PL-01

FLUOROCONTAINING SUBSTITUENTS AND THEIR ROLE IN CREATION CHEMICAL COMPOUNDS WITH PECULIAR PROPERTIES

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Brilliant and novel works performed by Ivan L. Knunyants, his passionate love of chemistry, sparkling ideas and extraordinary energy exert great influence upon the development of fluorine chemistry in Ukraine.

More then during half a century the investigations in the field of aromatic and heterocyclic compounds with fluorocontaining substituents were carried out in the Institute of Organic Chemistry NAS Ukraine. More then 60 new fluorocontaining substituents were introduced into organic molecules, their electronic nature was determined as well as their influence towards reaction ability, acidic – basic and spectroscopic properties, colour and biological activity.

In order to obtain different types of fluororganic and inorganic molecules it was developed the new reaction of electrophilic perfluoroalkylation by firstly obtained by us reagents – arylperfluoroalkyliodonium and sulfonium salts. New reactions of nucleophilic trifluoromethylation were investigated using Me_3SiCF_3/F^- and heterocumulenes such as CO_2, SO_2, COS, RNCO, RNCS, RNSO, as well as anhydrides, imines, fluoroanhydrides of sulfinic and sulfonic acids.

Reactions such as trifluormethylsulfonyl- and trifluoromethylsulfinylethylations of organic compounds were developed – this investigations we started together with Professor Ivan L. Knunyants.

Flurocontaining substituents introduction allows to change the orientation of aromatic compounds with tricoordinated nitrogen atom (as substituent) in electrophilic reactions, to obtain stable σ-complexes of aromatic compounds without nitro groups, to synthesize azodyes that show negative halochromy.

Synthetic approach to synthesize different molecules type containing nitrogen atom bonded to fluorinated chains was developed, among compounds obtained are dyes, ionic liquids, biologically active preparations.

Optically active sulfoxides with polyfluoroalkyl groups at sulfur atom were firstly prepared. The methods to obtain principally new cyanine dyes and polyfluoromethine conjugated systems in which electronic influence is propagated via CF=CF units were elaborated.

We proposed a new principle of constructing superstrong electron-acceptor substituents and superacids through replacement of their sp^2 oxygen atoms by the group $=NSO_2CF_3$. That open the way to create electron-acceptor substituents not only with central carbon atom, but also with central sulfur, selenium, phosphorus, iodine atoms, that exceed two or even three nitro groups in the electron-withdrawing effect, their σ_p-constants are 1.4-1.77 in Hammett scale. In order to obtain the strongest of known organic acids we synthesized analog of trifluoromethanesulfonic acid in which two oxygen atoms were substituted to $=NSO_2CF_3$ groups. By using this strategy we realized the aza-Curtius reaction that permit to obtain fluorine-containing carbodiimides istead of isocyanates. By substitution of oxygen atoms to $=NSO_2CF_3$ the deeply colored dyes, that absorbed in near infrared region, were obtained.

PL-02

FLUORINE CHEMISTRY AT 3M COMPANY RESEARCH TO IMPLEMENT NEW PRODUCTS

Yu. Cheburkov, M. D. Barrera, G. L. Bauer, F. E. Behr, G. Birznieks, S. Brinduse, D. F. Hagen, J. C. Hansen, G. D. Johnson, C. R. Kessel, T. A. Kestner, T. Kruger, W. M. Lamanna, G. J. Lillquist, J. S. Marhevka, G. G. I. Moore, K. S. Moorhouse, M. E. Mueller, M. C. Pallazotto, M. J. Parent, V. Pothapragada, F. L. DeRoos, P. M. Savu, Y. Zhang

3M Company , 3M Center, St. Paul, MN 55144-1000, USA
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Our first meeting with I. L. Knunyants and how have I joined 3M Company.
Eleven years at 3M solving the following problems in Fluorine Chemistry:

- Perfluoroisobutene (PFIB) analysis and removal from 3M "Fluorinerts"
- Using PFIB-Methanol adduct for HFC-236 fa and Hexafluoroacetone preparation
- Hexafluoropropene dimer as a homolog of PFIB: HFC-4310 mf synthesis
- Hydrofluoroethers – new method of preparation from Perfluoroalcohols
- Electrochemical fluorination and by-products ($C_3 – C_6$ Perfluoroalkanes) pyrolysis to PFIB and perfluoroaromatics
- Perfluoroalkanesulfonyl fluorides
    - Reaction fluorolefins with oleum
    - Synthesis Pentafluoroethanesulfonyl fluoride from Hexafluoropropan-beta-sultone and from Tetrafluoroethylene
    - Perfluorodalkylsulfones reactivity
    - Tris(pentafluoroethanesulfonyl)methane and its value in Microlithography

PL-03

ORGANOFLUORINE CHEMISTY AT THE BIOMEDICAL INTERFACE

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It has been shown that the introduction of fluorine to a bioative molecule causes minimal steric alterations, hence can facilitate interactions of a fluorinated biomolecule with enzyme active sites, receptor recognition sites, transport mechanisms, and other biological systems. At the same time, however, the introduction of fluorine alters significantly the physico-chemical properties of the bioactive molecule because of its large electronegativity. Thus, this type of modification, in turn, can induce modified biological responses. Rational designs exploiting these special properties of fluorine have been successful in the development of new and effective biochemical tools as well as medicinal and therapeutic agents. Fluorinated congeners can also serve as excellent probes for the investigation of biochemical mechanisms. ^{19}F-NMR can provide unique and powerful tools for the mechanistic investigations in chemical biology. This lecture presents the organofluorine chemistry at the biomedical interface, exploiting the unique nature of this element mentioned above, including taxane anticancer agents as a showcase in this field of research.

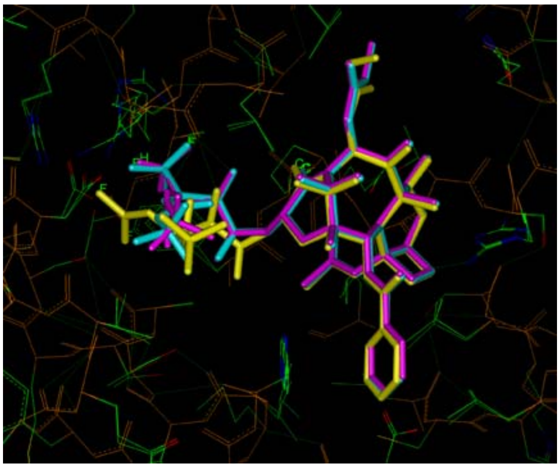

Figure 1. Overlay of CF_2H-, CF_3- and CF_2=CH-taxoids bound to tubulin

This research was supported by a grant from the National Cancer Institute (R01 CA 103314).

Kuznetsova L. V. *et al. J. Fluorine Chem.* 2004, **125**, 487-500.
Ojima I. *et al. Chem. Bio. Chem,* 2004, **5**, 628-635.
Ojima I. *et al.* In *Fluorine-containing Synthons* (V. A Soloshonok, Ed.), *ACS Symp. Ser. 911*, American Chemical Society/Oxford Press, Washington, D. C. (2005); pp 544-561.

PL-04

EXPLORING PROFESSOR I. L. KNUNYANTS'S CHEMISTRY: PAST AND PRESENT – A PERSONAL VIEW

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The results of I. L. Knunyants's research group especially in the field of phosphorus chemistry influenced and stimulated our own work to a large extent. The impact on some of our early and later achievements will be outlined and in this connection some aspects of our recent results will be discussed.

PL-05

NEW ASPECTS OF POLYFLUOROAROMATIC CHEMISTRY: REPLACEMENT OF –SH BY Cl AND Br; ORGANOZINC COMPOUNDS FROM POLYFLUOROGALOGENO- AND PERFLUOROARENES.

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A convenient route for introduction of chlorine and bromine into polyfluoroaromatic ring is demonstrated. This route consists in the replacement of –SH in polyfluoroarene thiols by chlorine and bromine in the copyrolysis of polyfluoroarene thiols with Cl_2 or Br_2 at 400-500°C in flow system. Chloro- and bromopolyfluoroarenes were obtained in good to excellent yields. Polyfluoroarene thiols were selected from benzene, indane, biphenyl and pyridine series. Several atoms of clorine or bromine can also be introduced into polyfluoroaromatic ring by this approach. The mechanism of replacement of –SH by Cl and Br is discussed.

A resonably general method of synthesis of polyfluoroaromatic organozinc compounds by the reactions of chloroperfluoroarenes with Zn in DMF or perfluoroarenes with Zn in DMF in the presence of $SnCl_2$ has been developed. When chloropolyfluoroarenes were used, polyfluoroaromatic organozinc compounds were formed at the C-Cl bond. In the case of perfluoroarenes, organozinc compounds were obtained as result of participation of the C-F bond in the process. Examles of this reaction pathway, which dominates over the classical organometallic formation with participation of the C-Cl bond, will also be described.

The application of these organozinc reagents in the reactions with some electrophiles directly or by means of Cu(I) for synthesis of iodo-, bromo- and allylpolyfluoroarenes as well as perfluorinated biaryls, N,N-dimethylaminobis(perfluoroaryl)methanes and polyfluoroaromatic ketones will be presented.

The mechanistic details of the formation and reactivity of polyfluoroaromatic organozinc compounds are discussed.

PL-06

ISOLATION AND APPLICATION OF A FLUORINATION ENZYME-THE FLUORINASE

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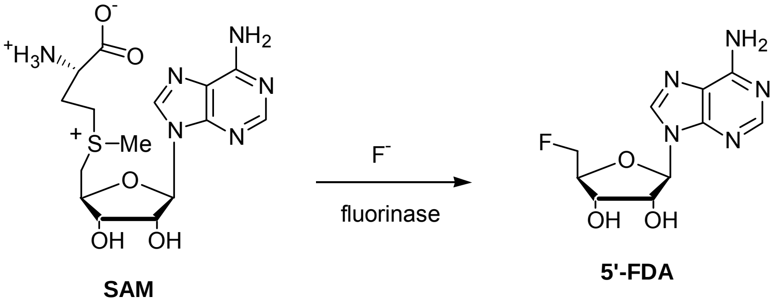
Although organo fluorine natural products are extremely rare, *Streptomyces cattleya* has the unusual capacity to biosynthesise organo-fluorine molecules. The fluorination enzyme has been identified and isolated from the organism. The 'fluorinase' has been shown to mediate a reaction between S-adenosyl-L-methionine (SAM) and fluoride ion to generate 5'-fluoro-5'-deoxyadenosine (5'-FDA). More recently the enzyme has been cloned, over-expressed and crystallised. X-Ray structure[1], stereochemical[2] and theory studies[3] suggest an S_N2 type mechanism. The substrate specificity has been explored and the prospects of developing this bio-transformation to a wider range of substrates will be discussed.



Our recent results investigating the isolation, mechanism and applications of the fluorinase including its use as a catalyst for ^{18}F-incorporation for positron emission tomography (PET)[4] will be highlighted.

This research was supported by the UK BBSRC and EPSRC Research Councils and by the Leverhulme Trust.

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[1] Dong C. *et al. Nature*, 2004, **427**, 561-564.

[2] Cadicamo C. *et al. ChemBioChem*, 2004, **5**, 685.

[3] Senn H.M. *et al. J. Am. Chem. Soc.,* 2005, **127**, 13643 – 13655

[4] Deng H. *et al. Chem. Commun*, 2006, 652-654.

PL-07

FLUORINE-CONTAINING OXO AND DIOXO ESTERS IN SYNTHESIS OF HETEROCYCLES

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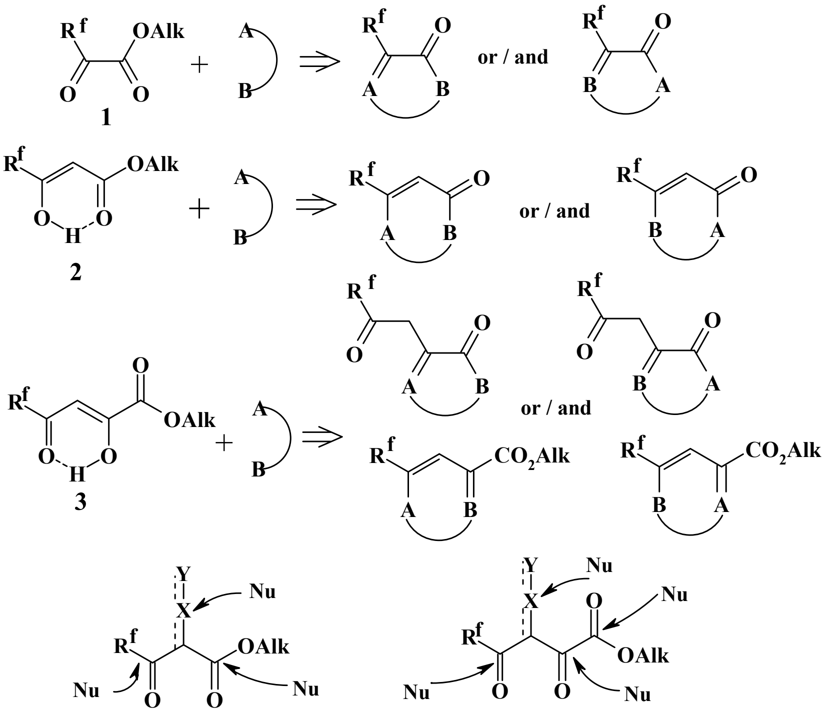
The questions of heterocyclic systems synthesis using fluorine-containing oxo esters **1-3** as the key block-syntones are discussed in the report. The reactions of 2-oxo and 3-oxo esters **1, 2** with various dinucleophiles at the corresponding α-keto- or β-ketoalkoxycarbonyl fragments lead to the formation of different heterocyclic systems. 2,4-Dioxo esters **3** having mutually combined α- and β-dicarbonyl moieties can react at both these fragments. The formation of regioisomeric products is possible in the reactions of esters **1-3** with non-symmetrical dinucleophiles. Introduction of different functional groups at the *mezo*-position of fluorine-containing 3-oxo esters **2** and 2,4-dioxo esters **3** is the perspective path for generation of new "building blocks" for heterocycles synthesis. Using derivatives of 3-oxo and 2,4-dioxo esters **2, 3** having perfluoroaryl substituents is especially interesting for creation of benzoannelated heterocycles due to intramolecular cyclization as a result of nucleophilic substitution of fluorine *ortho*-atom. The reactivity of fluorine-containing esters **1-3** is discussed in comparison with non-fluorinated analogues.



This work was supported by the State Programme for Supporting Leading Scientific Schools (grant № SS-9178.2006.3) and Russian Science Support Foundation.

PL-08

THE DIVERSE AND SYNTHETICALLY-USEFUL CHEMICAL REACTIVITY OF OCTAFLUORO[2.2]PARACYCLOPHANE (AF4)

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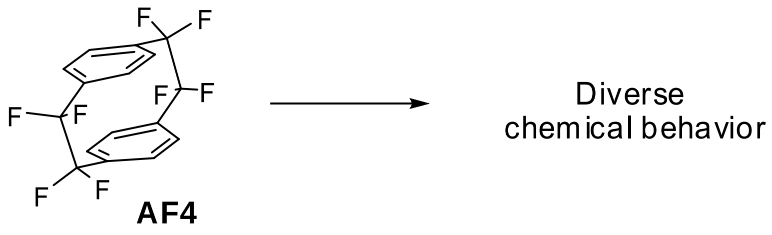
Octafluoro[2.2]paracyclophane (AF4) is widely recognized as the CVD precursor of the highly thermally stable thin film polymer, Parylene-HT®. Because of its inherent strain energy and the great electron deficiency of its component benzene rings, it also exhibits a uniquely versatile chemical reactivity with respect to aromatic substitution.

Such diverse chemical behavior of AF4 and its derivatives will be the subject of this lecture. The discussion will include (a) simple electrophilic substitution reactions, (b) free radical chemistry, (c) a wide variety of aryne chemistry, (d0 SET ($S_{RN}1$) chemistry, and finally (e) reactions that cleanly destroy the cyclophane system.



PL-09

TRIFLUOROMETHYLATED IMINIUMS AND ENONES AS GOOD TOOLS FOR THE EXPEDIENT SYNTHESIS OF TRIFLUOROMETHYL-CONTAINING CYCLES

**B. R. Langlois[a], T. Billard[a], G. Blond[a], S. Gille[a], A. Ferry[a], A. Barthelemy[a],
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α-(Trifluoromethyl)- allylamines and homoallylamines, as well as β-(trifluoromethyl)-enones can be easily synthesized in one-pot, respectively in two and three steps, from hemiaminals of trifluoroacetaldehyde (fluoral), via trifluoromethylated iminium intermediates.

After N-allylation or propargylation, α-(trifluoromethyl)-ω–unsaturated amines can undergo ring closure methathesis (eventually followed by a Diels-Alder cyclisation) or Pauson-Khand reactions leading to α-trifluoromethylated unsaturated nitrogen cycles (from 6- to 14-membered rings) and bicycles (octahydroisoquinolines, piperidinocyclopentanones).[1]

β-(Trifluoromethyl)enones can be involved in Diels-Alder cyclisations (affording 6-membered cycles or bicycles), Robinson annelation (leading to cyclohexenones) or Michael addition followed by ring-closure imination (delivering proline derivatives).

Unsaturated oxygen cycles and bicycles can be obtained, by analogous strategies, from hemiketals of fluoral.[2]

Cyclic trifluoromethyl-containing cycles can be thus prepared in a very limited number of steps.

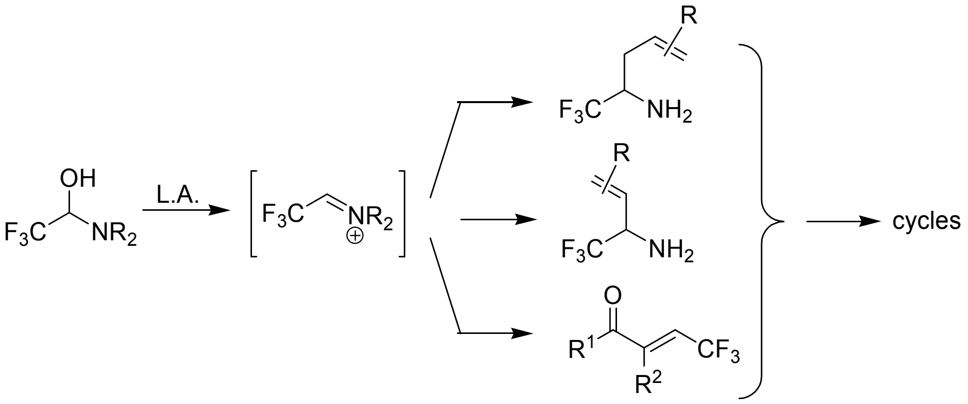

Fig. 1. α-(Trifluoromethyl)-ω-unsaturated amines and β-(trifluoromethyl)-enones

This research was supported financially by the French Ministry of Research and the “Centre National de la Recherche Scientifique” (CNRS).

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[1] T. Billard *et al. J. Fluorine Chem.* 2005, **126**, 189-196.
[2] S. Hartong *et al. Synthesis. 2005* (13), 2253-2263.

PL-10

α-FLUOROALKYLAMINES ARE NEW SOURCES OF UNHYDRATED FLUORIDE ION

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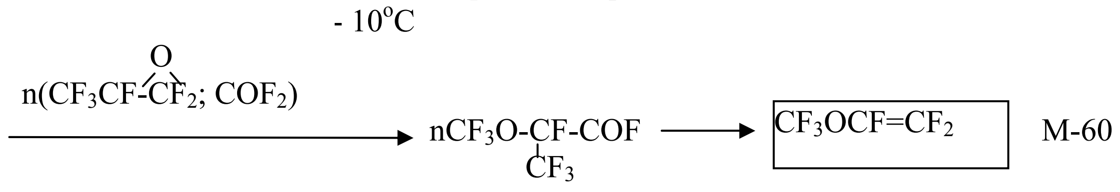
The paper covers the studies by I.L.Knunyants and his school in the field of chemistry of organofluoric compounds with fluorine anion involved.

I.L.Knunyants was firmly convinced that fluorine anion would play the same enormous part in the chemistry of organofluoric compounds as proton in the chemistry of organic compounds.

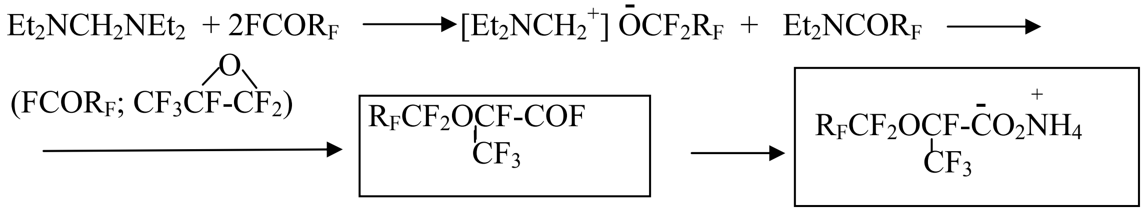
The choice of sources of fluorine anion was limited to caesium fluoride, rubidium fluoride, potassium fluoride and sodium fluoride. The low solubility of fluorides in media required for effecting a synthesis restricted potentialities of the method, and then I.L.Knunyants tasked to find new sources of fluorine anion permitting to enlarge the field of application of such processes. As a result of the studies α-fluoroalkylamines have found a wide application in reactions for the preparation of fluorinated aliphatic and aromatic compounds.

At present these processes are one of the main trends of the preparative and industrial synthesis of perfluoroalkyl-substituted compounds. The capability of dialkylaminofluoromethane to act as a source of fluorine anion in reactions with perfluorocarbonyl compounds has been realized in processes for the preparation of perfluorovinyl ethers and surfactants at the pilot plant of “Russian Scientific Center “Applied chemistry” Perm Branch.



$$2COF_2 + Et_2NCH_2NEt_2 \xrightarrow[-10^{\circ}C]{} [Et_2NCH_2^{+}]\,OCF_3 + Et_2NCOF \longrightarrow$$

$$\xrightarrow{n(CF_3CF\overset{O}{-}CF_2;\ COF_2)} nCF_3O\text{-}\underset{CF_3}{CF}\text{-}COF \longrightarrow \boxed{CF_3OCF{=}CF_2} \quad \text{M-60}$$



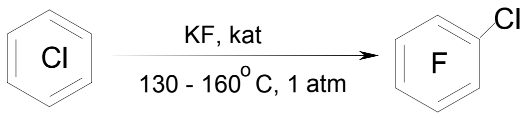
$$Et_2NCH_2NEt_2 + 2FCOR_F \longrightarrow [Et_2NCH_2^{+}]\,\bar{O}CF_2R_F + Et_2NCOR_F \longrightarrow$$

$$\xrightarrow{(FCOR_F;\ CF_3CF\overset{O}{-}CF_2)} \boxed{R_FCF_2O\underset{CF_3}{CF}\text{-}COF} \longrightarrow \boxed{R_FCF_2O\underset{CF_3}{CF}\text{-}\bar{C}O_2\overset{+}{N}H_4}$$

$R_F = C_4F_9, C_6F_{13}$

эмульгаторы

Unique properties of the new sources of fluorine anion have also found a use in the production of fluoroaromatic compounds prepared on an industrial scale at the pilot plant of “RSC “Applied chemistry” PB.



PL-11

SELECTIVE REDUCTIVE DEHALOGENATION – A CONSISE ROUTE FROM BASE TO DIFFICULTLY ACCESSIBLE POLYFLOROARENES AND BENZOAZOHETEROCYCLES ON THEIR BASIS

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Partially fluorinated arenes and their functional derivatives, containing 2÷4 fluorine atoms in a benzene ring, are valuable base building blocks for synthesis of practically useful substances and materials. Their utilisation in such a capacity is essentially restrained by small availability because the routes to them from hydrocarbon analogues, as a rule, are multistage and require several consecutive procedures of fluorine introduction into an aromatic ring. The classical method to introduce fluorine into aromatic nucleus, based on chlorine replacement by the action of metal fluorides, renders readily accessible perfluoro- and perfluorochloroarenes, thus becoming attractive precursors for their essentially less accessible partially fluorinated analogues. As an universal means for the selective removal of fluorine or chlorine atom, the simplest reductive system – zinc in the ammonia containing medium (liquid or aqueous ammonia) is offered and its applicability for obtaining partially fluorinated arenes, their trifluoromethyl-, carboxy- and cyanoderivatives has been shown. Introduction of an amino group keeps an opportunity to remove chlorine, but blocks hydrodefluorinaton. This blocking effect is suppressed by N-acetylation which, besides, allows to remove fluorine atom selectively from position *ortho* to an acetamido group. Such an orientation has been shown to be caused by presence of zinc cations. With use of quantum chemical and electrochemical methods, the notions of the hydrodefluorinaton mechanism and the factors causing its regioselectivity have been substantiated. The opportunity of selective *ortho*-defluorination of polyfluorine-N-acetylamines affords a favorable structural situation for implementing various heterocyclizations and, thus, opens the shortest way to earlier inaccessible poyfluorobenzoazoheterocycles. *ortho*-Defluorinated N-acetyl derivatives of poyfluoroarylamines has been shown to be immediately involved into the Skraup synthesis. A number of formerly difficultly accessible or unknown quinolines with the fluorinated benzene ring has been synthesized by this way, their various functionalizations on the benzene ring has been implemented, based on fluorine nucleophilic substitution, hydrolysis of trifluoromethyl group, and subsequent transformations of carboxylic group thus generated.

PL-12

GENERAL APPROACHES FOR THE INTRODUCTION OF SHORT-LIVED FLUORINE-18 INTO THE STRUCTURES OF BIOLOGICALLY ACTIVE MOLECULES

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Positron emission tomography (PET) is a modern noninvasive nuclear imaging technique, which provides an *in-vivo* information on the physiological and biochemical processes abnormalities on molecular level. The potential of PET is based on the application of short-lived positron emitting radionuclides (^{15}O, ^{13}N, ^{11}C, ^{18}F), available from medical cyclotrons. Among them fluorine-18 has the longest half-life (110 min), therefore the duration of syntheses can be scaled up to 4 hours. Also, several clinical doses of radiopharmaceuticals (RPs) can be produced in a single batch and delivered to remote-site hospitals which are not equipped with an expensive cyclotron. The incorporation of fluorine-18 into the structure of various molecules can be achieved via nucleophilic or electrophlic fluorination reactions. Historically, electrophilic method has been pioneered in the synthesis of ^{18}F-labelled compounds. However this method has well-known limitations mainly due to technical difficulties in generating ^{18}F via ^{20}Ne(d,α)^{18}F or ^{18}O(p,n)^{18}F nuclear reactions by irradiation gas cyclotron target. The complete recovery of radionuclide from gas target necessitates the addition of molecular fluorine as a carrier. As a result, the radiotracers obtained have low specific activity, which is crucial for certain classes RPs, like labeled toxic substrates, receptors radioligands and others. The widely accepted synthetic way involves nucleophilic radiofluorination reactions. Here the radionuclide is produced via ^{18}O(p,n)^{18}F nuclear reaction during irradiation of enriched water-^{18}O and recovered from the target as an aqueous ^{18}F-fluoride. The main advantages of this approach are high starting radioactivity of ^{18}F (up to 12 Ci) and availability of ^{18}F without carrier. To activate ^{18}F-fluoride for nucleophilic substitution, it is transferred in aprotic solvents media while fluorinations are performed in the presence of phase transfer catalysts (kryptofix 2.2.2, tetrabutyl ammonium salts).

Direct introduction of the label via nucleophilic displacement of suitable "leaving group" by the fluorine-18 complex, $[K/K2.2.2]^{+18}F^{-}$, has found to be an optimal way to ^{18}F-labelled RPs. Other functional groups in the substrate molecule bearing labile hydrogen have to be protected. De-protection step (hydrolysis) has to be performed after radiofluorination. This approach was applied in a synthesis of 2-[^{18}F]fluoro-2-deoxy-D-glucose (^{18}F-FDG), an unique radiotracer of glycolysis which is utilized in more than 80% of PET studies. However, direct introduction of ^{18}F-label into the molecule is limited by several examples. Preparation of many important classes of ^{18}F-radiotracers involves a wide range of chemical transformations which requires a complex multi-step labelling procedure. First stage of this process is a synthesis of high reactive agents (synthons): [^{18}F]fluoro- benzaldehydes, alkyl halides, alkyl sulphonates, fluorinated amines etc. For example, to introduce ^{18}F-label into aromatic ring of tyrosine derivative, an original approach has been developed in INEOS RAS. The key synthesis step is asymmetric alkylation of chiral glycine-based Ni (II) complexes with the corresponding [^{18}F]fluorobenzyl bromide. Following major synthesis steps, the preparation of RPs is finalized by semi preparative HPLC purification, pH adjustment and sterilization. For implementation of new synthetic approaches for ^{18}F-labeling, the possibility of automation has to be considered as an important issue, due to the necessity to minimize radiation doses on the personal. In this report various production aspects for ^{18}F-labelled RPs will be discussed with a major focus on the new synthetic methods.

PL-13

FLUORINATED CYANOETHYLENES AS PRECURSORS OF CF_2X-SUBSTITUTED HITROGEN-CONTAINING HETEROCYCLES

N. D. Chkanikov, V. Yu. Tyutin, K. V. Komarov, P. V. Pasternak, A. F. Shidlovskii, A. S. Golubev, V. I. Muhanov, Yu. E. Pavlova, A. S. Peregudov, M. Yu. Antipin

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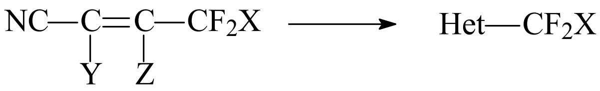
The syntheses of highly electrophilic cyanoethylenes containing CF_2X-group adjacent to the double bond have been developed. Pyrazole, pyridine, quinoline, pyrimidine, pyrazolo[3,4-b]pyridine, pyrazolo[1,5-a]pyrimidine, pyrido[1,2-a]pyrimidin, pyrano[2,3-c]pyrazole, and pyrido[2,1-a]isoquinoline derivatives have been synthesized from the above synthones (Scheme).



$$NC-\underset{Y}{C}=\underset{Z}{C}-CF_2X \longrightarrow Het-CF_2X$$

X = F, H, Br, Cl, $PO(OEt)_2$, SAr
Y, Z = CN, COOAlk, Cl, CF_3, CF_2H, CF_2Cl,
$PO(OEt)_2$, Ar, HetAr

Scheme

In most cases the transformations studied are specific for β-CF_2X-substituted acrylonitriles and have no direct analogies among non-fluorinated compounds. The approach to the synthesis of CF_2X-substituted heterocycles that we performed makes it possible the preparation of a number of new compounds that exhibit high biological activity in a number of cases.

A significant part of this work was financially supported by E. I. DuPont de Nemours and Co., Inc. within the framework of the Agreement with the International Science and Technology Center(ISTC) (Project ISTC-1016).

PL-14

NEW MATERIALS BASED ON MODIFIED[*] POLYTETRAFLUOROETHYLENE

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Политетрафторэтилен (ПТФЭ) имеет широкое применение во многих областях, однако практика требует новых приложений, которые могут обеспечить материалы, полученные модифицированием промышленных марок ПТФЭ. Модифицирование может быть достигнуто тепловой, химической, радиационной, механической обработкой промышленного ПТФЭ, а также комбинацией перечисленных методов. Кроме того, имеется проблема переработки отходов ПТФЭ, возникающих в производственном процессе.

В докладе делается обзор новых материалов различного морфологического строения (порошки, волокна, пленки, микротрубки, покрытия на твердых поверхностях), полученных отмеченными методами модифицирования. Обсуждаются особенности молекулярного, супрамолекулярного, морфологического строения материалов, выявленные исследованиями с применением набора физических методов: электронной и зондовой микроскопии, колебательной и ЯМР–спектроскопии, дериватографии, рентгеновской дифракции и др.

При определенных условиях, из газообразных продуктов пиролиза ПТФЭ удается получить ультрадисперсные порошки, состоящие из сфероподобных частиц со среднестатистическим размером 550 нм. Частицы имеют многоуровневую иерархическую структуру, нижний уровень которой составляют наноблоки размером 20 – 50 нм. Установлено наличие в порошке низкомолекулярной фракции ПТФЭ, макромолекулы в которых построены из несколько десятков мономеров, наряду с основной высокомолекулярной фракцией с молекулярной массой макромолекул в несколько сотен тысяч. Молекулы низкомолекулярной фракции имеют концевые CF_3 - и $CF{=}CF_2$ – группы. Этот факт и малые размеры макромолекул обуславливают существенное различие тепловых, динамических и структурных свойств низко- и высокомолекулярных фаз. Наличие низкомолекулярной фракции, растворимой в ряде растворителей, в том числе в сверхкритическом CO_2, расширяет технологические возможности использования материала для нанесения фторполимерных покрытий и капсулирования различных веществ в тефлоновые оболочки. Другой особенностью ультрадисперсного порошка ПТФЭ является возможность создать на его основе композитные металл - полимерные материалы – наночастицы металлов на поверхности микрочастиц фторполимера.

Установлены особенности морфологические строения микроволокон фторполимера, полученных лазерным воздействием на блочный ПТФЭ. Наблюдается сложная структура, образованная упаковкой наноблоков, размером 50 – 100 нм, вдоль оси волокна. Анализируется влияние радиационного и радиационно-механического воздействия на морфологическое строение модифицированных материалов.

Изучены особенности морфологического строения покрытий, полученных нанесением модифицированных материалов различными способами: втиранием, из растворов и газовой фазы.

Обсуждаются области практического применения новых материалов, перспективы их производства, в том числе из отходов, и коммерческой реализации товарных продуктов из них.

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[*] The author did not submit an English version.

PL-15

A NEW ACCESS TO FUNCTIONALIZED NANOSCOPIC METAL FLUORIDES: APPLICATIONS AND PERSPECTIVES

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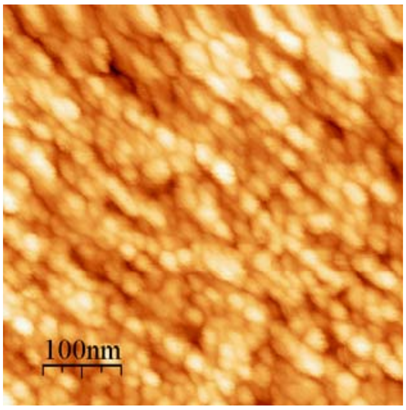
Optical and catalytic properties of metal fluorides – in several cases – are superior to that of metal oxides. In contrast to that, their use in optics and catalysis is very restricted. This is, besides economic factors, mainly due to the fact that the synthetic approach and utilization for metal fluorides is less developed as compared to metal oxides.

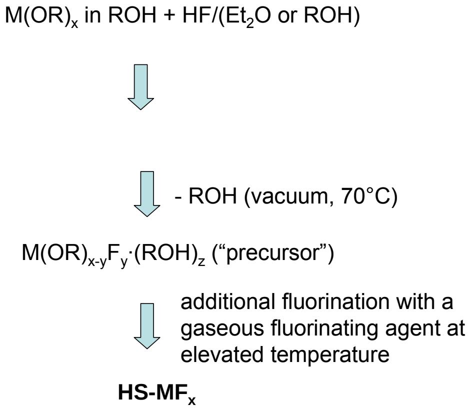
An extensive arsenal of synthetic methods is available for tailor-made metal oxides for many different applications. Without any doubt, sol-gel synthesis of metal oxides is one of the most powerful and most important synthesis routes.

In this presentation, a new synthetic access to metal fluorides with exceptional high surface areas and narrow particle size distribution on a low nano meter scale will be introduced. This new synthesis route opens the way to a wide range of nano-scopic, mesoporous metal fluorides for many applications in catalysis, for optical materials and/or for surface coating (optics, hydrophobic layers etc.).

The general path way of this new synthesis route will be presented for selected systems, including mechanistic details. The high potential of these new materials for several catalytic as well as optical applications will be presented.



AFM presentation of a spin-coated MgF_2 layer on a silica wafer



Reaction route for sol-gel-synthesis of metal fluorides

This new field of applications for nano-scopic metal fluorides is presently intensively investigated inside an EC-funded project involving 7 groups of several European countries. Hence, the FUNFLUOS-consortium gratefully acknowledges financial support through the 6th Framework Programme (Contract No. NMP3-CT-2004-5005575).

For literature references see the FUNFLUOS homepage: www.funfluos.com

PL-16

POLYMERIC PROTON CONDUCTING MEMBRANES FOR FUEL CELLS: STRUCTURE, PROPERTIES, ACHIEVEMENTS AND PROBLEMS

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The scientific fundamentals for the selection of perfluorinated proton conducting polymer membrane electrolytes (Nafion, Flemion, MS-4SK etc.) as well as the advances in their synthesis and commercial production processes are overviewed on the basis of the analysis of patents, research publications and obtained experimental data.

The optimum performances of membrane polymers are discussed with a particular consideration of the issues relating to the complexity of the initial fluoro-monomers synthesis and technological features of copolymerization processes. The possibilities for the optimization and improvement of performing the stages of sulfo-containing comonomer preparation and copolymerization, conditions providing the required copolymer composition and molecular weight as well as the effect of the copolymer end groups on the polymer membrane stability under fuel cell exploration conditions are analyzed. Another aspect of the discussion relates to the proton conductivity mechanism of Nafion-like polymer membranes and possible approaches to the modification of proton conducting properties for fluorinated polymer membranes with retaining their strength performances.

A particular consideration is devoted to the new R&D area on obtaining proton-conducting polymer membranes based on heat resistant polycondensation compounds such as poly(arylene sulfones), modified polyimides and other promising materials. Approaches to membrane thickness control, membrane reinforcement and modification by the incorporation of nanodispersed silica and other additives are summarized.

The presentation also includes the analysis of recent patents and advertising announcements on the development of new types of polymer membrane systems functioning under ambient conditions and featuring with availability, low cost, relatively simple preparation processes and reduced exploration expenses.

PL-17

NON-OZONE-DEPLETING HYDROFLUOROCARBONS

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Considered is the current state of Russian ODS-manufacturing chemical sector changeover to non-ozone-depleting substances (NODS). The report summarizes the studies conducted by FSUE «RSC "Applied Chemistry"» (St.Petersburg) that involve:

- background for the choice of the most promising non-ozone-depleting hydrofluorocarbons nomenclature;
- grounds for their manufacture methods;
- most probable chemical mechanisms for their synthesis;
- basis for standard process flow diagrams to be used in their full-scale manufacture;
- information on actual and newly created NODS production facilities in the Russian Federation.

PL-18

PERFLUOROCARBON EMULSIONS IN CLINIC [*]

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Идея создания кровезаменителя на основе эмульсий перфторорганических соединений (ПФОС) привлекательна во многих аспектах: все компоненты искусственного происхождения, ПФОС химически и метаболически инертны, при трансфузии эмульсий ПФОС исключается перенос инфекции, нет антигенной специфичности и благодаря этому эмульсии универсальны для всех реципиентов и, наконец, возможна организация промышленного производства кровезаменителя. Простота идеи оказалась кажущейся: так образующие стабильные эмульсии ПФОС, например, перфтортрибутиламин, задерживаются в тканях организма на всю жизнь, а сурфактанты, эффективно стабилизирующие эмульсии, разрывают клеточные мембраны. Долго не находила решения проблема получения биологически безопасных, стабильных по свойствам, высокоочищенных ПФОС и сурфактантов. Японские исследователи “Green Cross Corporation” создали в 1981 г. Fluosol-DA, который при выходе на клинический «простор» оказался реактогенным. В СССР к 1984 г. были созданы более приемлемые для практической медицины препараты. Высокоэффективные, изящные способы получения и очистки ПФОС, синтез оригинальных соединений, новые методы тестирования качества - все это результат исследований школы академика И. Л. Кнунянца, в первую очередь совместных усилий К. Н. Макарова, Л. Л. Гервица, блестящей плеяды химиков ГИПХа и технологов химических предприятий. Первостепенную роль в создании эмульсий ПФОС медицинского назначения сыграл профессор Ф. Ф. Белоярцев: его инициатива, энергия, понимание возможностей медико-биологического использования ПФОС. Производство нетоксичного сурфактанта обеспечила лаборатория Г. И. Быстрицкого. Оригинальный гомогенизатор высокого давления был создан в Черноголовке. Консолидация усилий в рамках целевой программы ОЦ-042 предопределила успех российской эмульсии ПФОС. На сегодня Перфторан - пока единственный разрешенный для клинического применения препарат эмульсии ПФОС. Благодаря участию в испытаниях и исследованиях таких клиницистов как Н. Л. Крылов, В. В. Мороз, Н. А. Онищенко, В. И. Шумаков, А. Н. Кайдаш, Л. В. Усенко, Е. Н. Клигуненко было определено и сегодня в полной мере оправдало себя использование перфторана: в лечении шоковых состояний, политравмы, кровопотери, различных видов ишемических нарушений, при кардиоплегии и в трансплантологии. Исследования В. В. Образцова дали толчок метаморфозе опасений в новые показания: вместо «ожидаемой» токсичности и канцерогенности сегодня перфторан используется как средство детоксикации, препятствующее развитию цирроза печени. Его высоко оценивают как средство лечения нарушений кровотока при различных облитерирующих заболеваниях сосудов и диабетических ангиопатий. Продолжаются пионерские патоморфологические исследования А. М. Голубева, изучение кинетики переноса газов и стабилизации эмульсии ПФОС- И. Н. Кузнецовой. Е. В. Терешина показала основные закономерности смены эмульгатора ПФОС в кровотоке. Мембранотропные и другие новые виды использования эмульсий ПФОС, связанные с участием гидрофобной фазы в нитрозилировании соединений крови, только начали выходить в клинику. Создание более стабильных, тонкодисперсных, минимально реактогенных эмульсий ПФОС – необходимое условие дальнейшего расширения их клинического использования не только в терапии кислороддефицитных состояний, но и в качестве эффективного регулятора воспаления, кровотока и иммунитета.

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[*] The authors did not submit an English version.

PL-19

FLUORINE CONTAINING UNSATURATED AMINO ACIDS. SYNTHESIS AND APPLICATION IN METAL CATALYSIS

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During last decade unsaturated α-amino acids have gained significant interest in the area of synthetic organic chemistry. They have proven useful building blocks for many transition metal-mediated fuctionalisations including different metathesis-type reactions[1].

We have developed a convenient synthetic methods for the preparation of unsaturated β-fluorocontaining α-amino acids and have demonstrated a possibility of their application in some metal-mediated transformations, *e.g.* such as intramolecular olefine and acetylene metathesis, cyclotrimerization reactions, 1,3-dipolar cycloaddition *etc*. A variety of new fluorinated cyclic amino acids can be synthesized by this methodology[2].

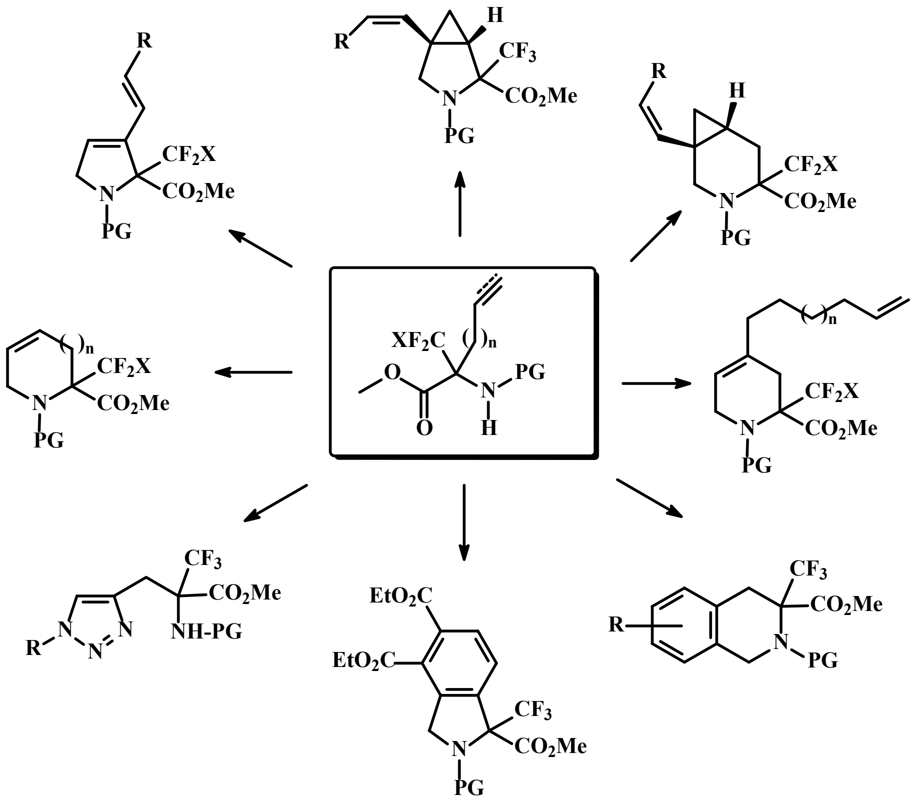

Рис. 1. Synthesis of cyclic fluoromethylsubstituted α-amino acids

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[1] J.Kaiser, S.S. Kinderman, B.C.J. van Esseveldt, F.L. van Delft, H.E. Schoemaker, R.H. Blaauw, F.P.J. Rutjes, *Org.Biomol.Chem*. **2005**, *3*, 3435.

[2] (a) S.N. Osipov, O.I. Artyushin, A.F. Kolomiets, C. Bruneau, M. Picquet, P.H. Dixneuf, *Eur. J. Org. Chem*. **2001**, *20*, 3891; (b) S.N. Osipov, P. H. Dixneuf, *Russ. J. Org. Chem*. **2003**, 39, *9*, 1211; (c) M. Eckert, F. Monnier, G.T. Shchetnikov, I.D. Titanyuk, S.N. Osipov, S. Derien, P.H. Dixneuf, *Org. Lett*. **2005**, 3741.

PL-20

CATALYTIC OLEFINATION REACTION – A NEW APROACH TO FLUORINATED COMPOUNDS

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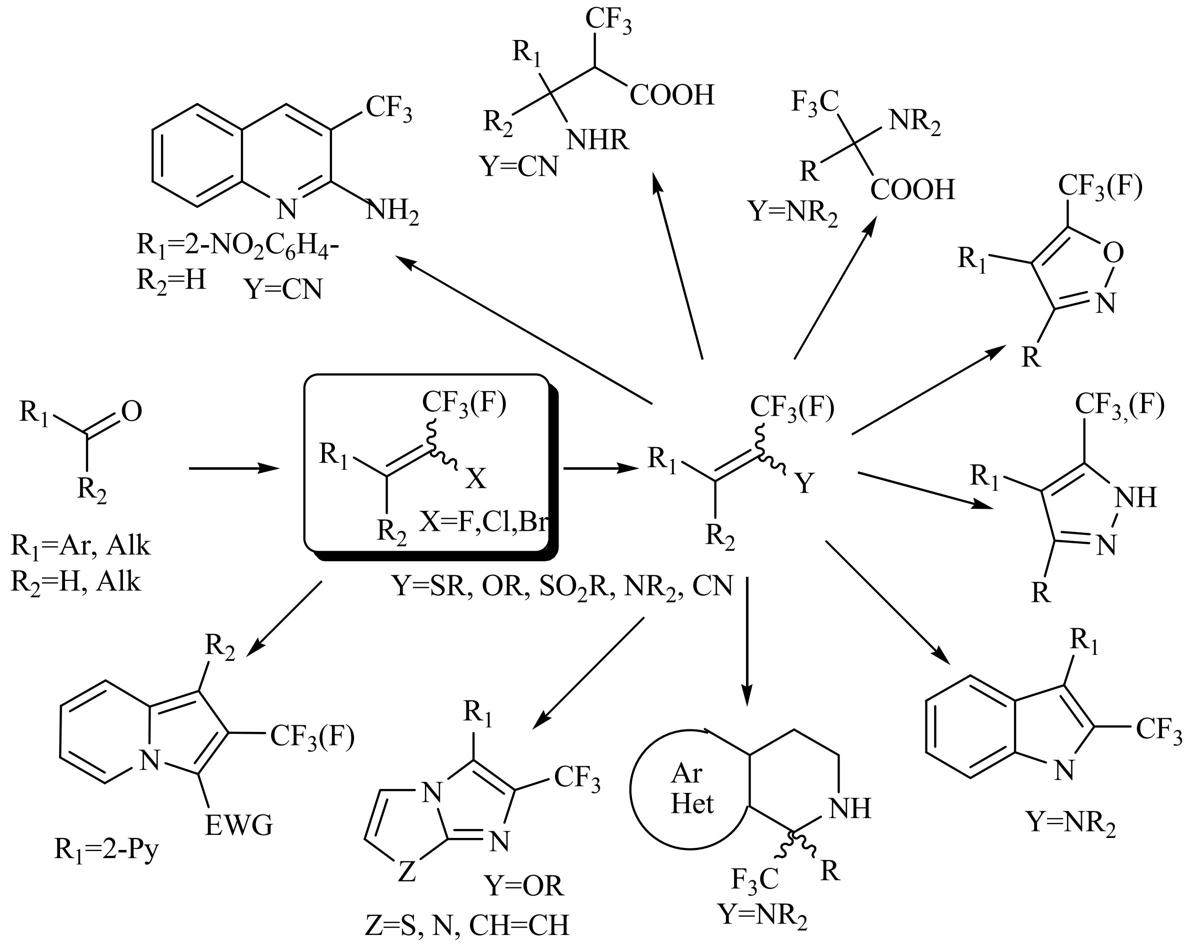
Organofluorine compounds are an object of increasing interest due to their biological activity. On the basis of catalytic olefination reaction we elaborated a novel method for synthesis of the fluorine containing alkenes. It was also shown, that these compounds are convenient starting materials for the synthesis of wide variety of fluorine-containing compounds. Aminoacids, quinolines, isoquinolines, isoxazoles, pyrazoles, indoles, indolizines, imidazopyridines, imidazothiazoles and other can be prepared using this approach.



O-01

NEW STEREOSELECTIVE SYNTHESIS OF POLYFLUORINATED *Exo*-NORBORNENES

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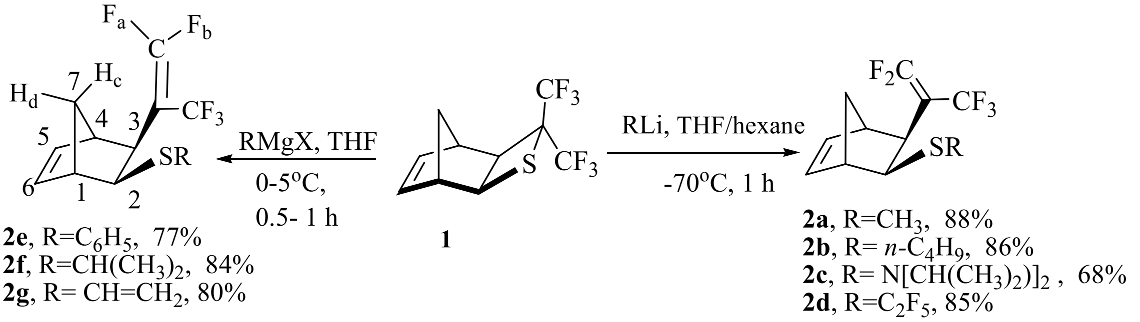
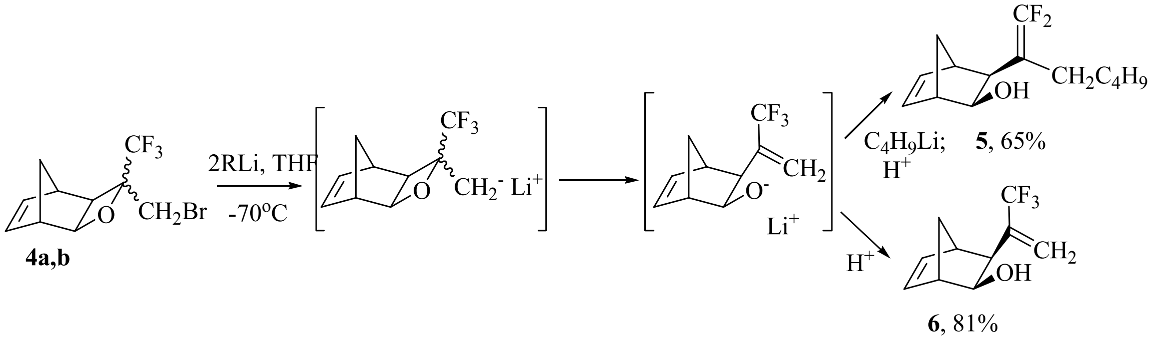
Recently we have developed a flexible synthesis of polyfluorinated *exo*-tricyclo[4.2.1.0$^{2.5}$]non-7-enes (tricyclononenes) through cycloaddition reaction of quadricyclane to polyfluorinated olefins, carbonyl-, nitrogen- and sulfur-containing compounds. In this work it was demonstrated that polyfluorinated *exo*- tricyclononenes due to their high configurational stability, can be used as feedstock for the stereoselective preparation of polyfluorinated *exo*-norbornenes.

Due to substantial positive charge on sulfur atom in compound **1**, it reacts with organolithium and magnesium compounds selectively producing the corresponding *exo-, exo*-norbornenes **2a-2g** in high yield.



exo-3-Oxa-4,4-bis(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-7-ene (**3**) has relatively low reactivity, but it slowly reacts with butyl lithium at ambient temperature. The replacement of one CF_3- by $BrCH_2$- group significantly enhances the reactivity. The reaction of **4a,b** with alkyl lithium reagents results in interesting ring opening process, leading to the formation of norbornene **5** (C_4H_9Li) or **6** (CH_3Li).



Scope and mechanism of ring opening reactions will be discussed.

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* Talk No 3408

O-02

CATALYTIC SYNTHESIS OF POLYFLUOROALKYLCHLOROSULFITES AND CATALYTIC REACTIONS WITH THEIR PARTICIPATION

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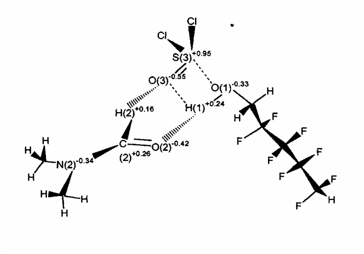
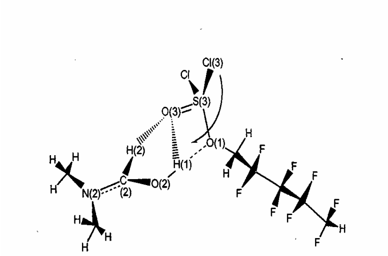
Polyfluoroalkylchlorosulfites (PFAChS) – unique compounds, characteristic stability to destruction on chloroalkanes, HCl, SO_2 [1].

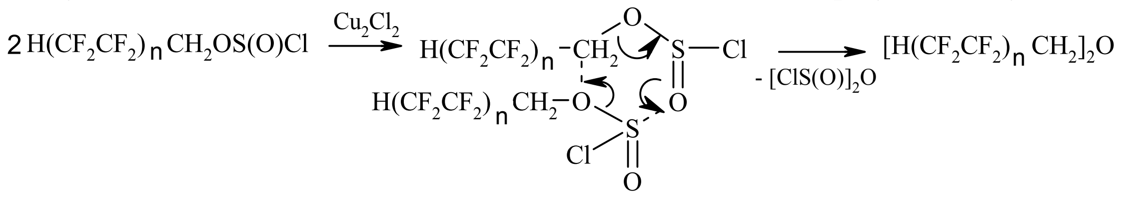
We worked out catalytic (amides, ketones) synthesis of PFAChS by reaction between polyfluoroalcohols (PFA) and $SOCl_2$. Quantum chemical calculation (method AM1) of more likely reaction steps indicate to bimolecular reaction of nucleophilic substitution of halogen going with polarization of reagents and formation next state:





Proton acceptor compounds (as acetone) catalysate this reaction. New reactions of PFAChS with HO-, HOOC-groups in PFA, aliphatic, olygomeric, polymeric alcohols, phenols, organic acids was opened. We worked out synthesis of polyfluoroalkylated esters and ethers. Reaction PFAChS with HO-groups in salicylic aldehyde lead to cyclic ester.

Catalytic (Cu_2Cl_2) reaction of destruction of PFAChS leads to di-polyfluoroalkyl ethers:



In such a manner worked out method polyfluoroalkylated functional compounds and polymers with using PFA.

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[1] Rakhimov A.I. *et al*. Zh. Gen. Khim. 2004, **74**(5) 5, 868-869.

O-03

PERFLUORINATED α-BROMOKETONES. SYNTHESIS

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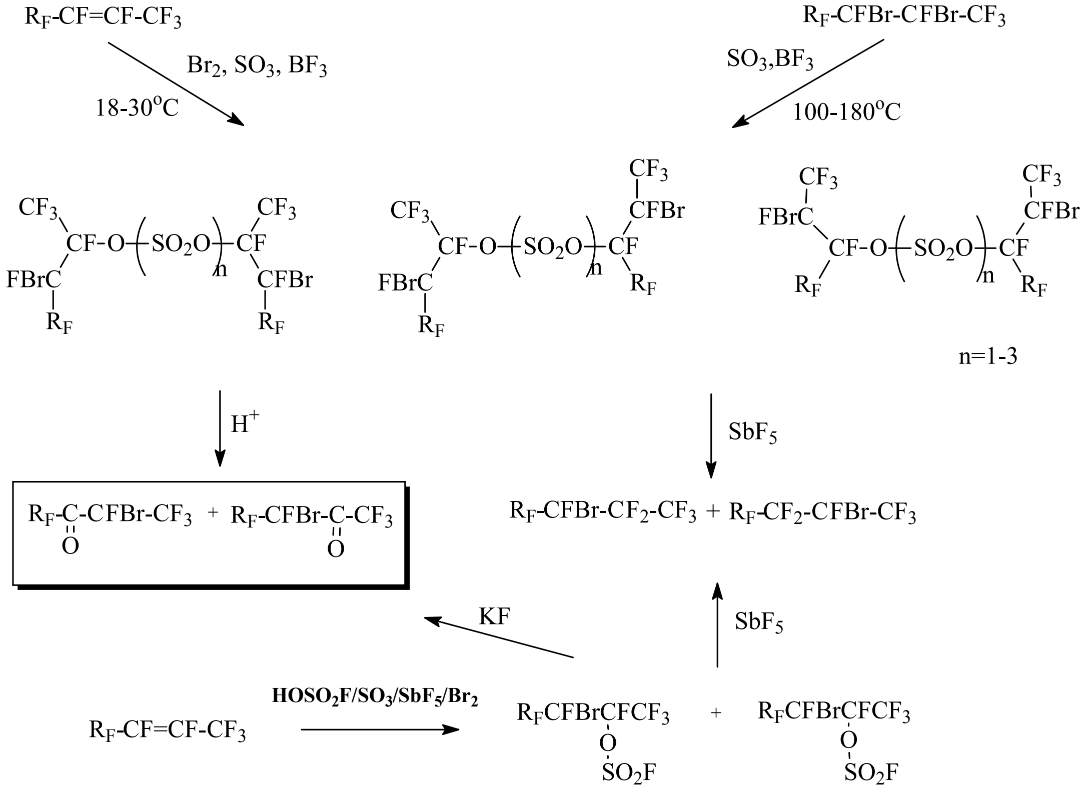
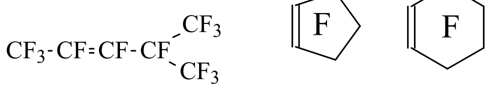
A novel method have been discovered for synthesizing perfluorinated α-sulfato bromides and α-fluorosulfato bromides by sulfatobromination of fluoroolefins of various structure and by sulfotrioxidation of vicinal dibromoperfluoroalkanes in the presence of electrophilic catalysts.



$CF_3\text{-}CF{=}CF\text{-}CF_3$ $CF_3\text{-}CF{=}CF\text{-}C_2F_5$

$CF_3\text{-}CF{=}CF\text{-}C_3F_7$


$CF_3\text{-}CF{=}CF\text{-}CF(CF_3)_2$

The reactivity of the synthesized α-sulfato bromides and ketones have been studied. Alternative synthesis methods are considered.

O-04

FLUORINATED LITHIUM 1,3-DIKETONATES – VALUABLE, CONVENIENT AND ACCESSIBLE SYNTHONS

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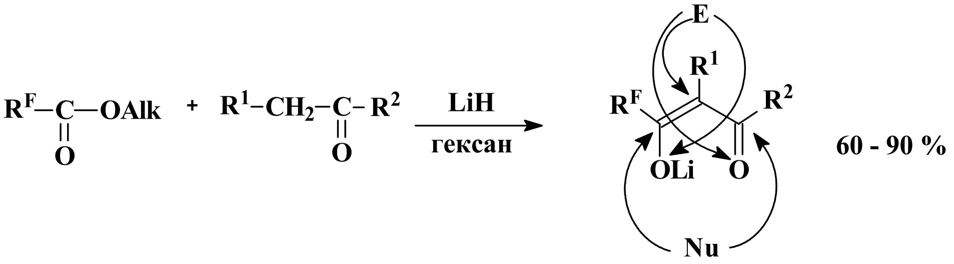
This presentation deals with the synthesis, structure and chemical properties of fluorinated litium 1,3-diketonates **1**.

Due to the presence of conjugated bonds and several electrophilic and nucleophilic centres in diketonates **1** these compounds are considered to be valuable polyfunctional synthons.



R^F=HCF_2, CF_3, $H(CF_2)_2$, $H(CF_2)_4$, C_4F_9, C_6F_{13}, C_8F_{17}
R^1 = H, R^1+R^2 = $(CH_2)_3$, R^1+R^2 = $(CH_2)_4$
R^2 = t-Bu, Me, Ph, CF_3, Bu, 4-Cl-C_6H_4, 4-CH_3-C_6H_4,

Diketonates **1** proved to be universal reagents for the synthesis of both a cyclic fluorine-containing compounds (β-diketones and their chelates β-hydroxyketones, regioisomeric enaminoketones) and a variety of fluorinated heterocycles (izoxazoles, pyrazoles, pyrimidines, 1,4-diazepines, pyrazines etc.)

X-Ray analysis of lithiums 4,4-difluoro-1-phenylbuta-1,3-dionate revealed its polymeric structure. In chains of bonds -O-Li-O- tetracoordinated lithium atoms alternates with square-bipyramidal centers which bearing four bonds Li-O and very poor interactions Li-F[1].

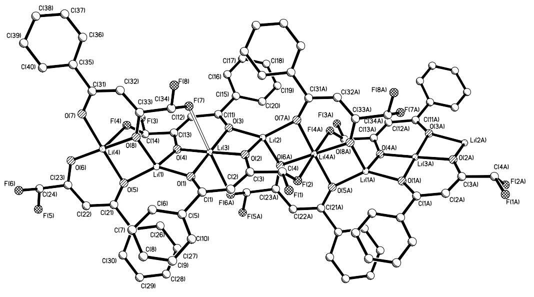


Fig.1. Coordination of Li cations in lithium 4,4-difluoro-1-phenylbuta-2,4-dionate.

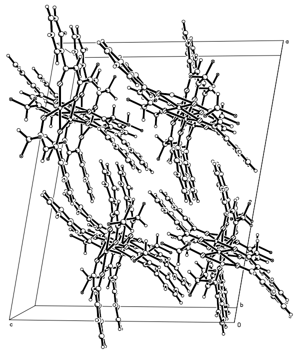


Fig.2. Packing of lithium 4,4-difluoro-1-phenylbuta-2,4-dionate in crystals.

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[1] Karpenko N.C. *et al. Zh. Struct. Khim.* 2005, **46**, 987-991.

O-05

1-HALOPERFLUOROALKYL DERIVATIVES OF AZOLES

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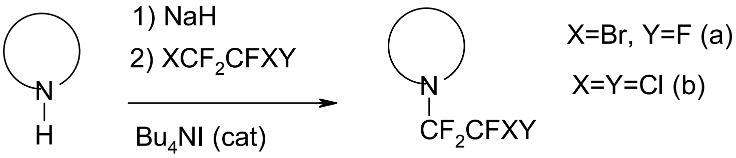
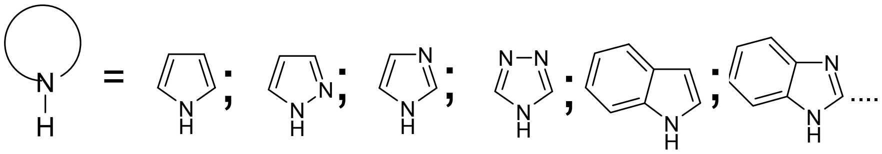
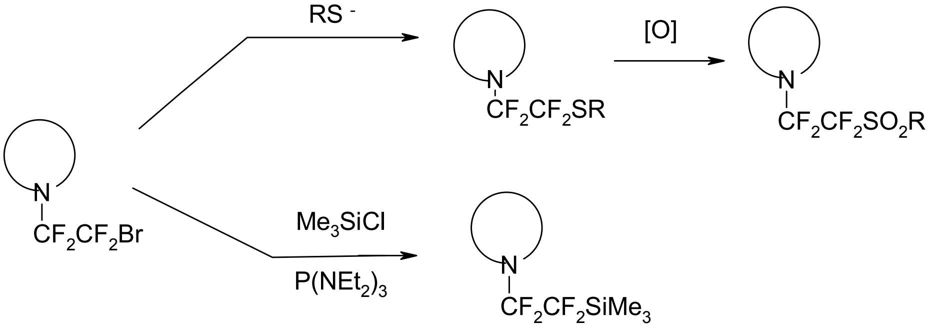
The reactions of nitrogen-containing heterocycle’s sodium derivatives with available haloperfluoroaethanes - $BrCF_2CF_2Br$ (Freon-114 B2) и $ClCF_2CFCl_2$ (Freon -113) were investigated. The correspondent heterocycles with new fluorinated substituents - 2-bromo-tetrafluoroethyl- and 2,2-dichlorotrifluoroethyl groups near the nitrogen atom (**1 a,b**) were obtained..



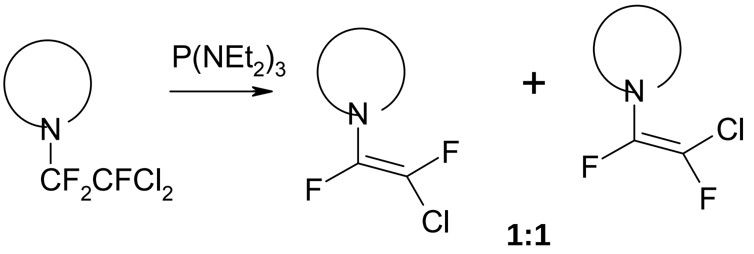
1 a,b



The reactions of the terminal bromine replacement in the compounds type **1a** were investigated. The new sulfides, sulfones, sulfinic acids and trimethylsilyl derivatives were obtained.



N-(2-Chlorodifluoro)ethenyl derivatives of azoles were obtained by interaction of the compounds type **1b** with tris(diethylamino)phosphine.



O-06

NOVEL THREE-COMPONENT REACTION AS A ROUTE TO THE SYNTHESIS OF 4-TRIFLUOROMETHYLPYRIDAZIN-3-ONES

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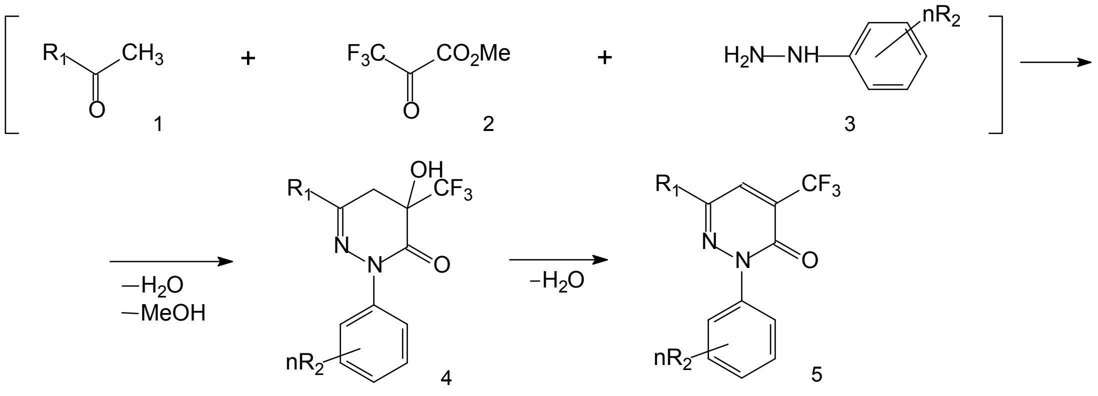
There are few multicomponent reactions that lead to heterocyclic compounds in organic chemistry. The most common of them are the Biginelly reaction, various Hantzch syntheses of 1,4-dihydropyrimidines, pyridines, and pyrroles, the Dauben reaction, the Doebner-Miller quinoline synthesis, the Ullman acridine synthesis.[1]

We have shown that interaction of equimolar amounts of ketone 1, methyltrifluoropyruvate 2 and phenylhydrazine 3 under reflux in toluene and other solvents for 6 to 8 h gives new 4-hydroxy-4-trifluoromethyl-4,5-dihydro-2H-pyridazine-3-ones 4 in 65-85% yield. When the reaction is carried out for 2 to 3 days, the end products are 4-trifluoromethyl-2H-pyridazine-3-one derivatives 5.



R_1 = Alk, Ar, Heter
R_2 = Alk, OMe, Hal, CF_3, NO_2

Dehydration of 4 can be significantly promoted using acid or basic catalysis. Further, compounds 4 can be readily transformed to 5 in quantitative yield by common dehydration agents.

Specific features and a mechanism of the reaction are considered. The three-component reaction we discovered is compared with the described syntheses of pyridazines. The scope of applicability of the novel strategy to the synthesis of this class of compounds is analyzed. Biological activities of derivatives **4** and **5** are compared with those for the other trifluoromethyl-containing pyridazinones.[1,2]

The structures of the compounds synthesized are confirmed by ^1H and ^{19}F NMR, GC-MS, and element analysis data.

This work was financially supported by E.I. Du Pont de Nemours Co. within the framework of the Agreement with the International Science and Technology Center (Project ISTC-1016).

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[1] K.V. Vatsuro, G.L. Mishchenko. Name Reactions in Organic Chemistry, Moscow, Khimiya, 1976.

[2] US Patent No. 6,333,413 B1, 2001.

[3] US Patent No. 6,482,773 B1, 2002.

O-07

SYNTHESIS OF 3,3,3-TRIFLUOROMETHYLARYLPROPYLAMINES AND FUSED 3-TRIFLUOROMETHYLPYRIDINES

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The trifluoromethyl group at β-position towards to the heterocyclic nitrogen atom in azines can be involved in irreversible enzyme inhibition[1], this makes it reasonable a search for cytotoxic antitumor agents among 3- trifluoromethylsubstituted pyridines.

Until now the synthesis of fused 3-CF_3-substituted pyridines has been reported only in one publication[2] where 3-CF_3-substituted pyridines were obtained from 3,3,3-trifluoro-2-methoxy-2-arylpropyonitrile.

We have shown that thiophene and indole derivatives cannot be obtained using the known scheme. To prepare the compounds containing the above aromatic moieties we have developed the synthesis schemes (Fig. 1) where 1-aryl-4-(trifluoromethyl)thieno[3,2-c]pyridines are obtained using trifluoroacetylthiophen and 3,3,3-trifluoro-1-nitropropene[3] is a key reagent for the synthesis of 1-aryl-4-trifluoromethyl-β-carbolines.

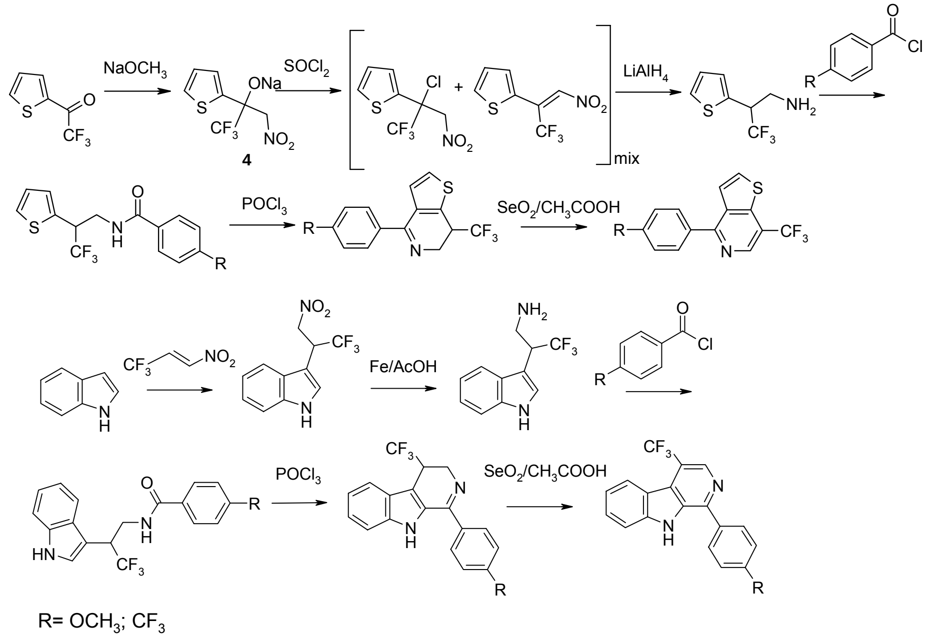

Fig. 1. Synthesis of 1-aryl-4-(trifluoromethyl)thieno[3,2-c]pyridines and 1-aryl-4-trifluoromethyl-β-carbolines

The possibility of synthesizing other 3-trifluoromethylpyridines from 3,3,3-trifluoro-1-nitropropene is considered.

This work was financially supported by E. I. DuPont de Nemours and Co., Inc. within the framework of the Agreement with International Agreement with the International Science and Technology Center(ISTC) (Project ISTC-1016) and Presidium of RAS, grant of CMSD RAS (Chemistry and Material Science Division) OX-10, CMSD Program “Biomolecular and Medical Chemistry “.

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[1] Sakai T.T. *et al. J. Med. Chem.* 1973, **16**, 1079.

[2] Poszavacz L. *et al. Tetrahedron* 2001, **57**, 8573-8580.

[3] Satoru I. *et al. Bull. Chem. Soc. Jpn.* 1993, **66**, 2432.

O-08

SYNTHESIS OF LOW PERFLUOROALKANES AT HIGH-TEMPERATURE INTERACTION BETWEEN GRAPHITE AND FLUORINE

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A number of lower perfluoroalkanes, such as tetrafluoromethane, hexafluoroethane, octafluoropropane and decafluorobutane, are inert gaseous fluorine-carriers used for silicon etching in semiconductor full-scale manufacture. Traditional industrial processes for hexafluoroethane and octafluoropropane synthesis make use of ozone-depleting chlorinated raw materials that have to be phased out. Therefore the development of the novel methods for those substances production is an urgent issue.

Currently tetrafluoromethane CF_4[1] and carbon polyfluoride $(CF_x)_n$[2] are produced in full-scale using carbon and fluoride for raw materials. Usually they apply fixed carbon powder layer, tetrafluoromethane is synthesized in burn regime at about 1500°C, while the regime of carbon polyfluoride production is nearly isothermal, and the temperature is about 450-500°C.

Our experimental studies have shown that not only CF_4 and $(CF_x)_n$, but also hexafluoroethane, octafluoropropane and decafluorobutane mixed with tetrafluoromethane are obtainable through the interaction between fluorine and graphite:

$$C_{\text{solid}} + F_{2\,\text{gas}} \longrightarrow CF_{4\,\text{gas}} + C_2F_{6\,\text{gas}} + C_3F_{8\,\text{gas}} + C_4F_{10\,\text{gas}}\,.$$

It was established that the nearly isothermal synthesis regime at 550-600°C results in a blend of perfluoroalkanes with the composition as follows: CF_4 about 40 by mass.%, C_2F_6 about 25 by mass%, C_3F_8 about 20 by mass.%, C_4F_{10} about 10 by mass.%. Fluoroolefines (tetrafluoroethylene and hexafluoropropylene) were also found among the reaction products, their total amount being 1-2%.

To provide thermostabilization of the reaction zone at laboratory conditions we applied dynamic graphite powder layers: circulating boiling bed, ascending gas-dust current or free-descending layer.

Reasoning from the experimental results we developed the basic technological flow diagram for the manufacture of CF_4, C_2F_6, C_3F_8, C_4F_{10} with the main substance content at least 99.9% starting with graphite and fluorine. For industrial applications we recommend the reactor with free-descending graphite powder layer.

A rectification unit is developed for splitting of the synthesized perfluoroalkanes.

Therefore, the research provides the scientific basis for the synthesis of tetrafluoromethane, hexafluoroethane, octafluoropropane and decafluorobutane from carbon and fluorine.

The research is financially supported by ISTC (project № 2198).

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[1] D.S.Pashkevich *et al.* Patent RF №2117652.

[2] Yu.B.Kutzenok *et al.* USSR Invention Certificate №577175.

O-09

STRUCTURE AND PROPERTIES OF SUPERFACIALLY FLUORINATED POLYMERS*

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Представлен систематический анализ и экспериментальные результаты по формированию поверхностно фторированных и сульфированных полимеров с максимальными гидрофобностью (близкой к фторсодержащим полимерам) и гидрофильностью, превосходящей известные традиционные полимеры, для реализации высоких характеристик полимера в целом. Рассмотрены кинетические особенности протекания процессов модификации, в основном фторирования и сульфирования, поверхности различных полимеров - полиолефинов, галогенсодержащих полимеров, эластомеров различного химического строения и степени предельности и ряда других.

Исследованы структура и химический состав поверхностных слоев, получаемых в результате модификации. Использованы как расчетные, так и экспериментальные методы анализа - электронная спектроскопия для химического анализа, электронная зондовая спектроскопия, ИК-спектрометрия, элементный химический анализ, гравиметрический анализ и другие.

Показано, что наиболее эффективными характеристиками модифицированного слоя, отражающими комплекс его свойств, и модифицированного полимера в целом являются состав трансформированного в результате обработки слоя, его условная толщина, концентрационный профиль по толщине и степень модификации.

Предложена структурная послойная модель гетерофазно модифицированных полимерных материалов. Определен состав поверхностного фторированного слоя, предложены и рассчитаны поверхностные и объемные характеристики полимеров-аналогов и рассмотрена термодинамическая совместимость поверхностного, переходного слоев и объема полимера. Рассчитана толщина модифицированных слоев в зависимости от условий обработки и проведен сравнительный анализ с измеренными толщинами слоев.

Смоделированы и экспериментально воспроизведены равномерные, ступенчатые и мультиплетные (множественные) поверхностные модифицированные макро- и наноструктуры, обладающие рядом оригинальных, не присущих полимерам, получаемым традиционными способами, свойствами. Исследованы смачиваемость жидкостями, проницаемость по низкомолекулярным веществам, диэлектрические, адгезионные, трибологические свойства, биостойкость и биосовместимость, теплофизические и механические характеристики фторированных полимеров.

Предложен подход к целенаправленному выбору полимера и способа модификации его поверхности на основе традиционных физико-химических параметров с достижением высокой устойчивости модифицированного полимера к внешним воздействиям, в первую очередь, низкой проницаемости по низкомолекулярным веществам. Продемонстрированы примеры разработанных технологий фторирования поверхности различных изделий из полимеров - труб, емкостей, топливных баков и пленок, изделий из эластомеров (манжет, сальников, уплотнительных прокладок и других) с комплексом высоких эксплуатационных характеристик.

Работа выполнена при финансовой поддержке РФФИ (проект № 04-03-08035)

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[*] The authors did not submit an English version.

O-10

OLIGOMERS AND POLYMERS WITH PERFLUOROALKYLENOXIDE LINKS

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At present, merely oligomeric perfluoroalkylenoxides can be achieved by anionic polymerization of perfluoroolefin oxides and photooxidation of perfluoroolefins. High molecular linear and cross-linked polymers with perfluoroalkylenoxide links can be synthesized from these oligomers with reactive end-groups (-CN, $OCF=CF_2$, etc.) or from perfluorooligoethers with peroxide links. For instance, linear and cross-linked polyperfluorooxaalkylentriazines specific of high thermal stability and cold-resistance were prepared from dinitriles.

The cold-resistance value of linear polymers depends on the elementary unit structure. It was identified through the empiric dependence $T_g = 283{,}5 - 370\ \alpha$ (K) where T_g – glass transition temperature, α – relation of the oxygen atoms number to the fluorine atoms number in the polymer unit. The identified dependence is also applicable to polymers of other classes containing perfluoroalkylenoxide units in the main and side macromolecule chains. High cold-resistance of these polymers, as was earlier demonstrated by V.A. Ponomarenko et al., results from very high thermodynamic and kinetic flexibility of macromolecules having [CF_2O and CF_2CF_2O] links.

A dependence of glass-transition and freeze temperature of oligomeric perfluorooxaalkylentriazines from their molecular mass value was also determined.

Oligomeric perfluorooxaalkylentriazines appeared to be efficient stabilizing agents for thermal destruction of perfluoropolyethers where the latter were in contact with various metals and their oxides at higher temperatures.

Cross-linked perfluorooxaalkylentriazines and perfluoropolyethers with the glass-transition temperature down to -145^0C were synthesized.

Polyperfluorooxaalkylentriazines were characterized by high thermal stability that was reasoned by high activation energy of the C-O-C bonds thermal degradation in polyperfluoroalkylenoxides. Additionally, the triazine cycle effectively prevents the polymer chain degradation in thermal destruction.

However the triazine cycle is relatively ready-destroyable as affected by nucleophilic reagents. We managed to prepare branched and cross-linked polyperfluorooxaalkylenbenzenes by having substituted the triazine cycles for aromatic ones. Oligomeric perfluorooxaalkylenbenzenes with the molecular mass 4000 – 8000, glass-transition temperature from -400 to -960 and 10%-mass loss temperature 400 – 4250 were synthesized. Such oligomers and polymers did not degrade in the presence of concentrated acids and alkalis at elevated temperatures.

O-11

PREDICTION OF FLUOROPOLYMER GLASS TRANSITION TEMPERATURE (T_g) DETERMINATION.

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It is known that low temperature properties of fluorinated rubbers and fluorocarbon oils are improved through the incorporation of ether groups into main or side chains. As previously shown by V.A. Ponomarenko and coworkers[1] for number of fluoropolymers intrinsic ratio (h_0^2/Nl_{desigh}^2) and conformational analysis data of polyperfluoroalkylenoxide polymers are indicative of $(CF_2CF_20)_n$, $(CF_2O)_n$ chains superflexibility. Internal interactions resulting in higher equilibrium flexibility also occur in fluoropolymers having pendent oxygen atoms.

Using as an example synthesized perfluorotriazine (PFT) polymers chain structure and length relationships of T_g between triazine rings are obtained in good quality. But T_g of most synthesized PFT did not fit in with design diagram of T_g estimation suggested by L.A. Askadsky and G.L. Slonimsky.

Assuming that backbone and side chain oxygen has different effect as well as on the basis of experimental data for T_g of synthesized by us PFT we have calculated numerical new values of increments K_i*:

N	Element	Symbols	Numerical value (cm^3/mol)
1	Oxygen in perfluorooxamethylene side chain	K_0* side	-3.760
2	Oxygen in backbone perfluoropropylenoxide units	K_{01}* main	+1.324
3	Oxygen in backbone perfluoroethylenoxide units	K_{02}* main	-1.220
4	Triazine ring	K_0* tr.	+32.077

Using these found numerical values of increments K_i* we have calculated T_g for a great many of PFT as well as for other categories of synthesized by us fluoropolymers (carbon-chain, fluoroalkoxyphosphazene, fluorosiloxane, fluoroacrylate etc.). for most fluoropolymers the deviation of experimental evidence T_g from desing data was within 0-5 K. it is shown that T_g drop effect of the fluoropolymers with perfluorooxamethylene side chains is distinct for polymers with more rigid main chain (carbon-chain).

Special attention must be given to the fact that for polymers with long perfluorooxamethylene side groups T_g tends to 102,5 K (-170,5°C). This is the lowest T_g among all the naturally known polymers.

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[1] Ponomarenko V.A. et al. *Vysokomol.* 1981(6), 403.

O-12

ENHANCEMENT OF COMMERCIAL PROPERTIES OF POLYMERIC ARTICLES BY DIRECT FLUORINATION

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Results of more than 20-years research of both fundamental features of the direct fluorination of polymers (i.e. treatment of polymer surfaces by gaseous fluorine and its blends) and physical-chemical properties of the surface modified layer and study of the possibilities to enhance gas separation properties of polymeric membranes and modules and barrier properties of polymeric articles are reviewed. More than 20 various polymers (including polyolefines, polycarbonates, polyimides, polysulfones, simple and complex polyethers, phenyl-containing polymers, silicon-containing polymers, polyacrylates, co-polymers, etc.) where studied. The following methods where used: FTIR spectroscopy, spectroscopy in the visible and near UV region of spectra, refractometry, electron microscopy, gas-chromatographic and volumetric measurement of transport properties of polymeric membranes, measurement of the surface energy, measurement of the permeability of liquids through polymer films, “*in situ*” interference method of investigation of the kinetics of formation of fluorinated layer, method of measurement of the density of fluorinated polymer layers (over 0.5-10 micrometer range). The process of the formation of fluorinated layer for all the studied polymers was diffusion controlled. Dependences of the thickness of fluorinated layer formed on the polymer surface on composition and pressure of the fluorinating mixture, fluorination duration and temperature were measured. The influence of treatment conditions on the polymer chemical composition, density, refraction index and surface energy were investigated. Kinetics of formation and termination of radicals, formed inside the fluorinated layer, was studied. A theoretical model, describing the kinetics and mechanism of the direct fluorination of polymers, has been developed on the basis of obtained data. A method to enhance the barrier properties of high density polyethylene with respect to petrol-methanol and petrol-ethanol mixtures has been developed. Direct fluorination can be successfully applied to enhance separation properties of polymer flat membranes and hollow fiber membrane modules. Fluorine treated membranes have enhanced gas separation selectivity accompanied with practically unchanged permeability of the main component of gaseous mixture. Fluorinated membranes can be used to purify hydrogen, separate helium, purify methane and so on.

The research was supported financially by ISF (grant No. NJG000), INTAS (grant No. 1277-96), NWO (grant No. 047.007.006) and 4 contract with the company “Air Products PLC” (UK).

O-13

STUDIES OF RADIATION DESTRUCTION OF POLYTETRAFLUOROETHYLENE.

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The discrepancy between the high chemical and thermal stability of polytetrafluoroethylene (PTFE) and its very low radiation stability remains a subject of discussion.

PTFE was labeled "very radiation-unstable synthetic polymer material". In contrast, the linear perfluoroalkanes, which are the low-molecular analogues of PTFE, have greater radiation stability (G = (1-5) molecules destruction per 100 eV adsorbed radiation energy) than their hydrocarbon analogues (G = (6-10)). In PTFE the radiation-chemical yield of PCs is very low (G=0.25). This yield is more than one order lower than for polyethylene (G=5.8).

Recently, the molecular mass of PTFE was deduced before and after irradiation in all its topographical structures by the TMS method. Before irradiation the variation of a thermomechanical curve of PTFE testifies to its amorphous-crystal structure. In a crystal phase, gamma-irradiation reduces the molecular mass of the crystalline chains of the low-melting modifications and also results in the disappearance of intermediate- and high-temperature melting crystal phases as a result of their transformation into the amorphous state.The radiation-chemical yield for PTFE destruction, averaged over the topographical blocks, was calculated from the molecular-mass dependence with irradiation dose. It does not exceed G=0.2 (in air) and G=0.1(in vacuum) of chain cleavage for 100 eV of absorbed energy. The value of the radiation-chemical yield for the PTFE destruction calculated from literature data indicates < 0.1 chain cleavage for 100 eV of absorbed energy. On the basis of such yields for chain destruction, this polymer is considered to be a radiation-chemically stable polymer. The radiation-chemical stability of PTFE is one order greater than that of polyethylene and two orders greater than those for cellulose and polysulfones. Thus, together with excellent thermal and chemical stability PTFE also has radiation-chemical stability.

Cleavage of C-F bonds is the basic radical process of the radiolysis of PTFE. The changes occurring in PTFE macromolecules as a result of $\sim CF_2C^{\bullet}FCF_2\sim$ radical formation were simulated by QCC using the geometry of n-$C_{20}F_{42}$ and the radical $CF_3(CF_2)_8C^{\bullet}F(CF_2)_9CF_3$. The results show the transformation of $C_{20}F_{42}$ into the radical $C_{20}F_{41}^{\bullet}$ is accompanied by reorganization of the molecular structure. In the solid state such reorganization should be accompanied by strong changes in the crystal structure. We suggested that the $\sim CF_2C^{\bullet}FCF_2\sim$ radicals formed during radiolysis of PTFE may be one of the main (or primary) sources of destruction of the crystal structure of the polymer.

The research was supported financially by the Cooperative Grants Program of the U.S. Civilian Research and Development Foundation (Project No. 15199).

O-14

RADIATION-CHEMICAL MODIFICATION OF POLYTETRAFLUOROETHYLENE IN MELT

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The paper gives a review of the current status of research on radiation-chemical processes in polytetrafluoroethylene (PTFE) and discusses the prospects of the practical application of PTFE radiation modification. There is a particular focus on the data obtained during the last decade.

Polytetrafluoroethylene (PTFE) is known to be one of the polymers possessing extremely low radiation resistance. Its exposure to ionizing radiations results in the rapid fall of the molecular weight and in the virtually total degradation of the mechanical properties. In this connection, the possibility of using radiation-chemical methods for improving the properties of PTFE has not, until recently, been seriously considered. The situation has changed drastically in the last decade, with the discovery of a phenomenon consisting in the change of the direction of radiation-chemical processes in the polymer. It turned out that, in a narrow temperature region, near the melting temperature of crystallites (327°C), irradiating PTFE results not in the destruction, but in the cross-linking of polymer chains, in the formation of short-chain branches, in the decrease of the degree of crystallinity and in the formation of a fluctuation network of cohesion sites. A peculiar feature of PTFE, distinguishing it from other polymers, is both the very existence of such a temperature region and the fact that radiation processes in this region are accompanied by anomalously great changes in the polymer’s macroscopic properties.

In the recent years, the field of radiation modification of PTFE has developed, both from the point of view of its scientific understanding and in terms of applied technology. In particular, this concerns the development of new-generation materials for tribotechnical and structural-material applications, including composite materials (with powder or fiber filling). This direction of activities is being actively pursued by scientific teams not only in Russia, but also in Japan and Germany.

The paper analyzes study results on the structure and properties of PTFE irradiated in melt, those on the mechanism of the radiation-chemical processes causing the observed effects, as well as applied problems related to the use of the new materials.

Presented in the paper are study results obtained at the Karpov Institute of Physical Chemistry on the durability, friction coefficient, creep, thermomechanical and strength properties of radiation-modified PTFE. A possible scenario of the radiation-chemical processes is discussed, allowing to account for the totality of the experimental results, including data obtained by infrared spectroscopy, nuclear magnetic resonance of ^{13}C, ^{19}F, electron spin resonance, differential scanning calorimetry, X-ray structural analysis, thermogravimetry, etc.

O-15

OBTAINING AND PROPERTIES OF FLUOROCONTAINING POLYCAPROAMIDE SYSTEMS

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Inclusion of polyfluorinated compounds (about 0.05-1% mass.) into polycaproamide (PCA) compositions improves their tribological properties.

We studied catalytic influence of 1,1,5-trihydroperfluoropentanol (TPFP) on destruction of ε-lactam cycle and participation of TPFP on step chain growth of hydrolytic polymerization of ε-caprolactam, that leads to obtaining polymer with higher molecular mass and higher thermostability. Inclusion of TPFP in PCA granules improves their hydrolytic and thermal stability. Obtained PCA fibres has more stability to oxidation "dark" and UV-destruction [1,2].

Formation of non-oriented PCA films obtained macromolecules by inclusion of TPFP. Macromolecules of PCA form hydrogen bonds between amide groups of neighboring layers and lead to increasing α-crystalline structures.

Polyfluoroalkylation of H_2N-, HOOC- end groups in olygo- and poly- ε-caproamides by TPFP or polyfluoroalkylchlorosulfites leads to materials (addition of T-2, MIK-T-2) with high flame resistance [3].

Fluoridation PCA fibres was recommended for obtaining surgical material rapid healing.

We worked out new cotton fabric with enclosure of PCA fibres. New material has high durability, better resistance to abrasion, resistance to cycle working load, good hydroscopic properties [4].

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[4] Novakov I.A., Storozhakova N.A. *at. el.* // Compozit-2004. Saratov. 2004. P. 316.

O-16

JOINT STOCK COMPANY "ASTOR" - MANUFACTURER OF HIGH PURITY FLUORINATED GASES

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Joint-Stock Company "ASTOR" was established in 1995г. Founders and shareholders of the company are leading specialists in the field of fluorine and the fluorinated compounds. They are former employees of Russian Scientific Center «Applied chemistry» - a head scientific-research institute of Russia in the field of fluorine and fluoro- compound chemistry.

JSC "ASTOR" main activity is manufacture of high purity fluorinated gases for microelectronics.

Now JSC "ASTOR" is scientific and production company. Following its establishment of "ASTOR" R&D laboratory has been directed for development and implementation in production the owned original technologies of high purity special fluorinated gases.

For time of the work of laboratory a number of unique technologies are created and more then twenty patents are obtained. Production complex of "ASTOR" and R&D laboratory are located in a settlement Kuzmolovsky near St.-Petersburg on "ASTOR"’s own facility. They are equipped with the modern process and analytical equipment.

Since 1996 "ASTOR" actively cooperates with the leading manufacturer of elementary fluorine in Russia – company Angarsk Electrolysis & Chemical Complex (AECC). Due to partnership relations the manufacture of tetrafluoromethane (CF_4) 6.0 with 500t/year capacity has been created. The new joint project is manufacture of nitrogen trifluoride (NF_3) 3.0. Process technologies of CF_4 6.0 and NF_3 3.0 are developed in "ASTOR" and transferred to AECC under the license agreements.

From the very beginning of business activity the effort of the company are directed on expand constantly a range of high purity fluorinated gases offered to our clients. In the company installations on pumping and filling of CF_4 6.0 with 300t/year capacity, on purification of octafluoropropane (C_3F_8) 5.0 and octafluorocyclobutane (c-C_4F_8) 5.0 – each per 100t/year capacity and on synthesis and purification of silicon tetrafluoride (SiF_4) 4.0 with 30t/year capacity are created.

Now process technologies of perspective gases for microelectronics 1,3-hexafluorobutadiene (C_4F_6) 4.0 and octafluorocyclopentene (c-C_5F_8) 4.0 are developed.

The company makes the big efforts for maintenance of stability of manufacture and quality of production. In 2005г the company is certificated under international standard ISO 9001:2000.

Cooperating with JSC "ASTOR" you will find not only highly qualitative production, but also operative technical support. We are ready to execute any customer order from manufacture of the product having not the standard specification to development of technology and creation of manufacture of product you are interested in.

O-17

A NEW COMPOSITE MATERIAL SUPERFLUVIS BASED ON FLUOROPLAST 4 AND CARBON FIBERS

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The market of composite materials based on fluoroplast-4 is believed to grow faster in contrast to that of pure PTFE. Novel types of machinery require the materials with high-tech characteristics to be competitive in quality and cost not to cede the rivals.

For a sufficiently long period Flubon and Fluvis have been considered as most promising among mass-produced in CIS antifrictional composites, and surpass much F4K20 one manufactured since 1960s. They present fluoroplast-4 filled with ground carbon fibers (CF) being more expensive than coke but ensuring high wear resistance, better heat conductivity and absence of any wear on the metal counterbody. This cuts cost on repair and justifies high price of the composite.

Based on the analysis of Fluvis material batch-produced since late 1990s, the authors have come to a conclusion that its characteristics can be improved considerably via raising process compatibility of its components. To that end, the character of wetting of the carbon fibers by the fluoroplastic was changed using an original method of modifying CF by the plasma-chemical formation of a fluoropolymer on their surface. The layer thickness makes up tens of nanometers.

Already the first samples have shown striking results. The composite density raised as much as 5-8%. This means that 5-8% of the volume of untreated fibers occupied the pores that were removed thanks to improved wettability. Breaking strength of the composite became 30-35 MPa, i.e. equal to that of the initial fluoroplast-4. Heat conductivity raised till 22-25 MPa and hardness by 20-30. Young's modulus has grown from 350-500 till 650-900 MPa. Yield strength at compression has increased from 18-21 till 35-36 MPa. Strength characteristics under elevated temperatures have improved noticeably. For comparison, yield strength of the analogues is rather low at compression, whereas that of the composite with modified CF is 6.5-7 MPa. Raised hardness and heat conductivity has lead to increased 1.5-3 times wear resistance.

Pilot production of the composite under a trademark Superfluvis was organized in 2005. At present it is tested at dozens of enterprises in CIS. The results obtained are a proof to high service characteristics of the material. Agitated interest at enterprises was met by the growth of output, amendment of the marketing strategy, being today the priority of our work.

O-18

THIN POLYMERIC FLUOROCONTAINING FILMS DEPOSITED FROM SUPERCRITICAL CO_2

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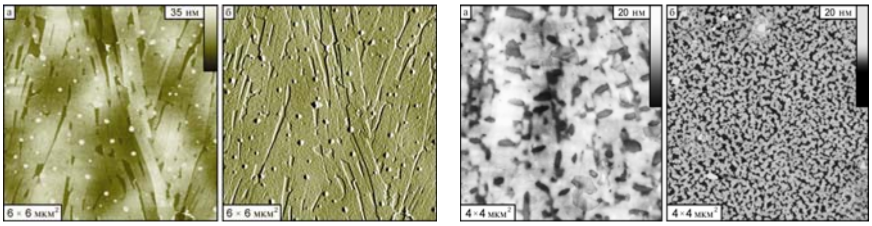
The main advantage of supercritical (sc) CO_2 (T_c=31,1°C, P_c=7,37 MPa) for preparation of thin-film coatings in comparison with liquid solvents is a dependence of dissolving power of sc CO_2 on temperature and pressure. It gives possibility to maintain optimal dynamics of polymer molecules precipitation onto different substrates. Besides the absence of liquid phase of CO_2 under atmospheric conditions excludes the re-orientation of deposited polymeric molecules on the substrate during the film drying (owing to surface tension forces) and solves the residual solvent problem. In this work we used ultrafine poly(tetrafluoroethylene) (UPTFE) for the polymer coating deposition from the supercritical CO_2 medium onto different substrates. The UPTFE is the product of thermal gas-dynamic destruction of industrial poly(tetrafluoroethylene) (Teflon) waste. We used also Teflon AF 2400 (DuPont, USA) with M_n=10^5, density 1.6 g/cm^3 and T_g=250 °C. It was experimentally established that from many fluorinated polymers these materials were soluble in sc CO_2. The mica (muscovite) and highly oriented pyrolytic graphite (pyrographite) were chosen as substrates for the polymer molecules deposition. Both materials allow one to obtain by cleaving the flat surface areas with angstrom- (mica) and nanometer- (graphite) level roughness. By the beginning of an exposure, the cleavage was performed to obtain clean substrate surface. The typical solubility area of polymers is situated in the region of T > 65 °C, P > 50 MPa. In this work we took out the polymers from solution in sc CO_2 by reduction of temperature of closed reaction chamber or by its depressurization. Fig. 1 illustrates thin films deposited on different substrates.



(a) (b) (c)

Fig. 1. Thin film of AF 2400 on pyrographite (a) and films of UPTFE on pyrographite (b) and on muscovite (c) substrates. Film thicknesses were from 4 to 8 nm.

Thin film coatings of AF 2400 and UPTFE deposited from sc CO_2 are very interesting regarding their potential application in optics, electronics and other technical areas.

This work was supported by the Russian Foundation for Basic Research (projects no. 04-03-32311, 04-03-39012, 04-03-32879, 04-03-08143, 04-03-32297 and 05-03-33046). The authors are also grateful to Russian Academy of Sciences (programs of Division of Chemistry and Material Sciences "Creation of new metallic, ceramic, glass, polymeric and composite materials" and "Creation and investigation of macromolecules and macromolecular structures of new generation") for financial support.

O-19

RADIATION-CHEMICAL METHOD OF PRODUCTION OF PROTECTING, HYDROPHOBIC AND ANTIFRICTIONAL COVERS USING TETRAFLUOROETHYLENE

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Concerning to insufficiency of polytetrafluoroethylene (PTFE) can be mentioned the insolubility in no one of known solvents that significantly limits its application and complicates of laying fluoropolymer covers. Using the radiation initiating method allows to product new materials on the base of TFE for hydrophobic and antifrictional covers. The significant preference of radiation-chemical method is independence of velocity of initiating reaction from a temperature and lack of chemical initiators, emulgators and catalizators of process that means the possibility of receiving of high pure products at ecological technology. In the report cites the data of production the soluble telomers of TFE as a result of radiation telomerizarion of monomer in the solvents. The kinetic and mechanism of reaction and properties of synthesized telomers were investigated. Received solutions can be used for creation of thin protecting covers. After treatment on the surface forms the thin film (1-5 mkm) which have properties nearby to those of PTFE. The laying of cover has no difficulties and not distinguishs from traditional way used at laying of laquer and paints (by paint-brush, plunge, pulverizer). The solutions can be storage in sealed vessel with no change of properties long time. The solution of telomere TFE can be used for impregnatiom of fabrics, wood, asbestos and other materials for attach them chemical stable, hydrophobic and antifrictional properties. The negligible thickness of cover allows to receive covers with good heatconductivity, transparency and profitable economic index. The physical-chemical properties of covers allows use the solutions for intensification of process of water condensation in heatexchanger apparatus and protecting of optic materials.

The another significant preference of radiation initiating is possibility of modification of surfaces by the method of post-irradiation graft polymerization at various temperatures. This method allows to realize grafting of TFE on various polymer materials, rubbers and its goods. The significant interest have graft polymerization onto surface of solid inorganic substances – metal oxides, natural minerals silica gels, microporous silica fibers, char coal and porous carbon sorbents. As a result had been received the products, combined the valuable properties of fluoropolymer and mineral support.

O-20

INHALATIONAL FLUOROETHER ANESTHETIC SEVOFLURANE

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Sevoflurane [fluoromethyl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl ether] was first introduced into clinical practice in 1994. The first commercial synthesis of this pharmaceutical is based on the fluoromethylation of hexafluoroisopropanol (HFIP) utilizing hydrogen fluoride, formaldehyde and sulfuric acid as a dehydrating agent:[1,2]

$$(CF_3)_2CHOH + (CH_2O)_x + HF + H_2SO_4 \rightarrow (CF_3)_2CHOCH_2F$$

We developed a three-step synthesis of sevoflurane:[3,4]

$$(CF_3)_2CHOH + (MeO)_2SO_2 \rightarrow (CF_3)_2CHOCH_3$$

$$(CF_3)_2CHOCH_3 + Cl_2 \rightarrow (CF_3)_2CHOCH_2Cl$$

$$(CF_3)_2CHOCH_2Cl + (i\text{-}Pr)_2(Et)N{\bullet}HF \rightarrow (CF_3)_2CHOCH_2F$$

Acid hydrolysis of sevoflurane precursors and by-products lead to the regeneration of HFIP, which substantially increases the overall yield of sevoflurane.[5]

Besides being an extremely valuable pharmaceutical product, sevoflurane possesses a number of very interesting chemical properties. For example, it can be used as a fluoride source in halogen-exchange reactions: [6]

$$CF_3CHClOCCl_3 + (CF_3)_2CHOCH_2F + SbCl_5 \rightarrow CF_3CHClOCCl_2F$$

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[2] Coon C.L. *et al.* US Patent 4,469,898, **1984** *(Baxter Travenol Laboratories).*
[3] Kudzma L.V. *et al.* US Patent 5,886,239, **1999** *(Baxter International Inc.).*
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O-21

SYNTHESIS AND TRANSFORMATION OF ALKOXYCARBONYL-5,6,7,8-TETRAFLUOROCHROMONES

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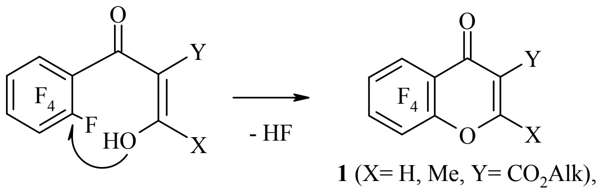
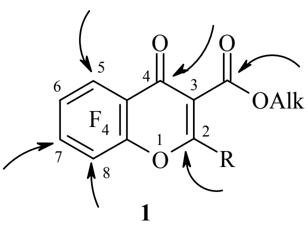
Chromone fragment is a significant structure component of biological active compounds both synthetic and natural origin, many of which are employed in medicine. Chromone derivatives are useful versatile molecules to preparation of the different compounds of various classes. We have developed convenient methods for synthesis of 2(3)-alkoxycarbonyl-5,6,7,8-tetrafluorochromones **1, 2** and studied paths of their transformations. Intramolecular cyclizations of compounds having vinyl fragment with vicinal pentafluorobenzoyl and hydroxyl groups were used for chromones **1, 2** synthesis. Chromones **1, 2** are polyfunctional compounds which can be transformed in the reactions with nucleophilic reagents. Nucleophilic attack depending on the reaction conditions and nucleophile type can be proceed: - at carbon atom C(2), at that nucleophile addition to C(2)=C(3) bond may be accompanied by pyrone cycle conservation or heterocycle opening to form 2-amino-4-(2-hydroxy-3,4,5,6-tetrafluorophenyl)-4-oxo-2-butenoic acid derivatives; - at carbonyl carbon atom C(4); at activated centers C(7) and C(5) of aromatic ring; - at alkoxycarbonyl group (centre C(9)).



1 (X= H, Me, Y= CO_2Alk),
2 (X= CO_2Alk, Y= H)



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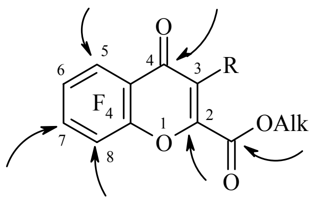

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This work was supported by the State Programme for Supporting Leading Scientific Schools (grant № SS-9178.2006.3) and Russian Science Support Foundation.

O-22

THE SYNTHESIS AND PROPERTIES OF FLUORINE-CONTAINING QUINOLONES, QUINAZOLINONES AND BENZOTHIAZINONES

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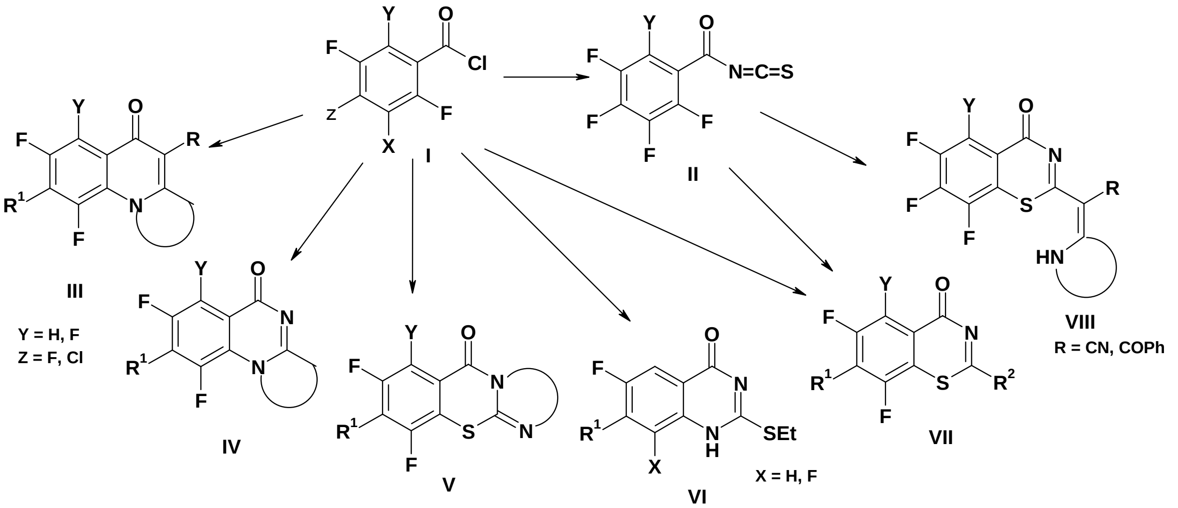
Condensed derivatives of azaheterocycles have been the subject of increasing interest since many compounds of this series proved to be biologically active.

We have developed new methods for the synthesis of pyrido- and benzimidazo[a]-annelated quinolones (III), azolo- and azino[a]-annelated quinazolinones (IV), imidazo[2,1-b]benzothiazine-4-ones (V), 1H-quinazoline-4-ones (VI) and 2-aryl(heteryl)[1,3]-benzothiazinones (VII) based on interaction of fluorinated benzoyl chlorides with nucleophiles.

We have used new fluorine-containing synton – polyfluorobenzoyl isothiocyanate – for construction of fluorinated heterocycles. Interaction of cycloalkylimines, aminoazines, aminoazoles and CH-active benzoimidazoles and pyridines with polyfluorobenzoyl isothiocyanates (II) results in formation of [1,3]benzathiazonone derivatives (VII, VIII). Amino-defluorination reactions of compounds obtained as well as substitution of moiety in position 2 of heterocycles (VI-VIII) by action of nucleophiles have been investigated.

(Polyfluorobenzoyl)thioureas obtained by addition of aryl(heteryl)amines, hydrazines, hydrazides, thiosemicarbazides and other N-nucleophiles to N=C bond of isothiocyanates (II) undergo cyclization with participation of not only fluorine atom in ortho-position of benzoyl isothiocyanates but also C=O and C=S bonds to give fluorine-containing [1,2,4]triazolo[4,3-a]pyrimidines, benzo[4,5]azolo[2,3-c][1,2,4]triazoles, 1,5-dihydro[1,2,4]triazole-5-thiones, thiazolidines and 1H-[1,2,4]triazoles.



Financial support of this research was provided by Russian Fund of fundamental investigations (projects № 06-03-32747, № 04-03-96107-Ural and № 04-03-96011-Ural), grants of Ministry of education and CRDF, Annex BF4M05, EK-005-X2[REC-005], “BRHE 2004 post-doctoral fellowship award” Y2-C-05-01 as well as the grant of president of Russian Federation MK-1492.2005.03 and HS-9178.2006.3.

O-23

PUSH-PULL ENAMINES IN THE SYNTHESIS OF TRIFLUOROMETHYL CONTAINING ALIPHATIC, CARBO- AND HETEROCYCLIC COMPOUNDS

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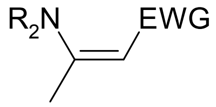
Fluoroorganic compounds exhibit unique properties and their potential is increasingly being exploited in various areas of life, particularly in pharmaceutical and agricultural industries. Introduction of fluorine atoms into aliphatic, carbo- and heterocyclic compounds allows substantially change their physico-chemical properties such as acidity and basicity, lipophilicity and hydrogen bonding ability. For successful search of drugs it is necessary to synthesize large number of compounds with different physico-chemical parameters. Nevertheless, direct introduction of trifluoromethyl group into already prepared substrate is often quite a difficult task.

We have developed the method for synthesis of trifluoromethyl containing aliphatic, carbo- and heterocyclic compounds using easily accessible push-pull enamines **1** and trifluoromethyl containing substrates **2-5.**[1-4]



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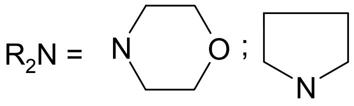
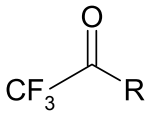
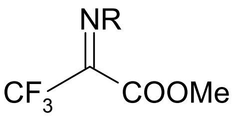


EWG = CN, COMe, COPh, COOEt



2

R = COOMe, Het, Ar



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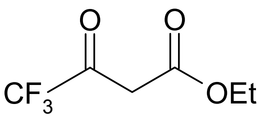

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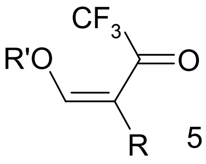
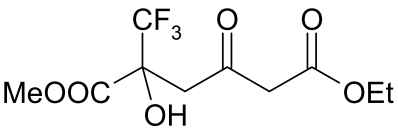


5

R = CF_3CO, COOEt, H



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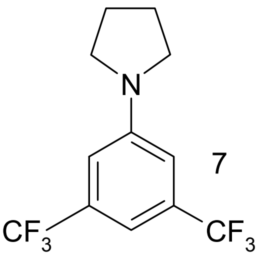

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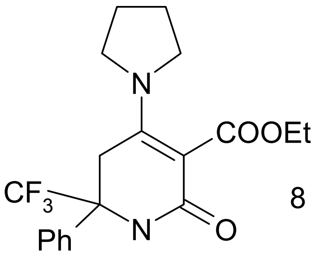

8

The method allowed us to prepare a set of new trifluoromethyl-containing derivatives, for example **6**-**8**.

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[1] Volochnyuk D. M. *et al. Tetrahedron.* 2005, **61**, 2839.
[2] Volochnyuk D.M. *et al, Tetrahedron*. 2004, **60**, 2361.
[3] Sibgatulin D. A. *et al. Synlett.* 2005, 1907-1911.
[4] Volochnyuk D.M. *et al. Synthesis*. 2004 (13), 2196

O-24

C-F…Na COORDINATION IN THE SOLUTIONS OF β-FLUOROENOLATES AND α-FLUOROVINYL(ACYL)RHENATES.

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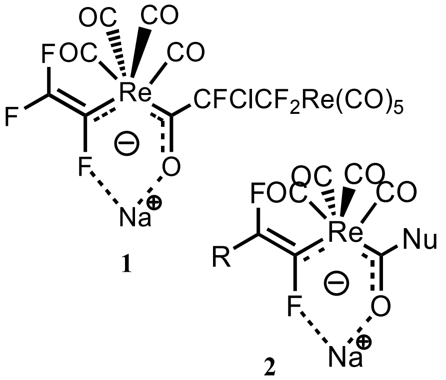
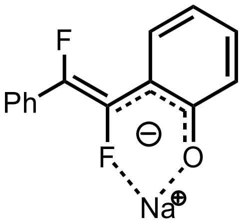
The ability of covalently bonded fluorine in organofluorine compounds to act as a hard donor atom for metal ions, obvious as it is, has not been recognized until the second half of the XX century.[3] Nowadays extensive data is available on CF…M^{n+} contacts in crystal phase, yet there are but a few cases, when such contacts persist in solution.



1

2



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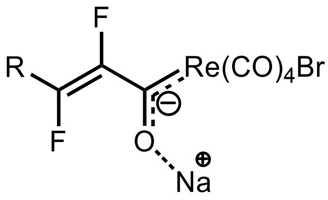
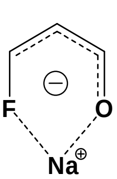


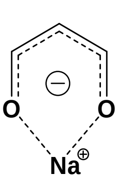
4

We observed that the resonance of α-F in NMR^{19}F spectrum of compound **1** in THF solution is broad and appears in unusually high field, but is shifted 10 ppm downfield and shrinks to ordinary linewidth on the addition of 18-crown-6 to the sample. Such behavior is characteristic of CF…Na coordination. As it turned out, the effect is common to a series of α-fluorovinyl(acyl)rhenates **2,** the downfield shift of α-F on the addition of 18-crown-6 approaching in some cases 15 ppm. The synthesis and NMR^{19}F study of a model compound **3** showed that, the presence of rhenium is not obligatory for CF…Na coordination in a β-fluoroenolate anion. However, in other β-F oxyanions which are isoelectronic to **1** – **3** such as **4** this effect is not observed in NMR^{19}F.

The anions discussed may be regarded as β-diketonate analogs where one oxygen atom is replaced with fluorine. To understand the origin of the increased coordination ability of certain C-F bonds a series of model CF…Na…OC chelates were studied quantum chemically (HF, MP2, B3LYP methods).



β–фторенолят



β–дикетонат

The research was supported financially by Russian Foundation for Basic Research (Project № 05-03-32905).

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[3] (a) Glusker J. P. *at.al. J.Am. Chem. Soc.* 1983, **105**(10), 3206; (b) Plenio H., *Chem. Rev.* 1997, **97** (8), 3363.

O-25

SYNTHESIS OF HETEROCYCLIC COMPOUNDS WITH PERFLUOROALKYL GPUPS ON THE BASIS OF ACTION PERFLUOROOLEFINS AND THEIR SOME DERIVATIVES WITH NUCLEOPHILIC REAGENTS

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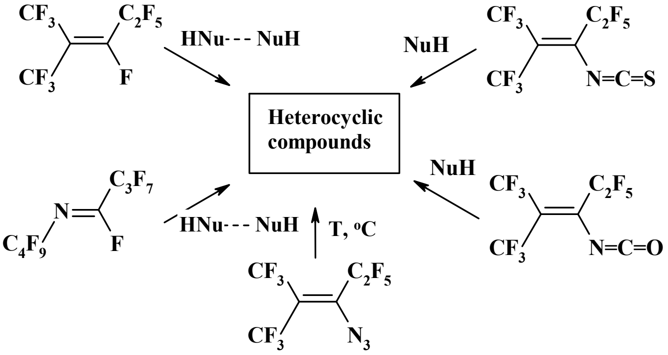
The review the prior work of the author on the systematic study of the synthesis of 3-7-membered and polycyclic fluorinated heterocycles with one or several heteroatoms. The heterocyclic compounds are prepared by reaction of bi-(1,1N, N is resulted; 1,2, N, N; N, O; 1,3 N, N; N, S; N, O; S, S; 1,4 N, N; N, O;) and mono-nucleophilic reagents with internal perfluoroolefins and perfluoroazaalkenes, them isothiocyanate and isocyanates derivatives in the presence of base.The structure compounds has been elucidated by X-ray crystallographic analysis.



Main tendencies were determinate in implementation of the approach that included generation of a new multiple bond and intermolecular nucleophilic cyclization. The following questions are investigated and discussed:

1) Influence of structural factors of a nucleophilic reagent on the direction of building a heterocyclic system was determinate.
2) An opportunity of transformation internal perfluoroolefins in terminal for the account isomerization under influence of the bases.
3) Correlation of the reactivity of perfluoroolefin and factors determinate generation of intermediate carbon ions and elimination of fluoride ion was observated.
4) Features of action binucleophilic reagents of system **a-b-c** on the nonsaturated compounds containing atoms of fluorine and what from atoms and or with participates in primary attack nucleophile.
5) What reasons of formation 5 or 6-membered heterocycles at use binucleophilic reagents of system **a-b-c** with various heteroatoms (N, S, O).

New heterocyclic compounds may serve as intermediates for propuction of medical and agricultural related products and for new modern materials in diverse fields of application.

Furin G.G. *Advances in Heterocyclic Chemistry,* 2004. Vol. 86. P. 129-224; 2005. Vol. 88. P. 231-309.
Furin G.G. *et al. Chemistry heterocycles compounds.* 2002, 147-171.

O-26

HALOGENATION OF FLUORINATED 1,3-DICARBONYL AND 1,3,5-TRICARBONYL COMPOUNDS

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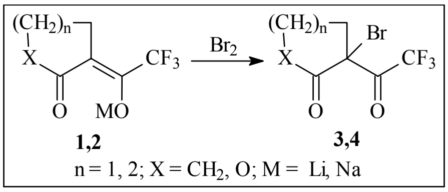
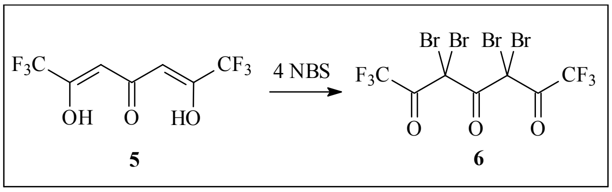
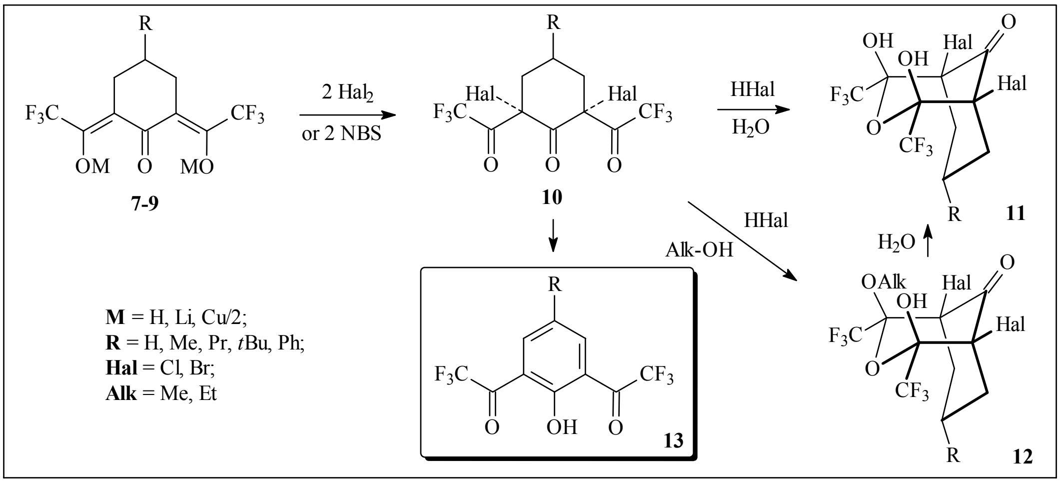
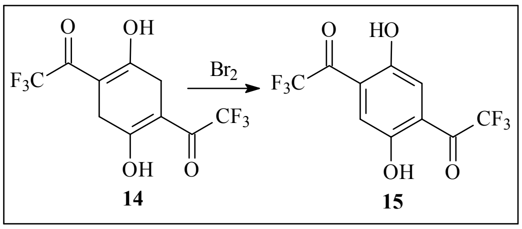
E-mail: sevenard@chemie.uni-bremen.de

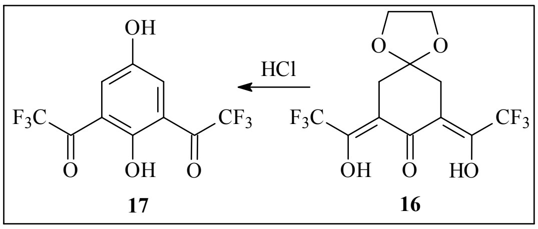
Given the synthetic importance of fluorinated 1,3-ketoesters with an additional halogen atom in 2-position[1] we examined the behaviour of diverse derivatives of cyclic 1,3-dicarbo-nyl- (**1**,**2**,**14**) and 1,3,5-tricarbonyl compounds (**5**,**7-9**) towards common halogenation reagents. A variety of mono- (**3**,**4**), di- (**10**) and tetrahalogenated (**6**) products was obtained. Transformations of **10** to bridged pyran-4-ones **11**,**12** and 2,6-bis(trifluoroacetyl)phenols **13** as well as the syntheses of isomeric hydroquinones **15** and **17** will be presented. Perspectives of further synthetic applications of **13**,**15**,**17** being only hardly obtainable otherwise will be discussed.











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[1](a) S. Archer, C. Perianayagam, *J. Med. Chem.* 1979, **22**, 306-309. (b) H.-G. Hahn et al. *J. Heterocyclic Chem.* 2000, **37**, 1003-1008.

O-27

APPLICATION OF THIOCARBONIC ACID DERIVATIVES FOR SYNTHESES OF FLUORO-SULFUR CONTAINING COMPOUNDS

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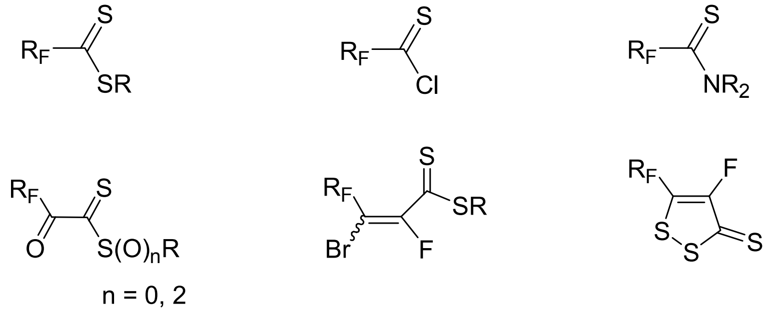
E-mail: vadim@bpci.kiev.ua
[b]*Laboratoire ‘Réactions Sélectives et Applications’, Associé au CNRS (UMR 6519), Université de Reims, Faculté des Sciences, B.P. 1039, 51687 Reims Cedex 2, France*

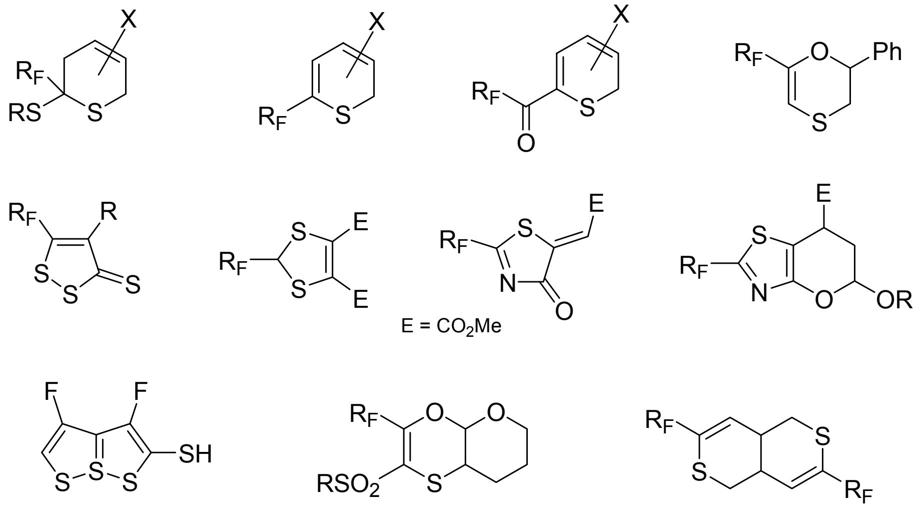
Thiocarbonyl compounds are well-known versatile tools in organic syntheses. Among fluoro-containing compounds of this class, a great attention was paid to studies of polyfluoroalkandithiocarbonic acid derivatives, the convenient preparative methods for the synthesis of which we have developed.



n = 0, 2

R_F = Alk_F, R = Alk, Ar

Due to the presence of electrono-withdrawing groups, the C=S double bond is very reactive in cycloaddition and thiophilic reactions. Applications of such building blocks to syntheses makes it possible preparation of various sulfur heterocycles with fluoroalkyl substituents such as thiins, oxathiins, dithioles, thiopyranes, trithiapentalenes, thiazolidines.



E = CO_2Me

O-28

UNUSUAL REACTION OF PHENYLTRIFLUOROSILANE WITH *β*-ALKANOLAMINES. A NEW ROUTE TO COMPOUNDS OF HYPERVALENT SILICON

M. G. Voronkov, E. A. Grebneva, O. M. Trofimova,
N. F. Chernov, A. I. Albanov, N. N. Chipanina

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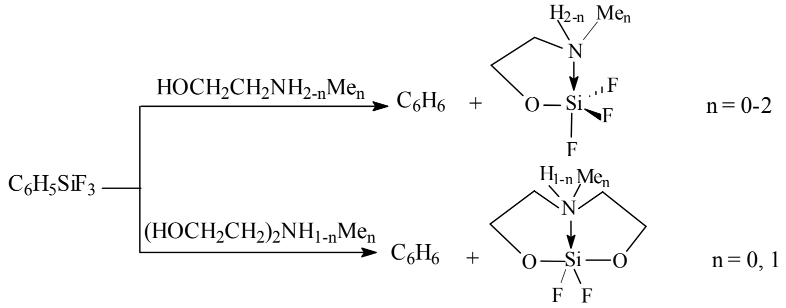
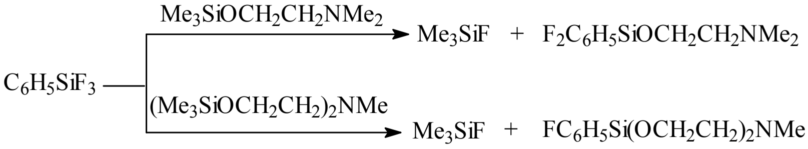
E-mail: voronkov@irioch.irk.ru

Recently it was shown that the protodesilylation reaction of phenyltrifluorosilane with 8-hydroxy- or 8-mercaptoquinoline affords the novel intramolecular heterocyclic complexes of (N→Si) 8-(trifluorosiloxy)- or (N→Si) 8-(trifluorosilylthio)quinoline containing a pentacoordinate silicon atom[4].

Now we found that treatment of phenyltrifluorosilane with 2-hydroxyethylamine, its mono- and di-*N*-methyl derivatives, or bis-(2-hydroxyethyl)amine and its *N*-methyl derivative resulted in the cleavage of the C-Si bond via elimination of benzene to give intramolecular heterocyclic complexes with the hypervalent silicon atom.



The reaction of phenyltrifluorosilane with trimethyl(2-dimethylaminoethoxy)silane or bis-[trimethyl(2-dimethylaminoethoxy)]silane occurs with retention of the Si-C bond. It is a process of trans-silylation which involves cleavage of the Si-F bond, followed by the elimination of trimethylfluorosilane and the formation of intramolecular complexes of (N→Si) phenyldifluoro(2-dimethylaminoethoxy)silane or 5-methyl-1-fluoro-1'-phenyl-2,2'-dioxa-5-aza-1-silacyclooctane, and five-membered ring closure.



$$C_6H_5SiF_3 \xrightarrow{Me_3SiOCH_2CH_2NMe_2} Me_3SiF + F_2C_6H_5SiOCH_2CH_2NMe_2$$

$$C_6H_5SiF_3 \xrightarrow{(Me_3SiOCH_2CH_2)_2NMe} Me_3SiF + FC_6H_5Si(OCH_2CH_2)_2NMe$$

The reaction of diphenyldifluorosilane with methyl-bis(2-hydroxyethyl)amine in a ratio 1:1 gave 5-methyl-1,1'-diphenyl-2,2'-dioxa-5-aza-1-silacyclooctane containing a tetracoordinate silicon atom.

$$(C_6H_5)_2SiF_2 + (HOCH_2CH_2)_2NMe \longrightarrow 2\ HF + (C_6H_5)_2Si(OCH_2CH_2)_2NMe$$

Structure of the synthesized compounds was confirmed by IR and multinuclear ^{1}H, ^{13}C, ^{19}F, ^{29}Si NMR spectroscopic methods.

We thank the Found of President of Russian Federation (Science Schools' Grant – 4575.2006.3) and the INTAS (Grant № 03-51-4164) for financial support.

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[4] Voronkov M.G., *et al. Appl. Organomet. Chem.*, 2005, **19**(4), 538-541.

O-29

NEW CYCLOADDITION REACTIONS OF 2,5-BIS(PERFLUOROALKYL)-1,3,4-OXADIAZOLES

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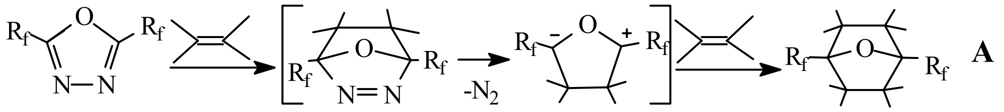
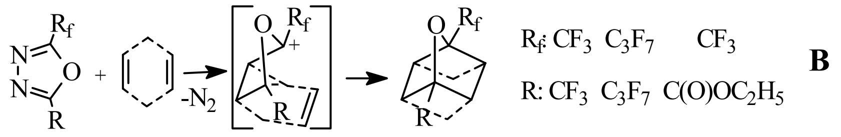
A. A. Bazhenov[a], G. V. Zatonskii[b]**

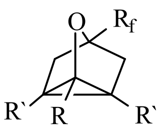
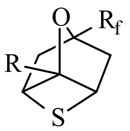
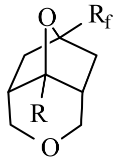
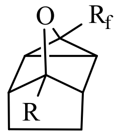
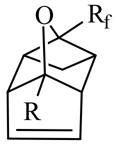
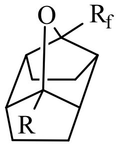
[a] *Military University of Radiation, Chemical, and Biological Protection, per. Brigadirskii 13, Moscow, 105005 Russian Federation. Phone: 2659318*
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii pr. 47, Moscow, 117913 Russian Federation. E-mail: Zatonsk@cacr.ioc.ac.ru*

It is well known that the interaction of fluorinated oxadiazoles with alkenes occurs as consecutive [2+4] cycloaddition, retro [2+3] cycloaddition with nitrogen elimination, and repeated [2+3] cycloaddition (route **A**) [1-3].



We studied the reactions of fluorinated 1,3,4-oxadiazoles with both acyclic and cyclic dienes. We found that, in a number of cases, cycloaddition occurred as an intramolecular reaction with the formation of various oxygen-containing framework structures (route **B**):



 R`: H, CH3					
1	**2**	**3**	**4**	**5**	**6**

Among acyclic dienes, butadiene, 2,3-dimethylbutadiene, divinyl sulfide, and diallyl ether enter into reactions **B**. In this case, tricyclic cage compounds **1-3** are primarily formed. Cyclic dienes (1,3-cyclohexadiene, cycloheptatriene, and 1,5-cyclooctadiene) are also prone to the predominant formation of tetracyclanes like compounds **4-6**. Note that the reactions of cyclic dienes, as well as acyclic dienes, is accompanied by the formation of an amount of bicycloheptanes in accordance with reaction **A**, whereas a number of dienes reacts only via this route (divinyl ether, diallyl phthalate, cyclopentadiene, 1,4-cyclohexadiene, and norbornadiene). Factors affecting the occurrence of intramolecular processes are discussed in this communication.

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[1] Vasil'ev N. V. *et al. Khim. Geterotsykl. Soedin.* 1987, 562.
[2] Seitz G. *et al. Chem. Zeit.*, 1988, **112**, 50.
[3] Vasiliev N. *et al. J. Fluorine Chem.,* 1993, **65**, 227.

O-30

THE ORIGIN OF NEGATIVE HYPERCONJUGATION AND OLAH SUPERACIDITY

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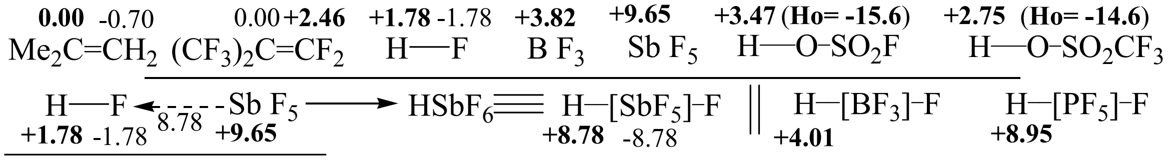
E-mail: agevork@sci.am

Recently we were able to show that L. Pauling's partial ionic character may be applied as an innate and quantitative merit for the estimation of chemical bond atom affinity in their intra- and intermolecular interactions. The problem is solved if the negative charges are ascribed to electronegative atoms of the bonds and positive charges – to less electronegative ones, both having the same (equal to bond partial ionic character) values. Then the approach was tested for the chemical reactivity solution problems, which remain inaccessible for the world-wide known concepts of organic chemistry. Therefore even the chemo-, regio- and stereoselectivity prediction of organic reactions become possible, as well as the quantification of Lewis acid reactivity forces and the hardness and softness of hard and soft acids and bases[1] etc. From this data one can conclude, that the affinity merit is revealed, which (as the carbon unit in mass characterization) helps to estimate the atoms affinities in those chemical reactions. Similarly we could clarify also the origin of negative hyperconjugation effect and G. Olah super acidity phenomenon. Thus one becomes capable to show, that the electrophylic addition direction onto perfluorinated and non-fluorinated ethylenes are controlled by the same general principle**:** always the reagent (electrophile) attack is directed namely (and only) to more electron donating atom (in the scheme they are marked by none-bolded charge figures) of the bond. Therefore the double bond regiochemistry becomes predictable without any fail and without any recourse to the conjugation (to negative hyperconjugation as well), mesomerism or any other indication of molecule. Similarly in the case of HF-SbF$_5$ as the F...Sb interaction has purely electronic nature, it leads to the "naked H-atom" formation, having electrophiliciy equal to the interacting atoms affinity difference (+9.65-1.78=+**8.78** units). It is also shown, that between these atom positive charge values and the acids Hammet Ho characteristics the expected parallelism is observed (scheme will be presented).



$$\overset{\mathbf{0.00}}{Me_2C}{=}\overset{-0.70}{CH_2}\quad (CF_3)_2\overset{0.00}{C}{=}\overset{\mathbf{+2.46}}{CF_2}\quad \overset{\mathbf{+1.78}}{H}\text{—}\overset{-1.78}{F}\quad \overset{\mathbf{+3.82}}{B}\,F_3\quad \overset{\mathbf{+9.65}}{Sb}\,F_5\quad \overset{\mathbf{+3.47}\ \mathbf{(Ho= -15.6)}}{H\text{—}O\text{–}SO_2F}\quad \overset{\mathbf{+2.75}\ \mathbf{(Ho= -14.6)}}{H\text{—}O\text{–}SO_2CF_3}$$

$$\underset{\mathbf{+1.78}}{H}\text{—}\underset{-1.78}{F}\xleftarrow[8.78]{\text{- - - -}}\underset{\mathbf{+9.65}}{Sb}\,F_5 \longrightarrow HSbF_6 \equiv \underset{\mathbf{+8.78}}{H}\text{—}\underset{-8.78}{[SbF_5]}\text{—}F\ \Big\Vert\ \underset{\mathbf{+4.01}}{H}\text{—}[BF_3]\text{—}F\quad \underset{\mathbf{+8.95}}{H}\text{—}[PF_5]\text{—}F$$

Where **0.70**= 0.35x2, 0.35=2.55-2.20. **2.46**=1.43x3; 1.43=3.98-2.55. **1.78**=3.98-2.20. **3.82**=1.94x3; 1.94= 3.98-2.04. **9.65**=1.93x5, 1.93=3.98-2.05. **8.78**=9.65-1.78. Figures 2.04, 2.05, 2.20, 2.55 and 3.98 - mean the electronegativities of **B**, **Sb**, **H**, **C** and **F**, correspondingly.

Pict. 1. The bond atoms charge estimation and charge alteration examples

Similarly were characterized the super-acidity of other magic acids and argued that in the super-acidic conditions namely (and only) the ion pairs are generated, having predictable stereochemical behavior (**frontal- and anti-frontal electrophilicity**), described by our group earlier[2]. This charge-lead approach hasn't any exception.

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[1] Gevorkyan A.A. *et al. Chem. J. of Armenia*. 2005, **58**(4), 92-107.

[2] Gevorkyan A. A. *et al.* J. Gen.Chem. 2001, **71**(5), 729-735.