needs. One of the possible applications of IMCs is catalytic hydrogenation of substituted alkynes to corresponding olefins. This reaction is of great importance for both industrial and laboratory practice [3].

Current research is focused on two main objectives: (1) to study of PdIn IMCs formation in the structure PdIn/Al_2O_3 catalyst and (2) to reveal the effect of isolation of Pd surface sites by indium atoms (Pd_1 single site structure) on the performance of PdIn/Al_2O_3 in hydrogenation of substituted alkynes. The catalyst was prepared using heterobimetallic PdIn acetate complex as an IMC precursor [4]. In this complex Pd and In components are strongly linked together via acetate bridges thus ensuring intimate contact of both metals within all stages of catalyst preparation and provides uniform stoichiometry of IMC nanoparticles in a final catalyst. Previously this approach was successfully applied for preparation of PdAg, PdZn and PdCu [5-7] catalysts.

XRD, FTIR-CO, H_2-TPD and TEM techniques were used for catalyst characterization. In accordance with XRD data formation of PdIn IMCs begins after mild reduction at 200°C with complete accomplishment after reduction at 400°C. FTIR-CO spectra demonstrate the disappearance of the CO band shift resulting from the lateral dipole–dipole interaction between adsorbed CO molecules. Additionally a disappearance of bridged adsorbed CO was observed indicating that the surface of PdIn nanoparticles contains predominantly single Pd atoms isolated by indium ones. A complete inhibition of PdHx species provides additional evidence of the formation of PdIn IMCs.

The PdIn catalysts demonstrate high selectivity in the hydrogenation of internal alkynes comparable with that of the commercial Lindlar catalyst. Note that similar activity/selectivity characteristics are reached at a significantly lower Pd content and in the absence of toxic Pb component. Studying the effect of In introduction on the catalytic performance reveals that the reaction selectivity is determined to a large extent by favorable adsorption–desorption equilibrium between the reactants and the reaction products.

The authors are grateful to the Russian Science Foundation (Grant RSF no. 16-13-10530) for financial support of this study.

References

[1] S. Furukawa, T. Komatsu, ACS Catal. 7 (2017) 735.
[2] M. Armbrüster, Intermetallic Compounds in Catalysis, In Encyclopedia of Catalysis, ed. I.T. Horváth, Wiley-VCH: Weinheim, Germany, 2011.
[3] A. Borodzinski, G.C. Bond, Catal. Rev. 48 (2006) 91.
[4] P.V. Markov, G.O. Bragina, G.N. Baeva. O.P. Tkachenko, I.S. Mashkovsky, I.A. Yakushev, M.N. Vargaftik, A.Yu. Stakheev, Kinet. Catal. 57 (2016) 617.
[5] A. V. Rassolov, P. V. Markov, G. O. Bragina, G. N. Baeva, I. S. Mashkovskii, I. A. Yakushev, M. N. Vargaftik, A. Yu. Stakheev, Kinet. Catal. 57 (2016) 853.
[6] I. S. Mashkovsky, P. V. Markov, G. O. Bragina, A. V. Rassolov, G. N. Baeva, A. Yu. Stakheev, Kinet. Catal. 58 (2017) 480.
[7] P.V. Markov, G.O. Bragina, A.V. Rassolov, G.N. Baeva, I.S. Mashkovsky, V.Yu. Murzin, Ya.V. Zubavichus, A.Yu. Stakheev, Mendeleev Commun. 26 (2016) 502.

NEW ATE COMPLEXES WITH 1,3,5-TRIHYDROXY-1,3,5-TRIAZACYCLOHEXANE LIGANDS

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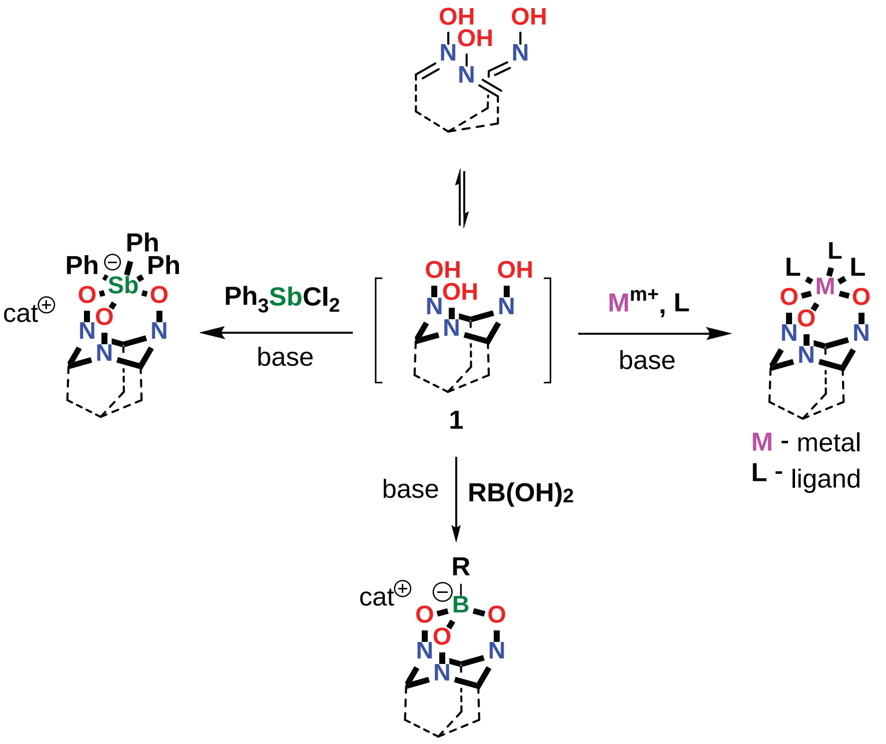
Ligands containing the N-OH unit as a coordinating group have gained considerable interest in the recent years due to their ability to stabilize metal ions in high oxidation states.[1] However, coordination chemistry of polydentate ligands bearing several N-oxy groups remains much less explored. In the present work, complexation of d-metal ions as well as some non-metal derivatives with 1,3,5-trihydroxy-1,3,5-triazacyclohexanes 1 (cyclotrimers of oximes) was explored (Scheme).



Scheme

We have demonstrated that under basic conditions unusual ate complexes of adamantoid structure are formed, in which metal ion or hypervalent p-element is coordinated by three oxygen atoms of deprotonated N-OH units (Scheme). In the presentation, synthesis, structure and properties of these new ate complexes are discussed in detail.

This work was supported by RFBR (Grant № 18-33-00647).

References:

1. (a) Edison S. E., Hotz R. P., Baldwin M. J., Chem. Commun., 2004, 10, 1212. (b) Boyko Y. D., Sukhorukov A. Y., Semakin A. N., Nelyubina Y. V., Ananyev I. V., Rangappa K. S., Ioffe S. L., Polyhedron, 2014, 71, 24.

REACTIONS OF OXIDATIVE COUPLING ACCOMPANIED BY S-N BOND FORMATION

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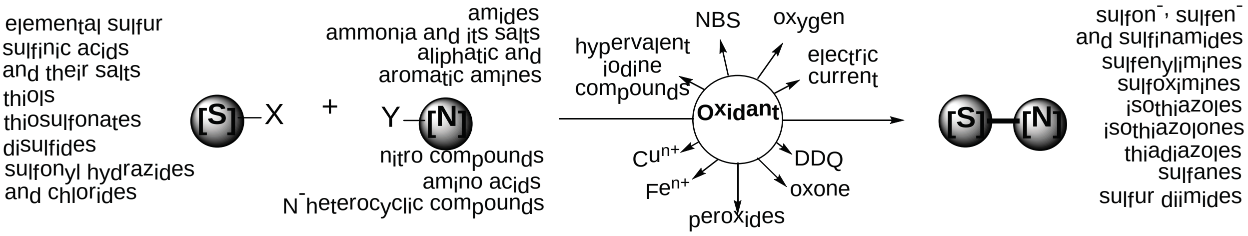
In recent decades much attention has been paid to the study of oxidative coupling reactions; in some fields of organic chemistry these processes seriously compete with reactions catalyzed by transition metals complexes and salts. The main advantage of oxidative strategies is no need for the introduction of leaving groups, and as a result, the number of synthetic stages is decreased.

Among these processes the reactions of oxidative S-N bond formation deserve considerable interest as an effective, convenient, and environment-friendly alternative for existing methodologies of the synthesis of a great variety of organic compounds widely used in organic and medicinal chemistry, such as sulfonamides, isothiazoles and thiadiazoles. Sulfinic acids and their salts, sulfonyl hydrazides, thiols, and thiosulfonates are generally used as S-reagents; aliphatic and aromatic amines are applied as N-reagents (Scheme 1).



Scheme 1. Oxidative S-N coupling.

The studies of oxidative S-N coupling processes are developing mainly in the field of extension of applied starting compounds and oxidants scope, as well as investigation of mechanisms of these processes. [1]

The work was supported by the Russian Science Foundation (grant № 18-13-00027)

References:
[1] Olga M. Mulina et al., Eur. J. Org. Chem., DOI: 10.1002/ejoc.201800838.

STYRYL AND THIENYL DERIVATIVES OF BENZAZINES AS PERSPECTIVE COMPONENTS FOR OPTICAL MATERIALS

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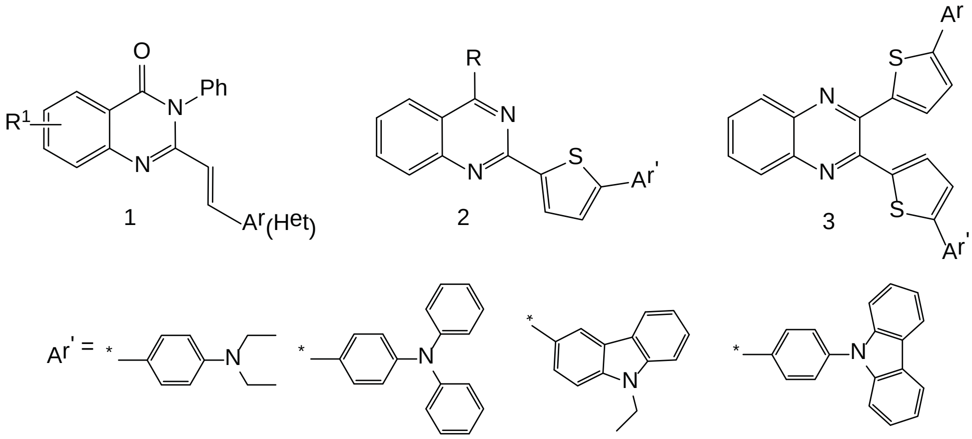
Novel styrylquinazolines 1 have been obtained by condensation of 2-methylquinazolin-4-ones with aromatic (heterocyclic) aldehydes in the presence of ZnCl2 (AcONa) or by the reaction of 2-methyl-3,1-benzoxazin-4-ones with the Shiff bases. Effects of aryl(heteryl) substituents on photophysical properties of (aryl/heteryl) quinazolinylethenes have been studied [1]. The synthesis of the series of push-pull aryl 2-(thiophen-2-yl) quinazoline derivatives 2 has been performed through bromination of (2-thienyl)quinazoline and subsequent palladium-catalyzed cross-coupling reactions. The effect of protonation has been studied, and the ability of some of these molecules to function as colorimetric and luminescent pH sensors has been demonstrated with significant color changes and luminescence switching upon the introduction of acid [2]. A series of novel V-shaped luminophores 3 containing electron withdrawing quinoxaline core and arylthienyl donor fragments at positions 2 and 3 have been successfully synthesized. Their photophysical properties in two solvents and halochromism have been studied [3].



Ar = Ph, 4-$Me_2NC_6H_4$, 4-FC_6H_4, 4-EtC_6H_4, 4-$MeOC_6H_4$, naphthyl; Het = 2-thienyl, 2-Py.
Figure 1. Structures of benzodiazines 1-3 possessing luminescent properties.

This work was supported by the Russian Scientific Foundation (grant 16-43-02020) and Russian Foundation for Basic Research (grant number 18-03-00112).

References:
[1] E.V. Nosova, T.V. Stupina, G.N. Lipunova, M.S. Valova, P.A. Slepukhin, V.N. Charushin. Int. J. Org. Chem., 2 (1), 56 (2012)
[2] E.V. Nosova, T.N. Moshkina, G.N. Lipunova, D.S. Kopchuk, P.A. Slepukhin, I.V. Baklanova, V.N. Charushin. Eur. J. Org. Chem., 2876 (2016)
[3] T.N. Moshkina, E.V. Nosova, G.N. Lipunova, M.S. Valova, V.N. Charushin. Asian J. Org. Chem., 7, 1080 (2018)

PREPARATION OF [1,2,4]OXADIAZINO[2,3-A]INDOLES BY MODIFICATION OF 2-AMINO-1-HYDROXYINDOLES

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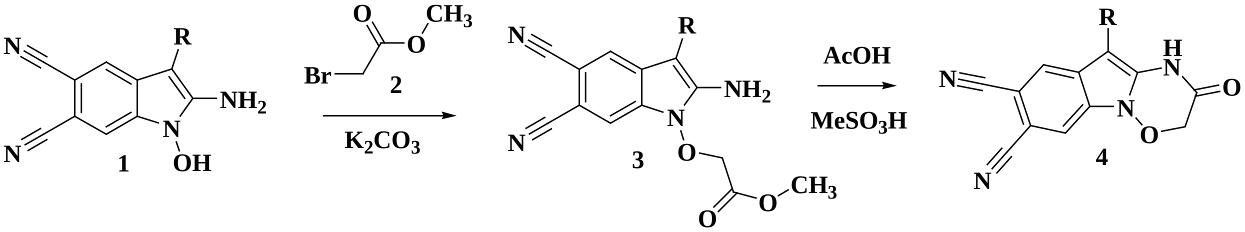
The condensed indole systems are included in compositions of natural products and alkaloids. In order to obtain new biologically active compounds the design of the methods for cyclization of 2-amino-1-hydroxyindoles to diffrent heterocyclic compounds by analogy with ortho-aminophenols is of certain synthetic interest.
The object of this work is the design of the methods for synthesis of new substituted [1,2,4]oxadiazino[2,3-a]indoles [1] (Scheme 1).



1, 3, 4: R = Ar
Scheme 1

In the first step 2-amino-1-hydroxyindoles 1 [2] were alkylated with methyl ester of bromoacetic acid 2 in the presence of potassium carbonate (deprotonating agent) to give esters 3 with the yield up to 82 %. Due to fact that hydrogen atom of hydroxy group is more labile than other hydrogen those the reaction only involves this group [3, 4].
In the second step the intramolecular amidation of esters 3 catalyzed with 20 mol % of MeSO3H was carried out in the acetic acid solution to form target heterocyclic compounds 4a-c with the yield up to 72 %.
The structures of obtained compounds 3 and 4 are determined from the total NMR and mass spectrometry data.

References:
[1] Zh. V. Chirkova, et al., Mendeleev Commun., 28, 86 (2018)
[2] S. I. Filimonov, et al., Chem. Heterocycl. Compd., 48, 427 (2012)
[3] Zh. V. Chirkova, et al., Russ. Chem. Bull., 66, 379 (2017)
[4] Zh. V. Chirkova, et al., Russ. J. Org. Chem., 53, 192 (2017)

SYNTHESIS AND BIOLOGICAL EVALUATION OF DISPIRO-INDOLINONES BASED ON 5-ARILYDENE -SUBSTITUTED HYDANTOINS AND RHODANINS

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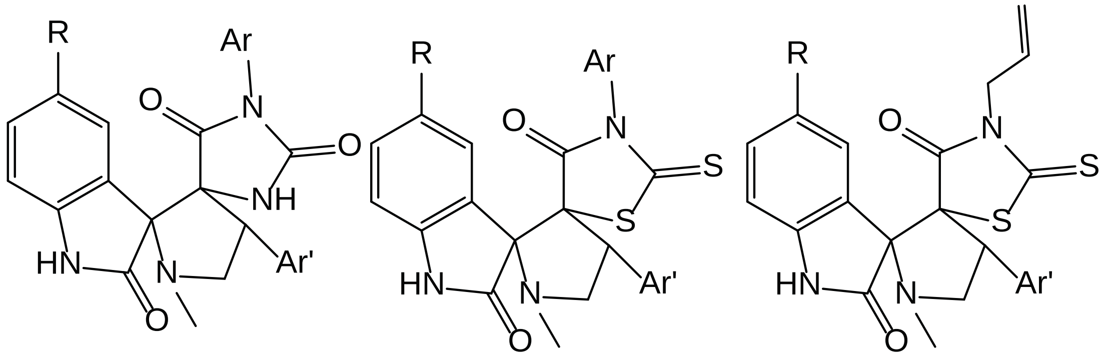
Around 8 millions of people die from cancer diseases all around the world every year. It was found that cancer cells are uncontrollably replicated due to a mutation of p53 protein. Therefore, it is necessary to inhibit the protein-protein interaction (PPI) of MDM2-p53 by small-molecular inhibitor that binds MDM2 to a stable complex and activates functions of p53 for apoptosis of cancer cells.

Previously in our group a «hit-compound» based on dispiro-oxindole core with the promising anticancer activity was found. In this work, a series of novel dispiro-indolinones shown below on the base of different types of heterocyclic compounds as 1,3-cycloaddition substrates were synthesized. Some compounds demonstrate significant cytotoxicity against cancer cell lines with IC50 in micromolar concentrations range comparable to Nutlin-3. Two of the synthesized dispiroindolinones show p53-related activity in p53 reporter activation test.



R=H, Br, Cl

References

1. K. Ding at al. Structure-Based Design of Potent Non-Peptide MDM2 Inhibitors // JACS. 2005. V.127, 29. P. 10130.
2. Yan A. Ivanenkov at al. Design, synthesis and biological evaluation of novel potent MDM2/p53 small-molecule inhibitors // Bio. Med. Chem. Let. 2015. V.25. P. 404-409

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BIOLOGICAL ACTIVE HETEROCYCLIC COMPOUNDS WITH CYCLOACETALIC FRAGMENTS

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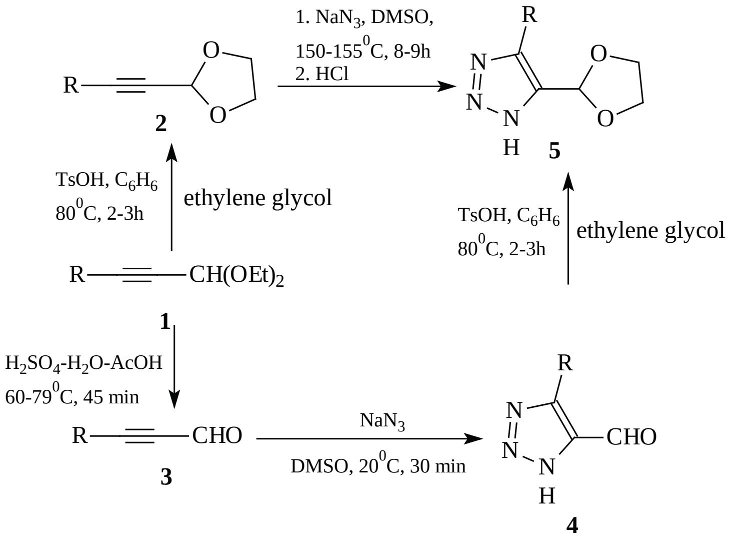
It is known that various nitrogen-containing heterocycles are widely used in pharmaceutical chemistry. Therefore we have developed methods for the synthesis of some substituted nitrogenous heterocycles containing cycloacetalic fragment. This group is useful as solvents and substrates in organic and aqueous media that allow to transport complex heterocycles through cell membranes.

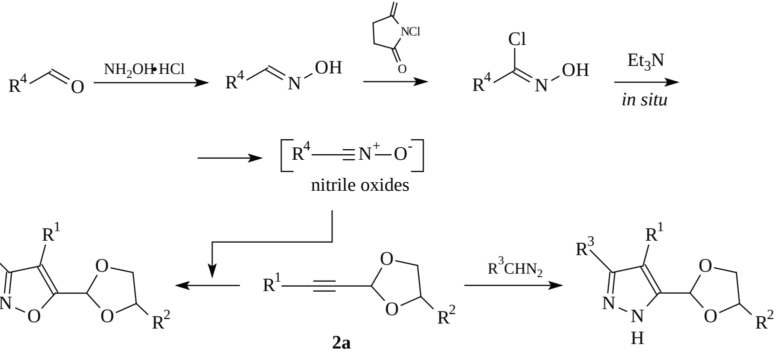
Substitutes 1,2,3-triazoles 5 have been obtained by two alternative methods based on linear acetals of acetylenic aldehydes 1.



The best yield of the desired product 5 was achieved by the two-step reaction via substrate 2. The steps, which involve reagents 3, 4 lead to the final product 5 with substantially poorer yields.

Moreover 1,2-oxazole and 1,2-diazole with 1,3-dioxolane substitutes were obtained from the cyclic acetals acetylenic aldehydes 2a. The yield of desired products does not exceed 70%. In the case of R^2=alkyl the individual *cis-* and *trans-* isomers have been isolated with a ratio of 6: 4, respectively.

Some of the obtained compounds showed antihistaminic and antiviral activity.



THE FIRST EXAMPLE OF REGIOSELECTIVE HYDROTHIOLATION OF CYCLOPROPYL ACETYLENE

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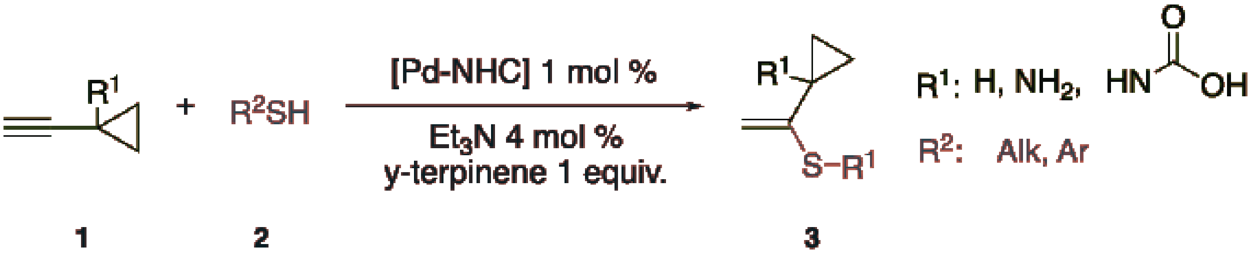
Vinyl sulfides represent an important class of compounds in organic chemistry. They are utilized in the synthesis of biologically active compounds, polymer chemistry and materials science. The interest to organosulfur compounds is due to their high prevalence in nature in the form of thiols, sulfides, disulfides and thiophene derivatives. Organosulfur compounds are found in coals, oil and natural gas; in living systems, they are represented by amino acids (methionine, cysteine, cystine) and vitamins (thiamine, biotin, lipoic acid, coenzyme A). In recent years several catalytic systems were studied to achieve atom-economic synthesis of organosulfur derivatives [1-2].

The aim of our work is to develop a stereoselective and efficient catalytic system for the synthesis of cyclopropyl-substituted vinyl sulfides and vinyl selenides. To achieve this goal, we studied functionalization of cyclopropyl acetylene with thiophenol in various catalytic systems based on nickel, palladium and platinum. Among many candidate catalysts, a palladium complex with N-heterocyclic carbene ligand (IMes)Pd(acac)Cl was found to be the most effective. This complex was subsequently used for optimization of the reaction conditions. The developed catalytic system is active for a wide range of thiols (Scheme 1). The structure and composition of products have been confirmed by NMR and MS in the isolated individual state.

Scheme 1. The developed thiol-yne click catalytic system provides an atom-economic access to vinyl(cyclopropyl) sulfides.



Vinylated derivatives of cyclopropane are highly reactive, due to the presence of double carbon-carbon bond in the vicinity of the strained three-membered ring. The study is underway to evaluate synthetic potential and possible applications of the obtained products.

The study was supported by Russian Science Foundation 14-50-00126 grant.

References:
[1] Degtyareva E, Burykina J, Fakhrutdinov A, Gordeev E, Khrustalev V, Ananikov V. ACS Catal. 5, 7208-7213 (2015).
[2] Ananikov V, Beletskaya I. Chem.Rev. 111, 1596-1636 (2011).

ELECTROCATALYTIC APPROACH TO THE DEPOSITION OF GE NANOPARTICLES ONTO COPPER SURFACES

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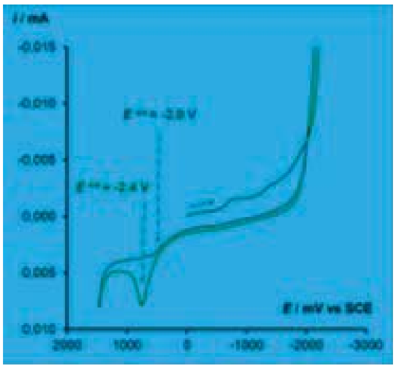
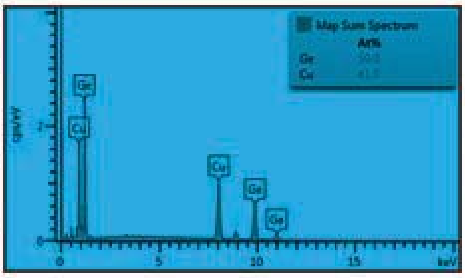
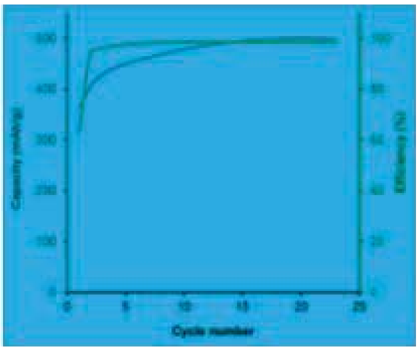
Nanoparticles of the 14 group elements, in particular of Ge and Si, are considered as a promising replacement of graphite in the anodes of modern Lithium-ion batteries able to significantly increase their energy capacity [1]. Almost all known methods of electrodeposition of the germanium nanoparticles are based on the use of its halides [2], usually germanium chloride, – a highly toxic and chemically labile compound.

We proposed a simple and convenient method of electrochemical precipitation of Ge nanoparticles from the solution of germanium citrate in propylene glycol. This substance is very stable and completely non-toxic; it can be easily obtained from GeO_2 and aqueous solution of citric acid. As shown by voltammetry, germanium citrate is an electrochemically inactive compound, and its reduction occurs due to hydrogen released in the cathodic electrolysis.







A dense black precipitate was formed from this electrolysis, mostly consisting of germanium particles with the size of about 200 nm. Half-cells of lithium-ion batteries based on these particles have shown a specific energy intensity of about 500 mAh/g at c rate, which greatly exceeds the maximum theoretical capacity of graphite (372 mAh/g).

This work was carried out with the financial support from Russian Science Foundation (RSF Grant 17-73-20281).

References
1. X. Xiao, X. Li, S. Zheng, J. Shao, H. Xue, H. Pang, Adv. Mater. Interfaces, 2017, 1600798
2. K. Nadarajah, A.F. Khan, N.A. Rahim, Recent Patents on Nanotechnology, 2016, 10, 26

NITROXYL RADICAL MODIFIED CHITOSANS WITH ENHANCED ANTIOXIDANT POTENTIAL

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Chitosan is a biocompatible glucosamine polymer with properties suitable for a great variety of biomedical applications. Water-soluble at neutral pH chitosan-(poly)nitroxyls (CPNs), differing in molecular weight of the saccharide backbone (Mw ~1 and ~10 kDa) and the nature of nitroxide radical (pyrroline and piperidine), were obtained and characterized. Fractions of modified glucosamines were in the range 0.15 – 0.28. Antioxidant potential of CPNs was studied on erythrocyte hemolysis and cellular oxidative stress models.
The dependence of delay time of 2,2-azobis-2-methylpropanimidamide dihydrochloride (AAPH)-induced erythrocyte hemolysis on the concentration of CPNs and data of electron paramagnetic resonance (EPR) spectra indicate their binding to the cell membrane. Because of this binding, CPNs demonstrate identical delay times of hemolysis at concentrations ~100 times lower than structurally similar low molecular nitroxyls. The proposed mechanism includes multiple breaking of oxidation chain through nitroxyl oxidation to oxoammonium cations and reduction of the latter by common biological reductants. Due to easier oxidation of piperidine nitroxyl by radicals RO_2• to oxoammonium cations, CPNs with attached 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) more effectively prevent hemolysis than their counterparts with 2,2,5,5-tetramethylpyrroline-1-oxyl.
In experiments on tumor (HeLa, A172, HepG2) and normal (Vero) cells it has been established that CPNs have low cytotoxicity ($IC_{50} \geq 2.5$ mM). The antioxidant effect of CPNs was studied on an oxidative stress model induced in these cells by tert-butyl hydroperoxide. Based on data on the accumulation of malonic dialdehyde and/or fluorescence with DCFDA, it was found that CPNs more efficiently inhibited the generation of reactive oxygen species (ROS) than low molecular weight nitroxyls. It is important that the maximum reduction in the ROS level was achieved for normal Vero cells. Therefore, CPNs are of interest as new biologically active materials with enhanced antioxidant properties.

The research was performed with the financial support of RSF grant No. 14-23-00018-P.

AN UNUSUAL ARENE HALOGENATION: REDUCTIVE HALOGENATION OF DIARYLHYDROXYLAMINES AND DIARYLNITROXYL RADICALS

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Diarylnitroxyl radicals Ar_2NO• are of interest as antioxidants, working material in Overhauser dynamic nuclear polarization magnetometers, molecular magnets, redox active materials for energy storage devices. Substituted diarylamines suitable for the preparation of Ar_2NO• are not easily accessible [1, 2]. On the examples of the available hydroxylamine $(4\text{-}tert\text{-}BuC_6H_4)_2NOH$ 1 and the corresponding nitroxyl $(4\text{-}tert\text{-}BuC_6H_4)2NO$• 2, we have found the possibility of selective halogenation of such compounds and thus the synthesis of new Ar_2NO•. Most arenes interact with chlorine and bromine by the mechanism of electrophilic substitution. Compounds 1 and 2 react with halogens by an unusual mechanism of reductive halogenation. Hydroxylamine 1, upon reaction with an equimolar amount of Br_2, is converted to dibromoamine 3 in 94% yield.

The transformation of hydroxylamine 1 to dibromoamine 3 proceeds through intermediate complex A, as evidenced by intense absorption bands at λ_{max} 406 and 308 nm. In complex A, the Br2 molecule appears to be coordinated with two benzene rings of hydroxylamine 1. In the rate limiting step of the reaction, the two ortho-hydrogen in complex A belonging to different rings are selectively replaced by bromine atoms and they themselves reduce the group >NOH to the amino group.

When radical 2 reacts with halogens, comparable amounts of di- 4 and trihalogenamines 5 are formed, the total yield is ⍰70%.

The reductive halogenation of nitroxyls to amines appears to proceed through intermediate hydroxylamines and aminyl radicals.

It is expected that in the ortho-halogen-substituted Ar_2NO•, obtained from amines of type 3-5, the aryl groups are twisted from the plane of the nitroxyl group. This should reduce the delocalization of the spin density on the aryl fragments and increase the stability of such radicals.

References:
[1] R. Suzuki et al., J. Mol. Struct. 1106, 399 (2016).
[2] T.V. Magdesieva et al., Russ. Chem. Rev. 87, 707 (2018).

SELECTIVE HYDROGENATION OF PHENYLACETYLENE OVER FE/SIO$_2$ AND FE-CU/SIO$_2$ CATALYSTS

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Selective hydrogenation of phenylacetylene possesses considerable importance because phenylacetylene is regarded as a harmful component in feedstocks for the industrial manufacture of polystyrene [1]. Pd-based catalysts are generally used in the selective hydrogenation of phenylacetylene. The main drawback of these catalysts is their high content of the active components and toxicity. The development and investigation of more effective and ecological catalytic systems remain important goals of modern catalysis. The Cu-Fe catalysts are considered as ecofriendly and low-cost alternative to precious metal catalysts. The method of preparation of the Cu-Fe catalyst influences its reducibility and the interaction between Cu and Fe components and, as a result, the catalytic properties [2].

Silica-supported mono- and bimetallic samples were synthesized via (1) co-deposition-precipitation of Cu and Fe precursors predominantly on the outer surface of the silica support powder using thermal hydrolysis of urea (DPU); (2) deposition of Cu and Fe precursors by consecutive incipient wetness impregnation (CI) of porous silica beads with an ammonium trioxalatoferrate solution and after intermediate drying, with copper (II) nitrate solutions, (3) co-deposition of Cu and Fe precursors inside the pores of the silica support using simultaneous incipient wetness impregnation with a solution containing metal nitrates and urea (SDU).

Variations in the preparation procedures influence the reducibility and the interaction between Cu and Fe components resulting in considerable changes of the catalytic activity and selectivity in hydrogenation of unsaturated carbon bonds. Complete reduction to a metallic state was reached at 300 °C if the DPU preparation method was applied. The bimetallic nanocomposites Fe-Cu prepared by the DPU procedure provide the highest catalytic activity and selectivity to styrene above 60 %.

Acknowledgment

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References
[1] Dongshun Deng, Yang Yang, Yutong Gong and et.al. Green Chem. 15 (2013) 2525
[2] Sun C, Mao D, Han L, Yu J. Catal. Commun. 2016;84:175–178.

DEAROMATIZATION OF AZOLOPYRIDINES BY NEUTRAL NUCLEOPHILES

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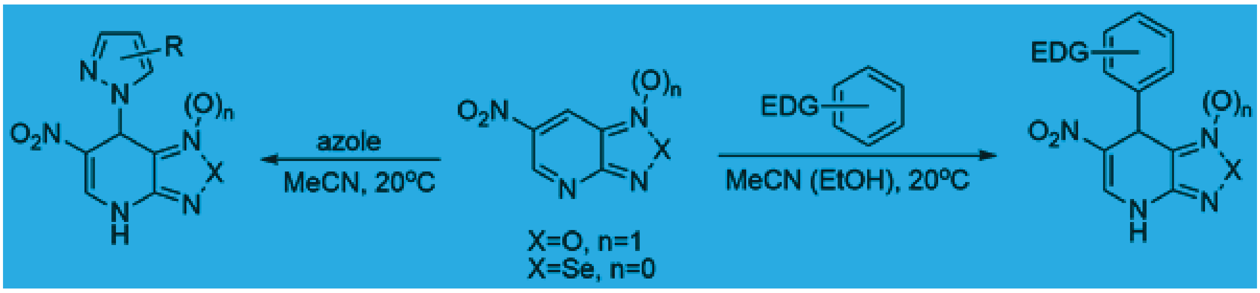
Recently [1] we discovered that 4-aza-6-nitrobenzofuroxan (ANBF) reacts with 1,3-dicarbonyl compounds and other CH-acids to give carbon-bonded 1,4-adducts. In case of most acidic β-diketones, the reactions proceed in the absence of any added base emphasizing strong electrophilic character of ANBF. Here we report on dearomatization of ANBF with π-excessive arenes and hetarenes [2]. In addition another highly electrophilic azolopyridine, namely 4-aza-6-nitrobenzo[1,2,5]selenadiazole was examined in reactions with both CH-acids and π-donor arenes [2]. Reactions of 4-aza-6-nitrobenzofuroxan and 4-aza-6-nitrobenzoselenadiazole with π-excessive (het)arenes resulted in formation of C-C- and N-C-bonded 1,4-adducts – 1,4-dihydropyridines fused with furoxan or selenadiazole ring. The reactions proceed in the absence of a base indicating highly electrophilic nature of studied fused pyridines. In highly polar solvents the adducts with azoles were found to undergo partial or complete elimination of the azole fragment leading to starting compounds. The influence of substituents in azole ring was observed. The resulting compounds combine in one molecule pharmacologically important 1,4-dihydropyridine fragment along with furoxan or selenadiazole ring and therefore can be considered as prospective platforms for the design of pharmacology-oriented heterocyclic systems.



This work was supported by the Russian Science Foundation (grant no. 14-50-00126).

References:
[1] Alexey M. Starosotnikov et al., Beilstein J. Org. Chem. 13, 2854 (2017).
[2] Alexey M. Starosotnikov et al. Mendeleev Commun., 28 (2018), accepted, DOI 10.1016/j.mencom.2018.11.025

SELECTIVE LIQUID-PHASE HYDROGENATION OF THE C≡C BOND UNDER MILD CONDITIONS ON FE-PD/γ-AL$_2$O$_3$ CATALYSTS

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Selective hydrogenation of carbon–carbon triple bonds to double bonds is a key step in the synthesis of many important compounds of petrochemical industry, as well as for the synthesis of fine and specialty chemicals (i.e., vitamins A and E, linalool) [1]. The supported Pd-containing catalysts are usually used as catalysts for selective hydrogenation of these compounds due to their unique ability to promote adsorption of hydrogen and relative stability in air environment and easy recyclability [2]. It is known that by adding a second metal or metal oxide to Pd-based catalysts and the use of some hybrid systems the activity and selectivity of catalysts can be increased [3]. There is increasing research interest in iron as a catalyst component for homogeneous and heterogeneous hydrogenation because this transition metal is abundant in nature and cheap, non-toxic and potentially amenable to magnetic recovery [4]. However, the influence Fe on the catalytic properties Pd catalysts in the selective hydrogenation of unsaturated compounds is scarcely.

The catalytic properties of the bimetallic catalysts depend on the conditions of thermal treatment of the samples. The calcination process has a significant influence on the palladium dispersion. The formation of Fe-Pd bimetallic phase in samples increases the reactivity and selectivity of the Fe-Pd/Al$_2$O$_3$ catalysts. The best results on the selectivity of styrene formation (91% at the 100% PhA conversion) and DMVC (95% at the 100% DMEC conversion) were obtained on the sample calcined in an N$_2$ flow at 400 °C and then reduced in an H$_2$ flow at 400 °C. Thus, the stable magnetic Fe-Pd/Al$_2$O$_3$ catalysts are a good alternative to the traditional toxic Lindlar catalyst in the alkyne selective hydrogenation in mild conditions.

The reported study was funded by RFBR according to the research project № 18-33-00040.

References
[1] N. Semagina, A. Renken, D. Laub, L. Kiwi-Minsker, J. Catal. 246 (2007) 308-314.
[2] W. Yu, H. Hou, Zh. Xin, Sh. Niu, Y. Xie, X. Ji, L. Shao, RSC Adv. 7 (2017) 15309-15312.
[3] V. Ananikov, E. Gordeev, M. Egorov, A. Sakharov, S. Zlotin, E. Redina, V. Isaeva, L. Kustov, M. Gening, N. Nifantiev, Mend. Commun. 26 (2016) 365-374.
[4] A. Reddy, Z. Yusop, J. Jaafar, Y. Reddy, A. Aris, Z. Majid, J. Talib, G. Madhavi J Environ. Chem. Eng. 4 (2016) 3537-3553.

INFLUENCE OF THE NATURE OF N-HETEROCYCLIC CARBENE ON THE STABILITY OF PD/NHC CATALYTIC SYSTEMS

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N-heterocyclic carbine complexes of transition metals are attractive catalysts of cross-coupling reactions. They are highly tunable due to the wide variety of available NHC structures and properties [1]. Among the large number of M/NHC complexes, a special emphasis is focused on Pd/NHC catalysts [2]. It has been previously believed that their excellent catalytic properties entirely depend on the strong Pd-NHC bonds. However, this belief was questioned by the evidence of formation of NHC-R species and production of free Pd, which may generate catalytic centers in the Heck reaction [3].

In spite of much attention to this chemistry, the influence of NHC's nature on the stability of palladium complexes remains understudied. The aim of this work was to study the specific influence of variously modified NHCs on the outcome of Ph–NHC coupling. According to the study design, the results of quantum chemical computational analysis were subjected to experimental validation by pressurized sample infusion electrospray ionization mass spectrometry (PSI-ESI-MS) monitoring.

The specific influence of NHCs nature on Ph–NHC coupling was investigated by using N-heterocycles of different size (5-, 6-, or 7-membered rings) with a variable N-substituent (2,4,6-trimethylphenyl or 2,6-diisopropylphenyl).

The calculated potential barriers indicate that the processes of Ph–NHC species formation are typical for all tested Pd/NHC complexes. The values of potential barriers are similar and fall within the range of 17.9 – 25.1 kcal/mol. The reaction is more efficient for NHCs with sterically bulky substituents. The results of the experimental part of the study were in a good agreement with the computational data.

The study was supported by Russian Science Foundation 14-50-00126 grant

References:
[1] Silva Díez-González et al., Chem. Rev. 109, 3612 (2009).
[2] Nilay Hazari et al., Nat. Rev. Chem. 1, 0001 (2017).
[3] Alexander V. Astakhov et al., Organometallics. 36, 1981 (2017).

A-FLUORONITROALKENES: PREPARATION AND APPLICATION IN ORGANIC SYNTHESIS

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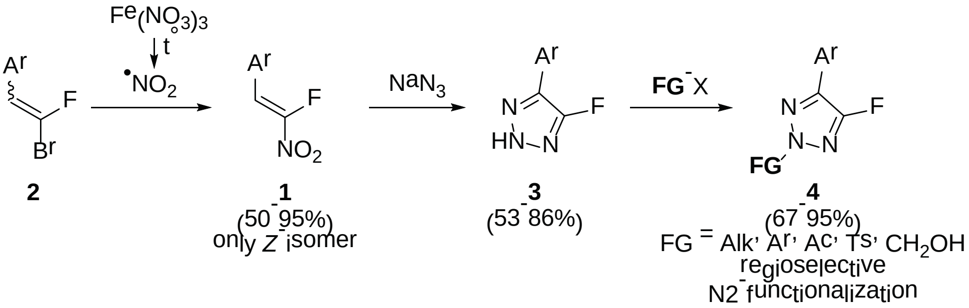
The chemistry of fluoroorganic compounds gained a significant interest in recent years.[1] Different unique properties of fluorine atom itself and carbon-fluorine bond draw attention of the chemists working in various fields such as medicinal chemistry, agrochemistry, material science. Hence, development of new fluorinated buidling blocks is highly desirable. We proposed that fluorine-possessing conjugated nitroalkenes 1 could be appropriate substrates for introduction of fluorine atom into organic molecules. A new method for the syntesis of nitroalkenes 1 was developed via radical nitration-debromination of available bromo-fluoro-styrenes 2. Target alkenes 1 were obtained in high yields with complete Z-selectivity.[2] Fluoronitroalkenes 1 were shown to smoothly react with various nucleophiles (dimethyl malonate, morpholine) giving corresponding addition products. Addition of sodium azide led to an array of hitherto unknown fluorinated 1,2,3-NH-triazoles 3.[3] Important discovered property of triazoles 3 is their selective functionalization (e.g. alkylation with alkyl halides, Chan-Lam arylation) at N2-atom.[3,4] Obtained diaryltriazoles 4 (FG = Ar) were shown to possess fluorescent properties emitting light in near-UV to visible violet-blue region.



The work was supported by Russian Science Foundation (grant 14-50-00126).

References:
[1] Y. Zhou et al., Chem. Rev. 116, 422 (2016).
[2] V. A. Motornov, et al., J. Org. Chem. 82, 5274 (2017).
[3] V. A. Motornov, et al., Eur. J. Org. Chem. 6851 (2017).
[4] V. A. Motornov, et al., Tetrahedron 74, 3897 (2018).

SYNTHESIS OF 1-METHOXY-2-PROPANOL FROM METHANOL AND PROPYLENE OXIDE IN THE PRESENCE OF COMPOSITION MATERIALS BASED ON ZIF-8 AND ALUMINA NANOFIBERS

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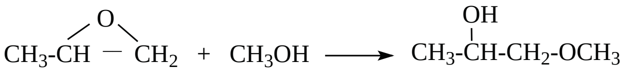
Propylene glycol methyl ether is considered to be important chemical that is widely used as industrial pollution-free solvent with the low toxicity in chemical and cosmetic industry, fine chemicals synthesis in pharmaceutical etc. Although there are several methods for synthesizing propylene glycol methyl ether, the propylene oxide route is the most convenient and industrially feasible in terms of atom-economy and energy efficiency.



$$CH_3\text{-}CH\overset{O}{—}CH_2 + CH_3OH \longrightarrow CH_3\text{-}\overset{OH}{CH}\text{-}CH_2\text{-}OCH_3$$

(PO) (I)

Although basic homogenous reaction shows high selectivity to secondary alcohols, they had the drawbacks of separation, liquid waste treating and corrosion problems. Thus, design of heterogeneous catalytic systems has been and still is an important task.

Herein we demonstrate application of novel composites based on zeolitic imidazolate framework (ZIF-8) and alumina nanofibers (Nafen) to synthesize propylene glycol ether. ZIF-8/Nafen composites were synthesized by a solvothermal method. It was found that modification of Nafen by ZIF-8 leads to the exfoliation of alumina nanofibers (Fig. 1). In sample 8.1%ZIF-8/Nafen we can reveal two regions. First region consists of few-layer sheets of nanofibers, where ZIF-8 crystals locate between two sheets of nanofibers. Other region consists of individual nanofibers, where ZIF-8 forms individual homogeneous distributed phase

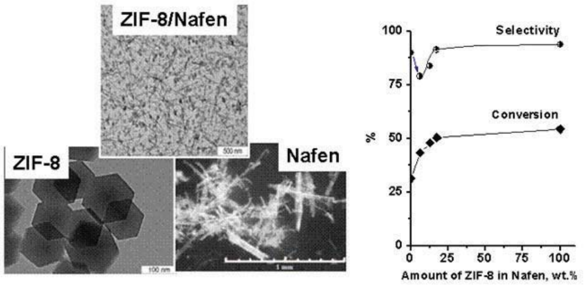


Figure 1. SEM data of ZIF-8, Nafen and 8.1% ZIF-8/Nafen, and dependence of conversion of PO and selectivity towards (I) on ZIF-8 content in ZIF-8/Nafen

According to DRIFT spectroscopy using CDCl3 as probe molecule, basic sites of Nafen are formed by bridging oxygen atom (Al-O-Al) and -OH groups, whereas Zn-OH groups and N-moieties of nonbridging linkers can act as basic sites of ZIF-8. The increasing ZIF-8 content in composite leads to rise amount of these basic sites. The strength of strongest basic sites of Nafen and ZIF-8 are 955 and 858 kJ/mol, respectively.

The catalytic properties of ZIF-8/Nafen composites were studied in the synthesis of propylene glycol methyl ethers from methanol and propylene oxide (PO) at 2.1 wt.% of catalyst, MeOH/PO molar ratio of 8 and 383 K. It was found that 1-methoxy-2-propanol (I) was the main product with 79.0-93.8% selectivity. Selectivity and reaction rate rose with increasing amount of basic sites that can be adjusted by ZIF-8 content in ZIF-8/Nafen (Fig. 1). Maximal activity and selectivity towards 1-methoxy-2-propanol (93.8%) was observed in the presence of ZIF-8. It was demonstrated that ZIF-8 can be used repeatedly without significant loss of catalytic activity during at least three catalytic cycles.

1,2-ZWITTERIONIC GA-COMPLEXES OF D–A CYCLOPROPANES AND METHYLIDENEMALONATES, AND THEIR TRANS-ADDITION TO ACETYLENES

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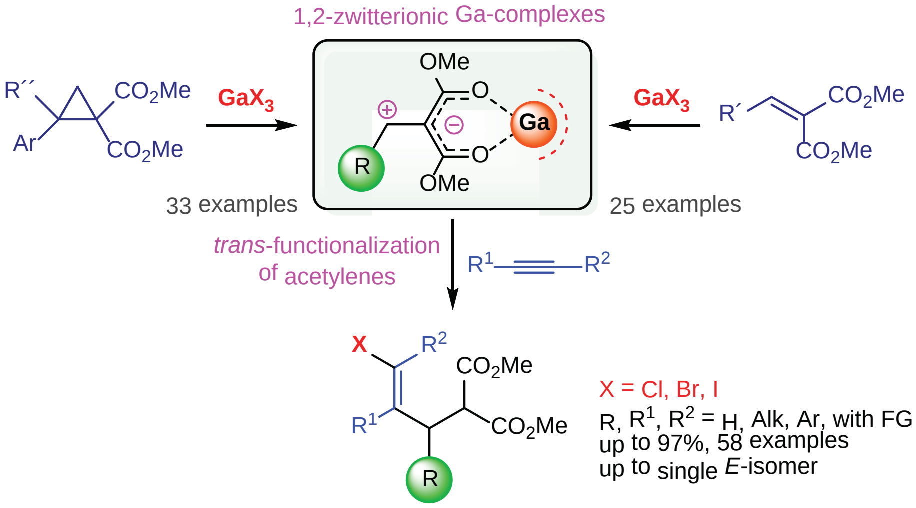
We have suggested and efficiently implemented a new strategy [1] to the three-component processes for donor-acceptor cyclopropanes (DAC) and methylidenemalonates based on generation of the 1,2-zwitterionic intermediates. [2,3] As an example of synthetic application, we have developed a new three-component addition of halide anions and acetylenes to DAC and methylidenemalonates. [1] This process is promoted by gallium(III) salts and occurs with high E-selectivity. The reaction readily occurs for a broad range of substrates and is tolerant to various functional groups. This methodology makes it possible to assemble highly functionalized vinyl halides. The latter are very convenient building blocks in organic synthesis. This reaction opens up a new group of processes involving DAC and methylidenemalonates, and it is a new chapter in their gallium chemistry. This process is of general nature and can be expanded to other objects in the future. A possible mechanism of this reaction and its stereochemical aspects were suggested and studied in details.



The work was supported by the Russian Science Foundation (grant no. 14-13-01054-P).

References:
[1] R.A. Novikov, D.D. Borisov, A.V. Tarasova, Y.V. Tkachev, Y.V. Tomilov. Angew. Chem. Int. Ed. 2018, 57, 10293–10298.
[2] R.A. Novikov, A.V. Tarasova, V.A. Korolev, V.P. Timofeev, Y.V. Tomilov. Angew. Chem. Int. Ed. 2014, 53, 3187–3191.
[3] D.D. Borisov, R.A. Novikov, Y.V. Tomilov. Angew. Chem. Int. Ed. 2016, 55, 12233–12237.

BIOGLYCANS: FROM STRUCTURE TO SPECTRUM AND FROM SPECTRUM TO STRUCTURE

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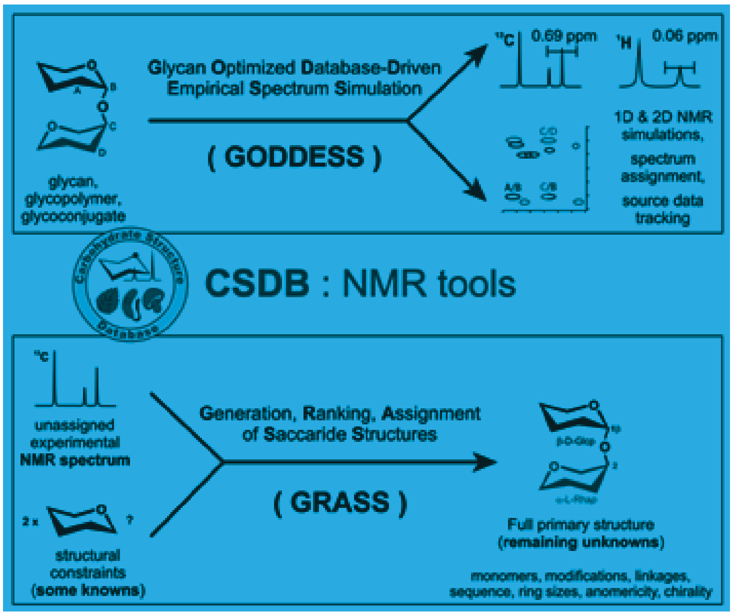
Glycan-Optimized Database-Driven Empirical Spectra Simulation (GODDESS) is a new method and web-service to simulate NMR spectra of bioglycans, including those containing rare sugars, amino acids, lipids, alditols, phosphates and other constituents. This approach exhibited NMR simulation with average accuracy of 0.69 ppm per ^{13}C resonance and 0.06 ppm per 1H resonance on a random pool of structures synthesized by microorganisms. The method was proved to be the most accurate method for NMR simulation of carbohydrates.[1] It is based on sequential generalization of the chemical surrounding of the atom under prediction and on subsequent heuristic averaging of matching data from a database of ~8000 NMR spectra of bioglycans. The generalization pathways are iteratively mutated to minimize the structure perturbation in the context of the specific carbohydrate descriptors.



Generation, Ranking and Assignment of Saccharide Structures (GRASS) is a method and web-service for automated elucidation of structures of glycans and derivatives which uses an unassigned 13C NMR spectrum and information from other methods. It is based on the iteration of structures according to the given constraints, and ranking of structural hypotheses according to the similarity between the simulated and experimental spectra. Top 500 matches obtained by the fast empirical prediction are further refined by accurate statistical method (GODDESS). According to the validation tests, it excels other methods in the diversity of supported structural features, accuracy and performance. [2]

Both services are built at the platform of the Carbohydrate Structure Database (CSDB) and rely upon all the NMR data accumulated in it. They allow prediction of structures and manual analysis of predictions, including 1D and 2D NMR simulation with cross peak size estimation (COSY, TOCSY, HSQC, HMBC and other) [3], spectrum assignment and comparison, estimation of a model trustworthiness and accuracy, tracking of data to original publications, and molecular geometry calculations. Free web services are available: http://csdb.glycoscience.ru/godess.html and http://csdb.glycoscience.ru/grass.html

This work was funded by the Russian Science Foundation (grant 18-14-00098).

References:
[1] R.R. Kapaev, Ph.V. Toukach, Analyt. Chem. 2015, 87, 7006-7010.
[2] R.R. Kapaev, Ph.V. Toukach, Bioinformatics 2018, 34, 957-963.
[3] R.R. Kapaev, Ph.V. Toukach, J. Chem. Inf. Model. 2016, 56, 1100-1104.

CSDB_GT:
A DATABASE ON CONFIRMED GLYCOSYLTRANSFERASES

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Carbohydrate-active enzymes (CAZy) assemble and process glycans in all living organisms. Reliable information on biochemical activities of CAZy facilitates their biotechnological and medical applications. Databases accumulating experimentally confirmed activities of various CAZy are highly demanded but underrepresented in modern bioinformatics resources.[1] We have developed CSDB_GT, a curated database on confirmed and predicted activities of glycosyltransferases (GTs) that participate in biosynthesis of natural glycans of plant and microbial origin.[2] CSDB_GT is a database at the platform of the Carbohydrate Structure Database (CSDB) project.[3] Currently, it provides the coverage on confirmed GT activities from Arabisopsis thaliana and confirmed and predicted GT activities from Escherichia coli. The coverage on Saccharomyces cerevisiae is expected in the nearest future. The data are manually retrieved by expert glycobiologists from original publications. CSDB_GT includes protein and gene identifiers (names, IDs and cross-links to other databases), activity data (linkage, donor and substrate), trust level (in vivo, in vitro, in silico), full glycan structure (if known), taxonomic data, and literature references. CSDB_GT supports search by IDs (CSDB_GT, UniProt, GenBank, etc.), enzyme name, activity and organism (Figure 1). CSDB_GT is freely available as a web-service at http://csdb.glycoscience.ru/gt.html.

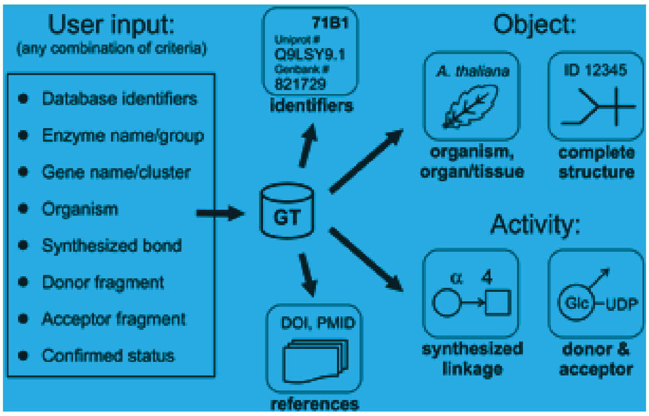

Figure 1. User input and output in CSDB_GT.

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References
[1] K. S. Egorova, Ph. V. Toukach, Angew. Chem. Int. Ed. 2018, ePub ahead of print, doi: 10.1002/anie.201803576.
[2] K. S. Egorova, Ph. V. Toukach, Glycobiology 2017, 27(4), 285-290.
[3] Ph. V. Toukach, K. S. Egorova, Nucleic Acids Res. 2016, 44(D1), D1229-D1236.

SYNTHESIS OF GEM-DIFLUORINATED PHOSPHONIUM SALTS AND THEIR VISIBLE LIGHT-MEDIATED TRANSFORMATIONS

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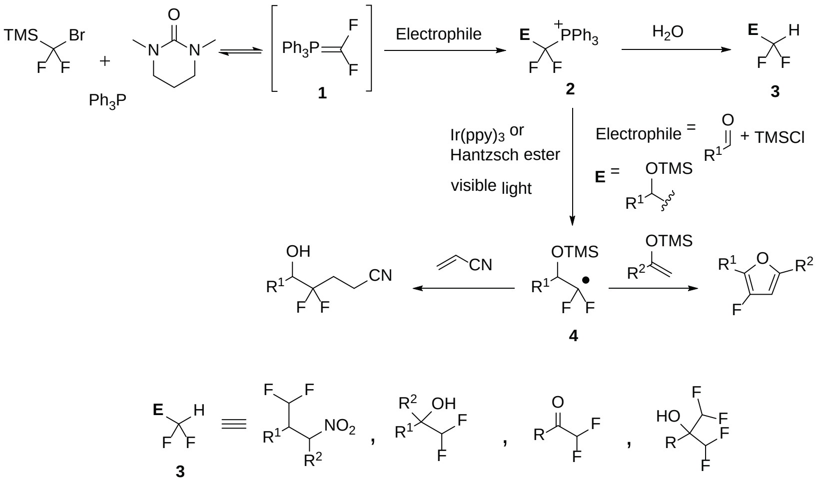
The importance of gem-difluorinated compounds for medicinal chemistry has stimulated intensive studies for the synthesis of compounds of this type. Besides classic approaches based on deoxofluorination and the application of building blocks, the use of difluorocarbene and related reagents has recently emerged as an attractive method for the straightforward access to CF2-substituted products.

A combination of (bromodifluoromethyl)trimethylsilane (Me_3SiCF_2Br), triphenylphosphine, and N,N'-Dimethylpropyleneurea (DMPU) serves as a source of difluorinated phosphorus ylide 1 under mild conditions. The system was used to effect nucleophilic difluoromethylation of ketones, nitroalkenes[1] and acyl chlorides.[2] gem-Difluorinated phosphonium salts 2 were hydrolyzed affording difluoromethylated products [3].

Phosphonium salts 2 can also serve as a source of radicals under reductive conditions if E is an aldehyde[3]. An iridium complex or Hantzsch ester was used as a one-electron reducing agent when irradiated with visible light. The fluorinated radicals 4 were trapped by silyl enol ethers or acrylonitrile leading to products either via a photoredox cycle (for the iridium catalyst) or via a hydrogen atom transfer (for the Hantzsch ester).



References

1. Trifonov, A.L.; Zemtsov, A.A.; Levin, V.V; Struchkova, M.I.; Dilman, A.D. Org. Lett., 2016, 18, 3458–3461.
2. Trifonov, A.L.; Levin, V.V; Struchkova, M.I.; Dilman, A.D. Org. Lett., 2017, 19, 5304–5307.
3. Panferova, L. I.; Tsymbal, A.V.; Levin, V.V; Struchkova, M.I.; Dilman, A.D Org. Lett., 2016, 18, 996–999.

SYNTHESIS OF NEUROACTIVE PROGESTERONE METABOLITES AND THEIR 16,17-CYCLOHEXANOANALOGS

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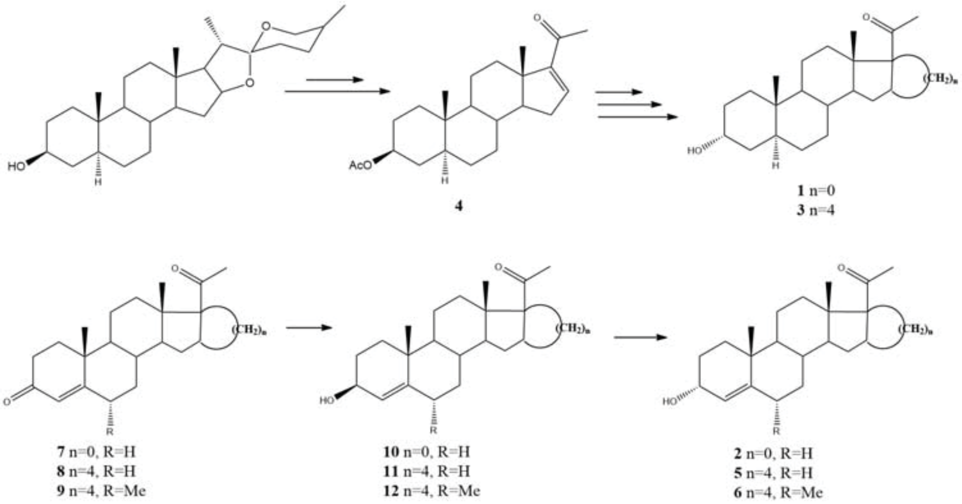
Conversion of endogenous progesterone by 5α-reductase and by 3α-hydroxysteroid dehydrogenase results in two basic metabolites: 5α-pregnan-3α-ol-20-one (allopregnanolone) 1 and Δ^4-pregn-3α-ol-20-one 2.

Allopregnanolone 1 is a potent allosteric modulator of γ-aminobutyric acid (GABAA) receptors and possesses a wide variety of effects, including antidepressant, anxiolytic, sedative, analgesic, anesthetic, anticonvulsant, neuroprotective, and neurogenic effects. At the same time both metabolites 1 and 2 can display other physiological functions in the body, for example, within breast tissue, proliferative and antiproliferative activities.

We have synthesized a new class of progestins with additional cyclohexano substituent at the 16α,17α-positions of the D ring (D'-pentaranes). These synthetic progestins are promising for practical application. Recently in our laboratory it was shown the similarity of the pathways of metabolism of D'-pentaranes and endogenous progesterone. We developed the convenient way for synthesis of progesterone metabolites and their pentarane analogs from commercially available natural source. Allopregnanolone 1 and its analog 3 were obtained starting from Δ16-pregnanolone 4. On the contrary, Δ^4-3α-hydroxy metabolites 2, 5, 6 were synthesized from progesterone 7 and 16α,17α-cyclohexanoprogesterones 8 and 9, correspondingly, by selective reduction α,β-unsaturated keto group into 3β-hydroxy compounds 10 - 12 and then into desired 2, 5, 6. The key stage of the synthesis of all metabolites was Mitsunobu reaction.



This work was supported by RFBR (grant 18-33-00913).

MAGNESIUM-ASSISTED MICHAEL ADDITION OF THE CYANIDE ANION TO IN SITU GENERATED NITROSOALKENES

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Addition of the cyanide anion to ene-nitrosoacetals was developed as a route to 5-amino-substituted isoxazoles starting from available nitronates and nitroalkanes. The tandem process involves in situ generation of unstable α-nitrosoalkenes, Michael addition of cyanide anion and subsequent cyclization of the resulting α-cyanooximes. The key feature of the developed procedure is the use of cyanide source in combination with magnesium perchlorate, which prevents anionic polymerization and side-processes on the Michael addition stage.

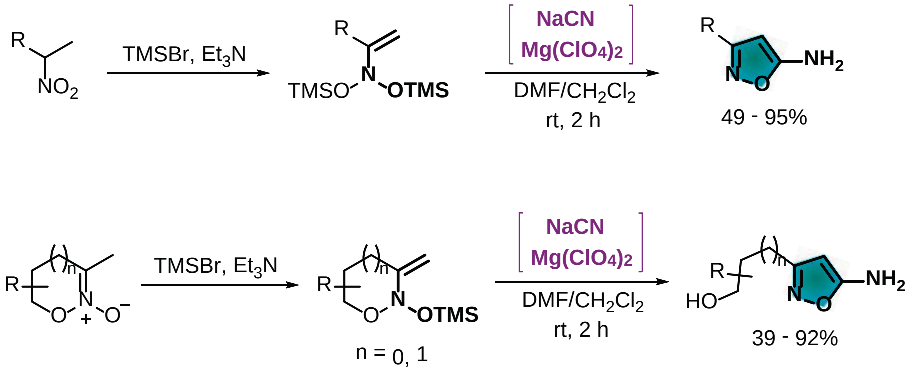

Figure 1. The developed route to 5-amino-substituted isoxazoles.

The developed nucleophilic cyanation system was successfully applied in reactions with various Michael acceptors and other electrophiles.

This work was supported by Russian Foundation for Basic Research (grant 17-03-01079_a).

DETERMINATION OF PHARMACOFORES OF FUCOSYLATED CHONDROITIN SULFATES USING RELATED SYNTHETIC OLIGOSACCHARIDES

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E.Yu. Borodina, M.I. Bilan, A.G. Gerbst,
A.I. Usov, N.E. Nifantiev

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Polysaccharides fucosylated chondroitin sulfates (FCS) isolated from sea cucumbers demonstrated a wide spectrum of biological activities such as anticoagulant, antithrombotic, antitumor, anti-inflammatory. FCS are glycosaminoglycans built up of a backbone [→3)-β-D-GalNAc-(1→4)-β-D-GlcA-(1→]$_n$ and fucosyl branches at O-3 of GlcA. We have performed structural study of a series of FCS from different sea cucumber species and have found out a series of unusual structural motives such as sulfated glucuronic acids in a backbone (Fig. 1) [1,2]. In this communication we report the synthesis of branched and linear compounds related to FCS together with their study using fluorescent cytometry and microscopy. As a result, structure-activity relationship within FCS was determined and a number of active compounds have been selected as a base for further development of antithrombotic and anti-inflammatory drugs. This work was supported by RSF grant 14-13-01325.

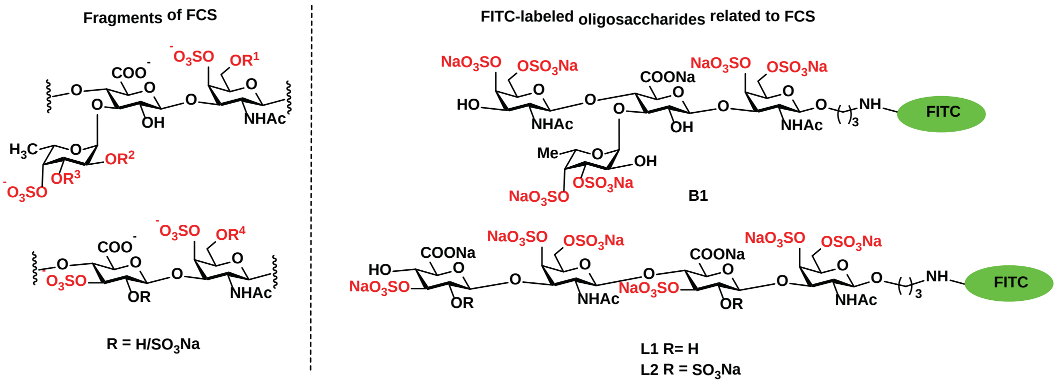

Figure 1. Examples of the structural fragments of fucosylated chondroitin sulfates (FCS) and related synthetic oligosaccharides bearing fluorescent label.

References:
[1] Nadezhda E. Ustyuzhanina et al., Glycobiol. 26, 449 (2016).
[2] Nadezhda E. Ustyuzhanina et al., Carbohydr. Polym. 165, 7 (2017).

B-HYDROXY-B-PEROXYLACTONES: STABLE CRIEGEE INTERMEDIATES OF BAEYER VILLIGER REACTION

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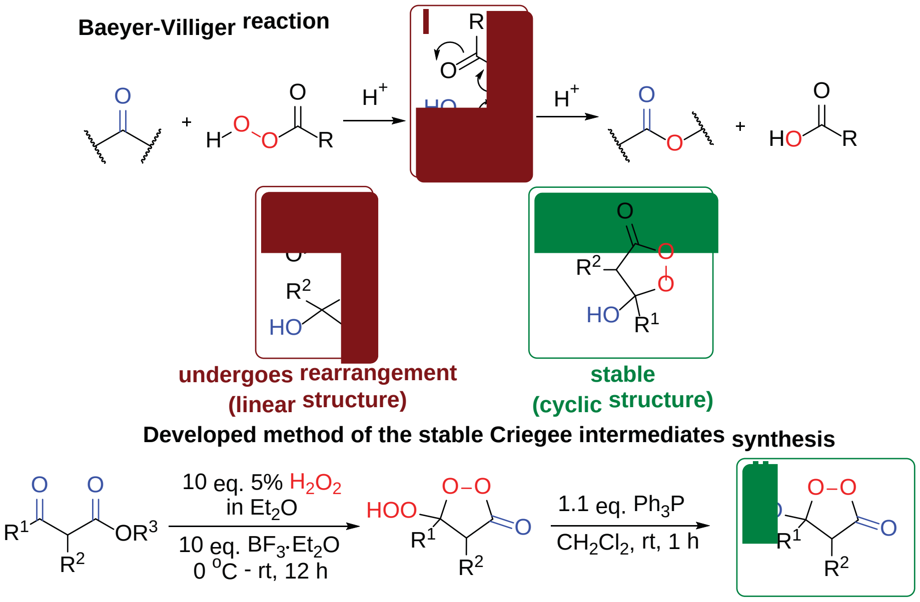
In 1899, Baeyer and Villiger reported a new reaction that could convert ketones into esters. More than a century later, this transformation still continues to provide a valuable connection between these key organic functional groups.[1] In 1948 Prof. Criegee proposed that the mechanism of the Baeyer-Villiger (BV) rearrangement involves a tetrahedral intermediate formed by the addition of a peroxyacid to the carbonyl group of a ketone (i.e., the Criegee intermediate).[2] Throughout the long history of the BV reaction, the parent hydroxy version of the Criegee intermediate was never isolated and structurally characterized because of its fleeting stability and high reactivity. It was discovered, that stable cyclic Criegee intermediates (β-hydroxy-β-peroxylactones) constrained within a five-membered ring can be prepared by mild reduction of the respective β-hydroperoxy-β-peroxylactones which were formed in high yields in reaction of β-ketoesters with BF_3•Et_2O/H_2O_2system.[3]



This study was supported by Russian Science Foundation (Grant № 18-73-00315).

References
[1] A. Baeyer, V. Villiger, Ber. Dtsch. Chem. Ges. 1899, 32, 3625–3633.
[2] R. Criegee, Justus Liebigs Ann. Chem. 1948, 560, 127–135.
[3] V. A. Vil', G. dos Passos Gomes, O. V. Bityukov, K. A. Lyssenko, G. I. Nikishin, I. V. Alabugin, A. O. Terent'ev, Angew. Chem. Int. Ed. 2018, 57, 3372–3376.

OZONE-FREE SYNTHESIS OF OZONIDES. OZONIDES AS PROMISING MEDICINAL AND AGRICULTURAL AGENTS.

I.A. Yaremenko[1,2], **Y.Yu. Belyakova**[1], **A.E. Vilikotskiy**[2],
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Organic peroxides have significant potential for creating on their basis new medicinal and agricultural agents. In recent decades, the chemistry of organic peroxides has been intensively developing due to the detection of antimalarial, anthelmintic, antitumor, growth regulation, and antitubercular activity.

The greatest progress in the development of medicinal agents on the base of synthetic peroxides is associated with compounds that contain an ozonide (1,2,4-trioxolane) moiety. Ozonides traditionally synthesized by using ozone via the reaction of ozone with alkenes or via ozonolysis of O-methyl oximes in the presence of acyclic or cyclic ketones (Griesbaum coozonolysis). However, ozone is significantly inferior to H_2O_2 due to a combination of factors that include cost, convenience, and toxicity. Therefore, development of synthetic ozone-free approaches to ozonides that utilize hydrogen peroxides and ketones represents an important fundamental and practical challenge.

In our studies, a general approach to the preparation of bicyclic ozonides is developed via reaction of 1,5-diketones with H_2O_2, promoted by such acids as $BF_3 \bullet Et_2O$, H_2SO_4, p-TsOH and HBF_4. This process leads to the stereoisomeric bridged ozonides and provides a rare example of selective synthesis of ozonides without the use of ozone.

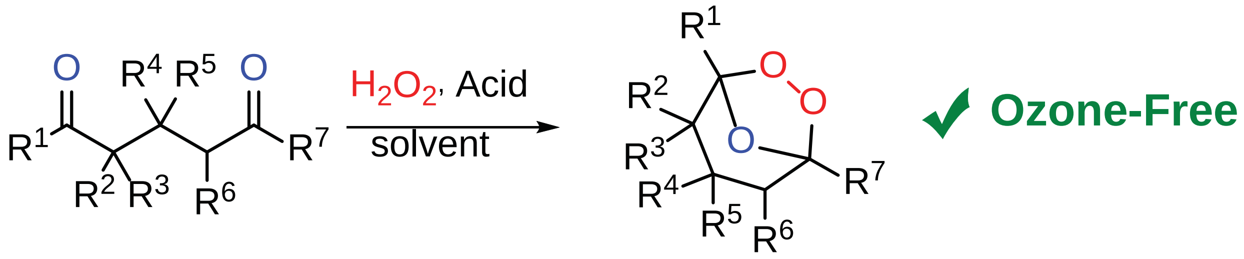

Figure 1. Ozone-free synthesis of ozonides.

Synthesized ozonides from 1,5-diketones and H_2O_2 were tested against phytopathogenic fungi, malaria, and cancer cell lines.

This work was supported by the Russian Science Foundation (Grant no. 17-73-10364).

References

[1]. G.d.P. Gomes, I.A. Yaremenko, P.S. Radulov, R.A. Novikov, V.V. Chernyshev, A.A. Korlyukov, G.I. Nikishin, I.V. Alabugin, A.O. Terent'ev, Angew. Chem. Int. Ed. 2017, 56, 4955

[2]. I.A. Yaremenko, G.d.P. Gomes, P.S. Radulov, Yu.Yu. Belyakova, A.E. Vilikotskiy, V.A. Vil', A.A. Korlyukov, G.I. Nikishin, I.V. Alabugin, A.O. Terent'ev J. Org. Chem. 2018, 83, 4402.

[3]. P. Coghi, I.A. Yaremenko, P. Prommana, P.S. Radulov, M.A. Syroeshkin, Y.J. Wu, J.Y. Gao, F.M. Gordillo-Martinez, S. Mok, V.K.W. Wong, C. Uthaipibull, A.O. Terent'ev. ChemMedChem 2018, 13, 902-908

A NOVEL APPROACH TO THE SYNTHESIS OF N-SUBSTITUTED MONOIMINOGLYCOLURILS FROM THE CORRESPONDING THIOGLYCOLURILS

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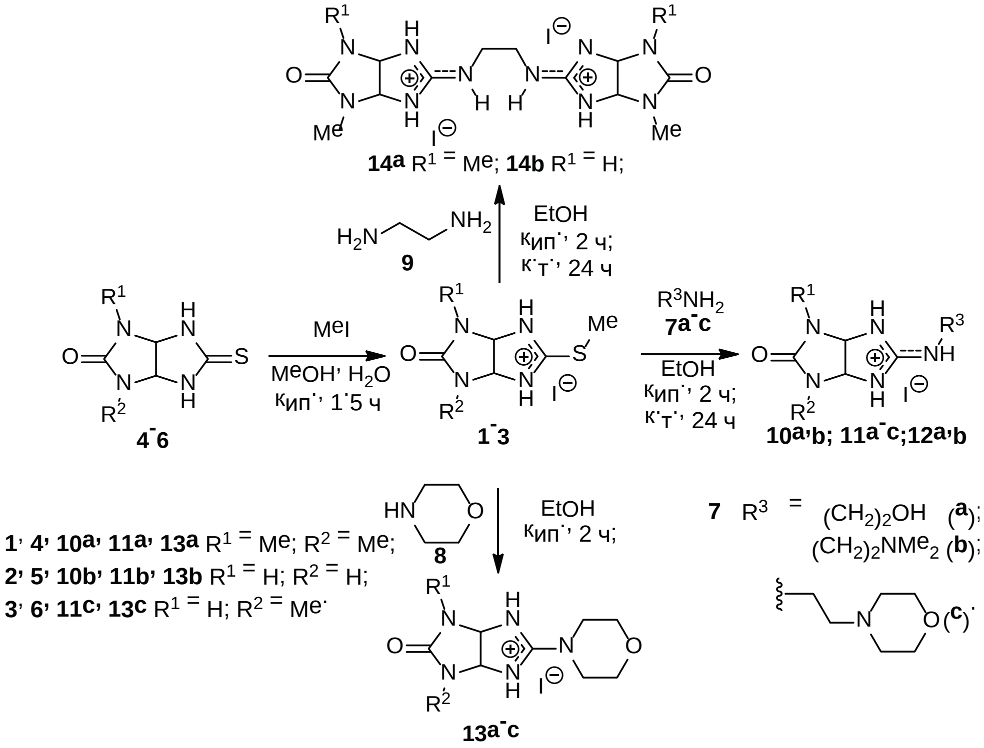
A novel general two-step approach for the synthesis of 2-imino-5-oxooctahydroimidazo[4,5-d]imidazol-1-ium iodides based on the reaction of thioglycolurils with MeI and various amines has been developed.

At the first step we synthesized isothiouronium salts 1-3 by the reaction of thioglycolurils 4-6 with MeI [1]. At the second step we studied the condensation of iodides 1-3 with primary amines 7a-c, morpholine 8 and ethylenediamine 9. The desired hydroiodides 10a,b, 11a-c, 12a,b, 13a-c and 14a,b with a guanidine moiety were obtained by the reaction of the salts 1-3 with $NH_2(CH_2)_2OH$ 7a, $NH_2(CH_2)_2NMe_2$ 7b, 2-morpholinoethanamine 7c, morpholine 8 and ethylenediamine 9 (Scheme 1).



References:

[1] Baranov, V. V.; Nelyubina, Y. V.; Kravchenko, A. N.; Kolotyrkina, N. G.; Biriukova, K. A. Tetrahedron Lett. 2015, 56, 6085-6088.

The work was supported by the Russian Science Foundation (Project 17-73-10415).

BISCATECHOLATE SILICON COMPLEXES WITH ACCEPTOR AND π-RICH NITROGEN HETEROCYCLIC BASES

D.Yu. Zinchenko[1,2], A.I. Nevezhina[1,2], E.N. Nikolaevskaya[1], I.V. Krylova,
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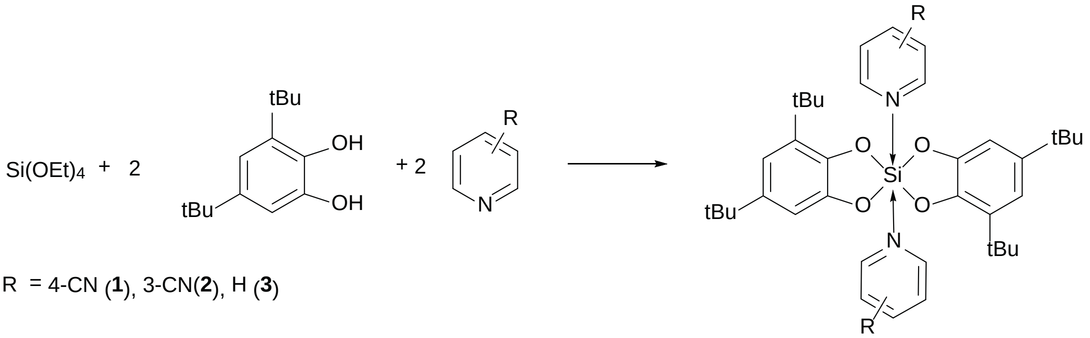
There are many reviews on high biological activity of silicon compounds [1-5]. However, the utility of hexacoordinated silicon in medicinal chemistry and chemical biology is still unclear. Meggers and co-workers synthesized hydrolytically stable hexacoordinated silicon compounds by using bulky bidentate building blocks [6]. The synthesized silicon complexes with catechol and 1,10-phenanthroline ligands had octahedral geometry and exhibited significant DNA-binding affinity. Hexacoordinated silicon derivatives are expected to be a novel class of structural templates for medicinal chemistry and chemical biology, with potential application to replace toxic transition metals.

The present work describes the synthesis of new hexacoordinated silicon complexes derived from 3,5-di-tert-butylcatechol (DTBC) and substituted pyridines (L). Their preparation includes the reaction of the catechol with tetraethoxysilane following by the addition of a π-rich nitrogen heterocyclic base (such as 4-cyanopyridine, 3-cyanopyridine, 2-cyanopyridine, 2,6-dicyanopyridine) in dry toluene media.



R = 4-CN (**1**), 3-CN(**2**), H (**3**)

The formed silicon complexes $(DTBC)_2SiL_2$ were characterized by elemental analysis, IR, ^1H, ^{13}C and ^{29}Si NMR spectroscopy.

This work was supported by Russian Scientific Foundation (grant № 17-73-20281).

References
[1] S. Fujii, Y. Hashimoto, Future Medicinal Chemistry, 2017, 9(5), 485–505.
[2] A.K. Franz, S.O. Wilson., J. Med. Chem., 2013, 56(2), 388–405.
[3] J.S. Mills, G.A. Showell, Expert Opin. Investig. Drugs, 2004, 13(9), 1149–1157.
[4] G.A. Showell, J.S. Mills, Drug Discov. Today, 2003, 8(12), 551–556.
[5] S. Gately, R. West, Drug. Dev. Res., 2007, 68(4), 156–163.
[6] Y. Xiang, C. Fu, T. Breiding, Chem. Commun., 2012, 48(57), 7131–7133

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