ABSTRACTS

The abstracts are printed in the authors' edition

L-01

SELECTIVE FLUORINATION. KEY FOR SYNTHESIS AND APPLICATION OF ANALOGS OF BIOLOGICALLY RELEVANT COMPOUNDS

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For the community of chemists it is quite obvious that the introduction of fluorine or fluorinated substituents into organic molecules results in a variety of modifications both of physico-chemical properties and biochemical behavior. However, the results cannot always be planned and frequently surprises must be expected.

The talk will illuminate the consequences of selective, partial fluorination on the properties of two groups of compounds:

(i) Tranylcypromine (*trans*-2-phenylcyclopropylamine) is a brain active drug applied for treatment of depression. Unfortunately, this compound is an unselective inhibitor of human monoamine oxidases (MAO) A and B. A series of monofluorinated phenylcyclopropylamines has been synthesized and the influence of regio- and stereoselective fluorine substitution on physico-chemical properties such as pK_a and log D values and consequences on the affinity and selectivity as MAO inhibitors *in vitro* will be detailed.

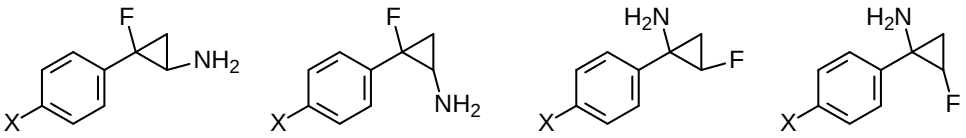

Figure 1. Fluorinated tranylcypromine analogs as potent MAO inhibitors.

(ii) Caspases (**c**ysteine **a**spartyl **s**pecific **p**rote**ases**) have been strongly implicated to play an essential role in apoptosis, the regulated destruction of cells. Inhibition of the so called effector caspases-3 and -7 slows down and even stops apoptosis *in vivo*.[1]

Ten years ago (*S*)-5-[1-(2-methoxymethylpyrrolidinyl)sulfonyl]isatin (**1**, R^1 = X = Y = H, R^2 = Me) has been identified as potent, non-peptide, competitive inhibitor of the mentioned effector caspases.[2] Here, we wish to present the synthesis and evaluation of several categories of substituted analogs of **1**. The influence of fluorinated groups at the binding site and in positions known to interact with the S_1, S_2 and S_3 pockets of the enzymes on the affinity and the selectivity as effector caspase inhibitors will be demonstrated.

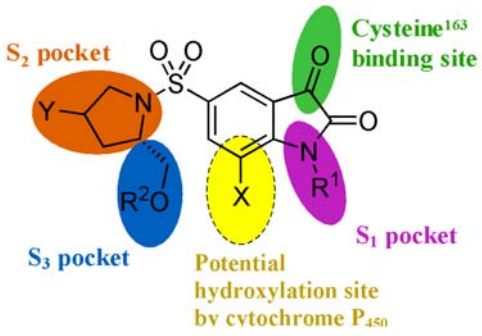

Figure 2. Isatin-based caspase inhibitors

The research was supported financially by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

1 M.O. Hengartner, *Nature* 2000, **407**, 770-776.
2 D. Lee, et al., *J. Med. Chem.* 2001, **44**, 2015-2026.

L-02

Dedicated to Professor Dr. Lev M. Yagupolskii memory

RECENT PROGRESS AND DEVELOPMENT OF "LEV YAGUPOLSKII PRINCIPLE" – SUBSTITUTION OF E=O FOR E=NSO_2CF_3

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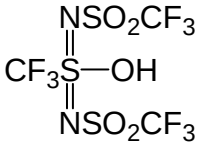
The lecture will summarize the last results obtained in the frame of ongoing investigations of the compounds constructed under the main idea to substitute E=O (E=C,S) moiety of various organic substrates for E=NSO_2CF_3 ("Yagupolskii principle") that led to unusual molecules with extreme behavior and properties. The main topics are as follows.

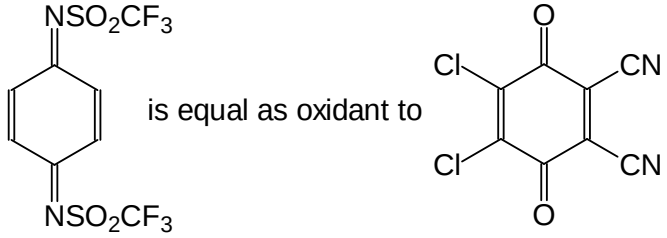
1. Synthesis, derivatives preparation, acidity evaluation and catalytic activity in organic molecules transformations of trifluoromethanesulfonic acid with both oxygen atoms substituted for =NSO_2CF_3 :



2. Nucleophilic rearrangements of carbonyl compounds derivatives bearing the strong electron-withdrawing group =NSO_2CF_3 instead of carbonyl oxygen atom - Arndt-Eistert type reaction.

   Ability of *N*-trifluoromethylsulfonyl-*N'*-arylcarbodiimide to react with various 1,3-dipoles and 1,2-phenylenediamine to form new heterocyclic compounds containing trifluoromethylsulfonylimino group will be presented.

3. Methods to construct bis(N,N'-trifluoromethylsulfonylimino) derivatives of 1,4-benzoquinone and 1,4-naphtoquinone will be presented. As a result, new compounds with high oxidation potential and increase of double bonds reactivity towards nucleophilic agents were obtained.



L-03

NUCLEOPHILIC TRIFLUOROMETHYLATION OF C=N AND C=C BONDS

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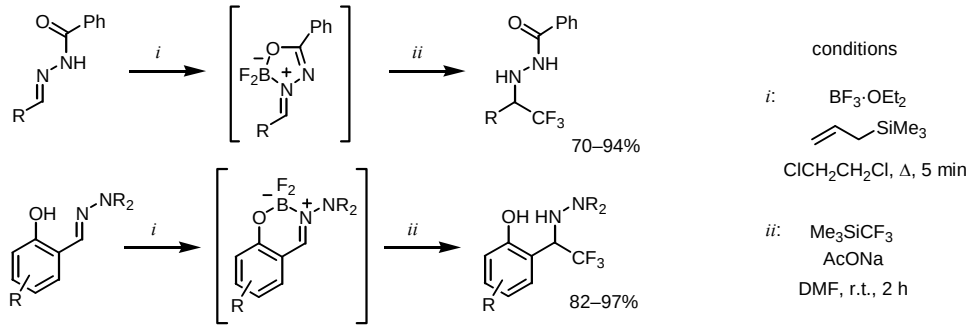
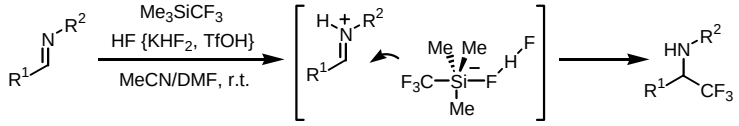
Nucleophilic trifluoromethylation constitutes a very attractive way for the direct introduction of CF_3-group into organic molecule.[1]

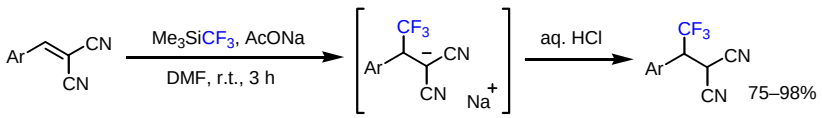
We have developed several methods for the addition of CF_3-carbanion to C=N bond using the Ruppert-Prakash reagent (Me_3SiCF_3). These reactions rely on the activation of azomethine fragment by means of Lewis or Brønsted acid. For example, substrates bearing an adjacent functional group, which is capable of coordinating Lewis acidic fragment, can be trifluoromethylated in high yields.[2-4]



Imines can be trifluoromethylated with Me_3SiCF_3 by using hydrofluoric acid generated *in situ*. It is believed that HF serves as a source of the proton for the activation of imine and as a source of fluoride for the activation of the silicon reagent.[5]



Trifluoromethylation of C=C bond can be readily achieved by using highly electrophilic Michael acceptors such as arylidenemalononitriles.[6]



This work was supported by Russian Academy of Sciences (program # 7), Russian Foundation for Basic Research (projects 08-03-00428, 10-03-91159), and the Federal program "Scientific and educational personnel of innovative Russia" (project 02.740.11.0258)

[1] G.K.S. Prakash *et al Chem. Rev.* 1997, 97, 757–786.
[2] A.D. Dilman *et al J. Org. Chem.* 2007, 72, 8604–8607.
[3] A.D. Dilman *et al J. Org. Chem.* 2008, 73, 5643–5646.
[4] A.D. Dilman *et al Medeleev Commun.* 2009, 19, 141–143.
[5] V.V. Levin *et al Eur. J. Org. Chem.* 2008, 5226–5230.
[6] A.D. Dilman *et al Tetrahedron Lett.* 2008, 49, 4352–4354.

L-04

FLUORINATED 2-METHYLIDENE-1,3-DICARBONYL COMPOUNDS IN ORGANIC SYNTHESIS

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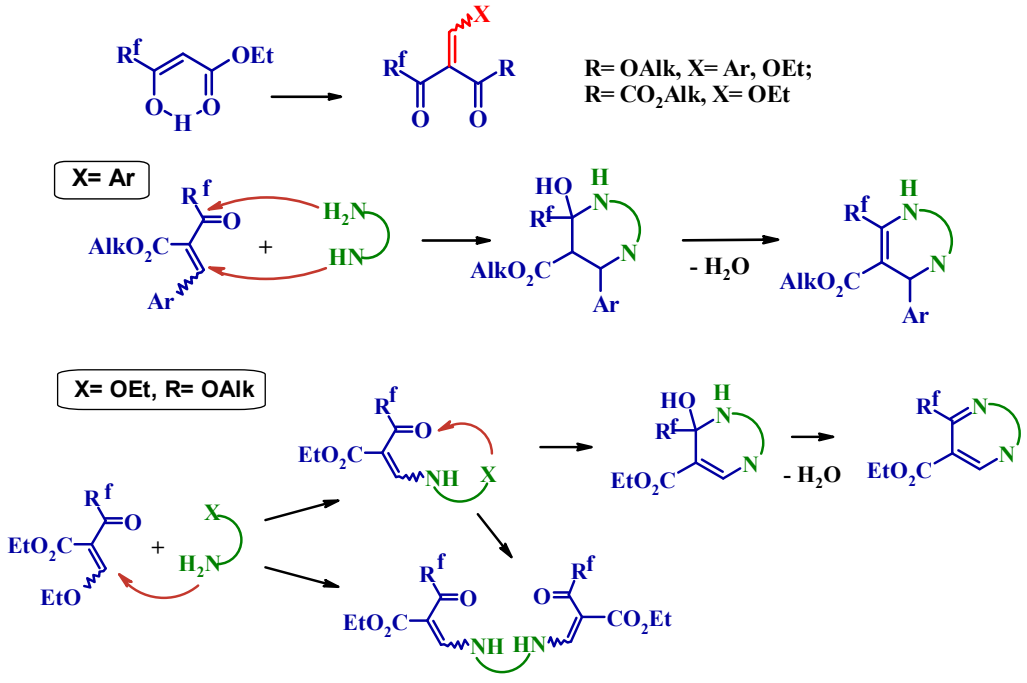
We have developed the synthetic methods for preparation of 2-methylidene-3-oxo-3-fluoroalkyl propionates containing the substituents having different leaving abilities at the methylidene fragment. As a result, a number of polyfluoroalkyl-substituted 2-aryl- and 2-ethoxymethylidene-3-oxo esters were synthesized as promising «block-synthones» for organic synthesis.

2-Arylmethylidene-3-oxo-3-fluoroalkyl propionates were found to react regioselectively with diamines mainly at the fluoroacyl-vinyl fragment; the reaction can be accompanied by water molecule elimination. When α- and *gem*-diamines are used, the further heterocyclization at fluoroacyl fragment is possible, while in the case of diamines having more remote amino groups, addition of the second ester's molecule occurs to give open-chain compounds. The latter can form metal complexes.



The research was financed by Russian Foundation for Basic Research (Project No. 10-03-96017), State contract No 02.740.11.0260, Program of Presidium UD RAS No 09-C-3-1002, Supporting program of Leading Scientific School (No 65261.2010.3)

L-05

FLUORINE MEETS PEPTIDES

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Despite its low abundance in naturally occurring biomolecules, fluorine's favorable impact on the pharmacokinetics and biological properties makes it an outstanding element for peptide and protein modification. Fluorine's effects trace back to its unique physicochemical properties, which are a very high electronegativity and electron affinity combined with a very low polarizability and high stability of the carbon-fluorine bond. As fluoroalkyl groups uniquely combine two contrary properties - polarity *and* hydrophobicity - their effects as substituents in native proteins are not easily predicted.

We have developed peptide-based models to systematically study the complex molecular interactions of fluoroalkyl groups within native polypeptides regarding space filling, lipophilicity and hydrogen-bonding. Using these *in vitro* investigations we determined how fluorinated amino acids influence the folding of native polypeptide motifs and established the key influence of the fluorine-flourine interactions on peptide and protein folding. The combination of the peptide model with analytical techniques and screening methods such as surface plasmon resonance (SPR) and phage display technology creates perfect systems to study the interaction pattern of a variety of fluorinated residues with all kinds of hydrophobic as well as charged amino acid side chains, respectively, within polypeptide environments. These studies pave the way to use the beneficial properties of fluorinated amino acids for the *de novo* design of biologically relevant peptide drugs as well as of fluorinated protein-based materials.

The research was supported financially by Deutsche Forschungsgemeinschaft (DFG Project No. KO 1976/2-2).

L-06

C-OXYALKYLATION OF NITROGEN-CONTAINING π-SYSTEMS WITH POLYFLUOROCARBONYL COMPOUNDS AS A PATHWAY TO NEW BIOLIGICALLY ACTIVE PRODUCTS

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Earlier we have thoroughly studied reactions of C-oxyalkylation of aryl amines, nitrogen-containing heterocycles and enamines with polyfluorocarbonyl compounds such as hexafluoroacetone and trifluoropyruvic acid esters.

We have shown that the similar transformation can be performed regioselectively at room temperature without catalysts to give the desired products in quantitative yields [1]. All these things make the above transformations especially attractive for creating new practically valuable compounds. This lecture considers the successes achieved in one of these directions, namely in the synthesis of biologically active compounds for the recent quarter of a century. For instance new plant growth regulators are discussed. The data on pharmacological activity of fluorinated preparations of this type are summarized. In addition regio- and stereoselective methods for obtaining new products of C-oxyalkylation with polyfluorocarbonyl compounds are discussed.

[1]Fokin, A.V., Dyachenko, V.I., Sviridov, V.D., Sizov, A.Yu**.,** Chkanikov, N.D. *Russian Chemical Bulletin* 1996, **45**, (5), 1178 – 1181; [2]Borisov, Yu.A., Chkanikov, N.D., Kolomiets, A.F., Fokin, A.V. *Russian Chemical Bulletin* 1993, **42,** (11), 1797 – 1799; [3]Chkanikov, N.D., Sviridov, V.D., Zelenin, A.E., Tyutin, V.Yu., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1992, **41**, (8.2), 1820 - 1831,1415 – 1424; [4]Golubev, A.S., Chkanikov, N.D., Antipin, M.Yu., Struchkov, Yu.T., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1992, **41**, (8.2), 1831 - 1836,1425 – 1429.

[5]Golubev, A.S., Tyutin, V.Yu., Chkanikov, N.D., Kolomiets, A. F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1992, **41**, (11.2), 2617 - 2623,2068 – 2073; [6]Sviridov, V.D., Chkanikov, N.D., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1991, **40**, (4.2), 847 – 849; [7]Sviridov, V.D., Chkanikov, N.D., Galakhov, M.V., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1990, **39**, (4.2), 853 – 855; [8]Chkanikov, N.D., Sviridov, V.D., Zelenin, A.E., Galakhov, M.V., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1990, **39**, (2.2), 323 – 328; [9]Sviridov, V.D., Chkanikov, N.D., Galakhov, M.V., Shklyaev, Yu.V., Shklyaev, V.S., et al. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1990, **39**, (6), 1268 – 1272.

[10]Komarov, K. V., Chkanikov, N.D., Suskina, V. I., Shapiro, A. B., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1989, **38**, (2.2), 415 – 417; [11]Sviridov, V.D., Chkanikov, N.D., Galakhov, M.V., Kolomiets,, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1989, **38**, (7.2), 1515 – 1518; [12]Sviridov, V.D., Chkanikov, N.D., Korbukh, I.A., Kolomiets,, A.F., Fokin, A.V., *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1989, **38**, (7.2), 1519 – 1522 ; [13]Sviridov, V.D., Chkanikov, N.D., Shapiro, A.B., Klimova, N. V., Pyatin, B. M., et al. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1989, **38**, (10), 2161 – 2162. Zelenin, A.E., Chkanikov, N.D., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1988, **37**, (1), 110 – 116; [14]Zelenin, A.E.; Chkanikov, N.D.; Ivanchenko, Yu.N.; Tkachev, V.D.; Rusakova, V.A.; Kolomiets, A.F.; Fokin, A.V., *Khimiya Geterotsiklicheskikh Soedinenii* 1987, (9), 1200-1; [15]Chkanikov, N.D., Vershinin, V.L., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1987, **36**, (3), 624 – 626; [16]Sviridov, V.D., Chkanykov, N.D., Galakhov, M. V., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1987, **36**, (6), 1326; [17]Zelenin, A.E., Chkanikov, N.D., Umnov, A.M., Kolomiets, A.F., Fokin, A.V., *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1986, **35**, 1890 – 1894; [18]Zelenin, A.E., Chkanikov, N.D., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1986, **35**, 1895 – 1900; [19]Chkanikov, N.D., Zelenin, A.E., Brondz, N.L., Galakhov, M.V., Kolomiets, A.F., Fokin, A.V., *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1986, **35**, (10), 2093 – 2098. [20]Zelenin, A. E., Chkanikov, N.D., Galakhov, M. V., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1985, **34**, (4), 850 – 853; [21]Zelenin, A. E., Chkanikov, N.D., Kolomiets, A.F., Fokin, A.V. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* 1985, **34**, (4), 873; [22]Chkanikov, N.D., Zelenin, A.E.; Galakhov, M.V.; Kolomiets, A.F.; Fokin, A.V. *Zhurnal Organicheskoi Khimii* 1985, **21,** (6), 1358-9.

L-07

ADVANCES IN CHEMISTRY OF POLYFLUOROALKYL AND SULFUR CONTAINING COMPOUNDS

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Highlights of the work of our group on the chemistry of sulfur containing compounds with polyfluorolkyl substituents are given. Starting from commercially available acyclic compounds (fluorinated alcohols or esters) a number of fluoroalkyl building blocks were developed for the preparation of sulfur-containing compounds with polyfluoroalkyl substituent. The elaborated methodologies of their usage are applied to the synthesis of various acyclic compounds (olefins, acetylenes, ketones, amines, imines, enamines, vinylazides, vinylisothiocyanates) as well as heterocycles (pyrroles, pyrazoles, triazoles, triazolidinethiones, uracils, pyrimidines)[3–6].

Series of thiocarbonyl compounds (amides, esters, thioesters of saturated and unsaturated fluoro-containing thionocarboxylic acids, β-ketodithioesters, and α-thioxo-β-oxosulfones) are obtained and their chemical properties are described. Main attention are paid to reactivity of fluoro alkyl thiocarbonyl compounds towards nucleophiles, viz. thiophilic addition with a concomitant β-fluoride elimination and the hetero-Diels-Alder reactions[7–9]. A new procedure developed are successfully applied in the synthesis of various fluoro-containing sulfur heterocyclic compounds such as dithiolenes, trithiapentalenes, thiopyrans, thiopyrylium salts, thiosugar analogues.

[1] V. Timoshenko, Yu. Shermolovich, *Ukr. Khim. Zhurn*. 1999, **65**(11-12), 10–16.
[2] Yu. Shermolovich, V. Timoshenko, *J. Fluorine Chem*. 2002, **114**(2), 157–161.
[3] Yu. Shermolovich *et al*. *Ross. Khim. Zhurn*. 2005, **XLIX**(6), 109–117.
[4] C. Portella *et al. Heteroatom Chem*. 2007, **18**(5), 500–508.
[5] S.S. Mikhailichenko *et al. J. Fluorine Chem*. 2007, **128**(7), 703–709.
[6] V.M. Timoshenko, C. Portella, *J. Fluorine Chem*. 2009, **130**(6), 586–590.
[7] V.M. Timoshenko *et al. J. Fluorine Chem.* 2010, **131,** 172–183.

L-08

PLANNED AND SURPRISING RESULTS IN ORGANOMETALLIC FLUORINE CHEMISTRY

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In order to study the chemistry of 1,1,4,4-tetraflurobutatriene[1] effective synthetic methods for the synthesis of fluorinated 1,3-butadienes based on C-C coupling reactions of C2 building has been developed.[2] 1,1,4,4-tetraflurobutatriene reacts with Vaska's complex forming the expected a triene complex[3] and with various dienes yielding the products of the Diels-Alder reaction. However, a rather unexpected complex shown in Fig. 1 (left) was isolated on reaction with $Fe_2(CO)_9$.

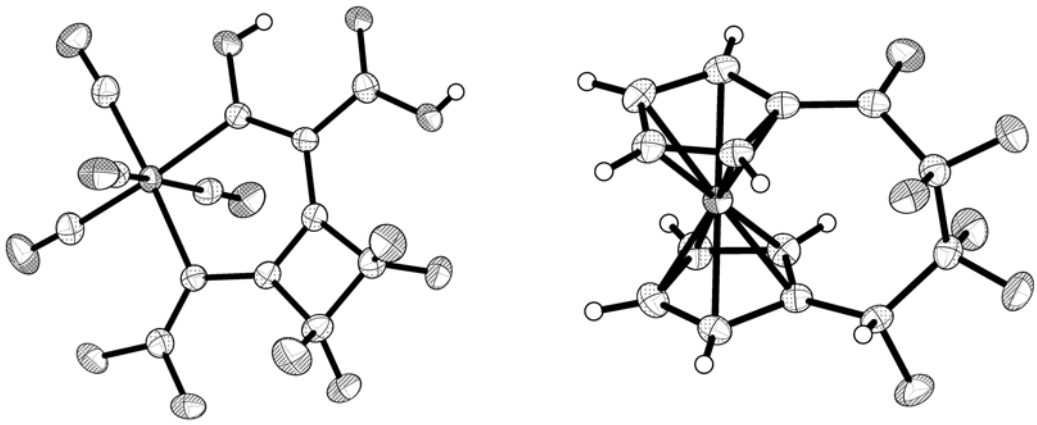

Figure 1.

The palladium catalyzed C-C coupling reactions have been expanded to the synthesis of trifluorovinyl substituted derivatives of ferrocene[4] and cymantrene. The synthesis of 1,1-bis(trifluorovinyl)ferrocene failed for a long time due to the high reactivity of this compound yielding *ansa* ferrocenes on contact with silica (Fig. 1 right).

The hydrometallation reaction of fluorinated allenes has been studied in detail, yielding substituted vinyl complexes.5 With Schwarz' reagent no stable hydrometallation product could be isolated on reaction with tetrafluoroallene. Trifluoroallene and 1,3-difluoroallene could be isolated.

1. A. Bach, D. Lentz*, P. Luger*, M. Messerschmidt, C. Olesch, M. Patzschke, *Angew. Chem.* 2002, **114**, 311-314.
2. F. A. Akkerman, R. Kickbusch, D. Lentz, *Chem. Asian J.* , 2008, **4**, 719-731.
3.. F. A. Akkerman, D. Lentz, *Angew. Chem.,* 2007, **119**, 4989-4991.
4. M. Roemer, D. Lentz, *Eur. J. Inorg. Chem.*, **2008**, 4875-4878.
5. M. F. Kühnel, D. Lentz, *Dalton Transactions*, **2009**, 4747-4755.

L-09

SYNTHESIS OF SYNTHESIS OF 4-FLUOROALKYL-SUBSTITUTED QUINOLINES AS PRECURSORS OF ANTITUMOR AGENTS

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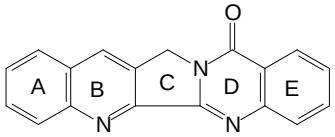
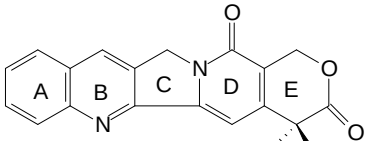
Luotonin A (**1**) is a pentacyclic alkaloid with antitumor activity. Structural similarities and biological associations between Luotonin A and the well-known antitumor alkaloid camptothecin (**2**) have stimulated much interest toward the synthesis of the former alkaloid and its analogs.

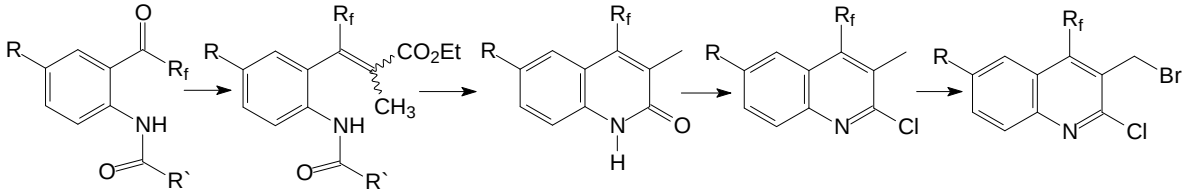


1

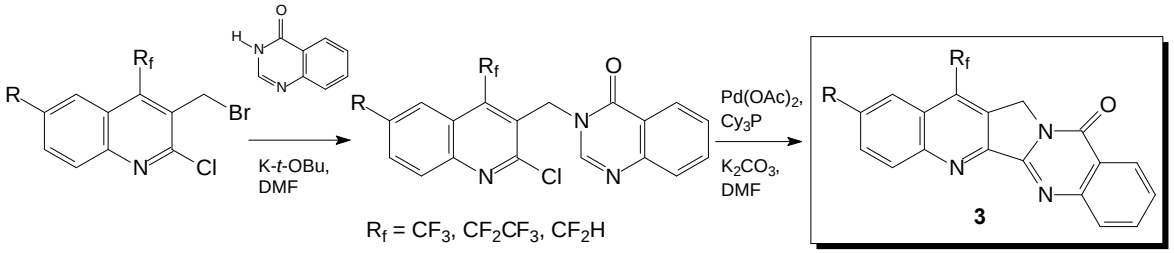


2

We report herein a synthesis of 7-fluoroalkyl-containing analogs of luotonin A (**3**). 3-Bromomethyl-2-chloro-4-(fluoroalkyl)quinolines are key intermediates of our synthesis. They were obtained from anilines bearing a suitable N-protective group according to a five-step synthetic scheme. It includes an ortho-acylation of the anilines, introduction of a C_2 chain extension by Wittig reaction, closure into a lactam cycle to form 3-methyl-2-chloro-4-fluoroalkylquinolin-2(1H)-ones, their transformation into 3-methyl-2-chloro-4-(fluoroalkyl)quinolines, and, at last, introduction an bromine atom into the 3-methyl group by NBS to form 3-bromomethyl-2-chloro-4-(fluoroalkyl)quinolines.



The final steps of our approach for 7-fluoroalkyl-containing luotonins involve the formation of the C-ring by connecting A/B- and D/E-fragments via an N-alkylation followed by an intramolecular Heck cyclisation.



R_f = CF_3, CF_2CF_3, CF_2H

The biological activity of 7-fluoroalkyl-containing analogs of luotonin A and details of their synthesis are discussed.

This work has been supported by Russian Foundation for Basic Research (project 08-04-13562).

L10

ELECTROCATALYTIC SYNTHESIS OF PARTIALLY FLUORINATED COMPOUNDS

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Partially fluorinated fluoroaliphatic compounds that combine physico-chemical properties specific both for fluoro- and hydrocarbons are of doubtless practical interest. It should be noted that the commercial application of such substances supposes the presence of vinylene moiety in their structure ensuring environmental protection.

A number of compounds that can be presented by general formula R_f-A-R_f (R_f = perfluoroalkyl, perfluoroalkoxyalkyl; A = saturated or unsaturated hydrocarbon moiety) has been obtained by anodic oxidation of fluorocarboxylic acids in the presence of unsaturated acceptors – acetylene, ethylene, α-dienes (additive Kolbe electrosynthesis).

It has been found that the composition of the reaction products depends on the nature of radical generated in the anodic process. Thus the share of additive Kolbe electrosynthesis products increases in the case of perfluoroalkoxyalkyl radicals (in comparison with their perfluoroalkyl analogues).

The correlation between electrochemical parameters of the process and the composition of the reaction products indicates at the competitive adsorption of the electrolyte components at the anode surface.

L-11

REACTIONS OF POLYFLUOROARENETHIOLS WITH ELECTROPHILES. SYNTHESIS AND SOME TRANSFORMATIONS OF ALLYL POLYFLUOROARYL SULFIDES AND SULFONES

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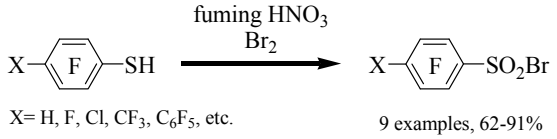
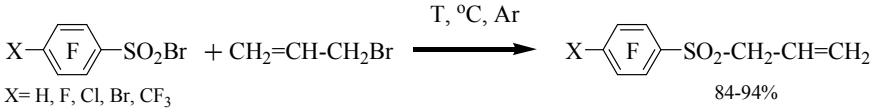
A new simple and efficient method for the synthesis of polyfluoroarenesulfonyl bromides by reaction of polyfluoroarenethiols with a mixture of bromine and fuming nitric acid is developed (Scheme 1)[10].



Scheme 1. Synthesis of polyfluoroarenesulfonyl bromides

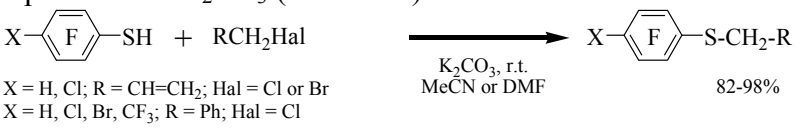
The reaction of polyfluoroarenesulfonyl bromides with allyl bromide proceeds with loss of bromine and leads to allyl polyfluoroaryl sulfones in good yields (Scheme 2).



Scheme 2. Synthesis of allyl polyfluoroaryl sulfones

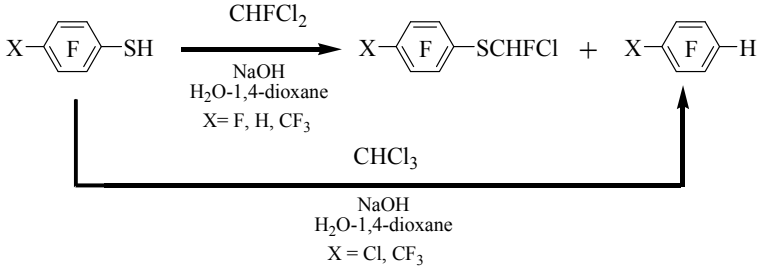
However, the reaction of pentafluorobenzenesulfonyl bromide with allyl chloride yielded no allyl pentafluorophenyl sulfone. In this case, addition of $C_6F_5SO_2Br$ to the double bond of allyl chloride took place.

Allyl and benzyl polyfluoroaryl sulfides are easily obtained by reaction of the corresponding arenethiols with allyl chloride or bromide in MeCN or with benzyl chloride in MeCN or DMF in the presence of K_2CO_3 (Scheme 3).



Scheme 3. Synthesis of allyl and benzylpolyfluoroaryl sulfides

Polyfluoroarenethiols react with $CHFCl_2$ in the presence of NaOH to give mixtures of the corresponding fluorochloromethyl polyfluoroaryl sulfides and hydropolyfluoroarenes. The reaction with $CHCl_3$ under analogous conditions gives mainly hydropolyfluoroarenes (Scheme 4).



Scheme 4. Reactions of polyfluoroarenethiols with $CHFCl_2$ and $CHCl_3$

Possible mechanisms of the reactions will be discussed.

[10] V.E. Platonov *et al. J.Fluorine Chem.* 2010, **131**(1), 13-16.

L-12

ADVANCES IN THE CHEMISTRY OF POLYFLUOROAROMATIC ORGANOZINC COMPOUNDS AND IN HYDROGENOLYSIS OF POLYFLUOROARENES UNDER THE ACTION OF ZINC

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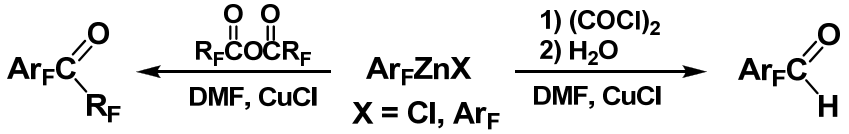
The methods of synthesis of polyfluoroaromatic organozinc compounds and their role as reactive intermediates in chemical transformations will be reviewed.

Novel synthetic methodology leading to polyfluoroaromatic organozinc compounds by the reactions of chloropolyfluoroarenes and perfluoroarenes with Zn in DMF in the presence of $SnCl_2$ or SnF_2 will be presented. The series of chloropolyfluoroarenes and perfluoroarenes includes chloropentafluorobenzene, 3-chloroheptafluorotoluene, octafluorotoluene, pentafluorobenzonitrile, ethyl pentafluorobenzoate, pentafluoropyridine, 3-chlorotetrafluoropyridine, perfluoroindan.

Polyfluoroaryl organozinc compound are used to obtain various functional derivatives of polyfluoroarenes. Reactions of polyfluoroarylzinc compounds with electrophiles will be considered.

Polyfluoroarenes, bromo- and iodopolyfluoroarenes, N,N-dimethylbis(polyfluoroaryl)-methanamines, perfluorinated symmetrical and asymmetrical biaryls are synthesized by reactions directly with polyfluoroarylzinc reagents, whereas the presence of copper (I) halide in addition to the latter is required for the synthesis of allylpolyfluoroarenes (from allylchloride), polyfluoroaromatic aldehydes and ketones. For example:



$Ar_F = C_6F_5$, 4-$CF_3C_6F_4$
$R_F = CF_3$, C_2F_5

$Ar_F = C_6F_5$, NC-(F)-, N(F)

The influence of the chemical structure of polyfluoroarenes on the hydrogenolysis of C-F and C-Cl bonds in polyfluoroaromatic compounds under the action of Zn(Cu)-DMF-H_2O is investigated.

Mechanistic aspects of the transformations are discussed.

The research was supported financially by the Interdisciplinary Integration Project of SB RAS (Project No.57).

L-13

PERSPECTIVES AND RECENT DEVELOPMENTS IN THE SYNTHESIS OF ^{18}F-LABELLED COMPOUNDS - RADIOTRACERS FOR POSITRON EMISSION TOMOGRAPHY (PET)

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Fluorine-18, a short-lived radioactive isotope of fluorine, is currently the radionuclide of choice for positron emission tomography (PET). PET is the most powerful nuclear imaging modality for the diagnosis of cancer, neurological and cardiovascular diseases. It allows quantitative evaluation of physiological, biochemical and pharmacological functions at the molecular level being a valuable tool in drug discovery and development. To date specific molecular probes (small molecules, peptides, antibodies) labelled with short-lived PET radionuclides have been suggested to trace various biological processes underlying the origin, pathogenesis and progress of diseases. Among four conventional cyclotron produced positron emitters, ^{18}F is considered as an ideal PET radionuclide due to its longer half-life (109.7 min) and relatively low positron energy providing high-contrast images. The radionuclide is easy available in large amounts from modern PET cyclotrons, while ^{18}F-labelled radiotracers can be delivered to imaging centers within a few half-lives of transportation time. This is a rational basis for cost-efficient clinical PET, as it was demonstrated by extremely successful application of PET with 2-[^{18}F]fluoro-2-deoxy-D-glucose in cancer diagnostics.

Over the last decade a versatile ^{18}F labeling chemistry has been developed; it was adapted to modern automated routine production under very high levels of radioactivity. In contrast to traditional methods for the preparation of fluoroorganics via electrophilic reagents, the fluorine-18 chemistry highly exploited the nucleophilic synthesis strategies based on [^{18}F]fluoride. No carrier added [^{18}F]fluoride is obtained via ^{18}O(p,n)^{18}F nuclear reaction occurred during protons bombardment of enriched $H_2{}^{18}O$ in a cyclotron target. The ^{18}F-recovery from the target water is achieved by the ion exchange or electrochemical methods. To react as nucleophile, ^{18}F is transferred into anhydrous form as a complex with phase transfer phase transfer catalyst (kryptofix 2.2.2) and potassium as a counter ion. The fluorinations are carried out at 80-180 ^{o}C in aprotic solvents; more recently the use of protic solvents has been suggested. For a very few radiotracers (small molecules) ^{18}F-labelling can be fullfilled by direct nucleophilic displacement of suitable leaving group in the aliphatic or aromatic substrate. For variety of ^{18}F-labelled compounds the cleavage of protecting groups in the labelling substrate in required after fluorination step. Electron rich aromatic systems can be substituted in the presence of an appropriate electron withdrawing leaving group and an auxiliary substituent (CHO, CN etc.). For biomolecules (aminoacids, peptides, drugs molecules) that cannot tolerate harsh fluorination conditions, the labeling is done by coupling ^{18}F-labeled prosthetic group or synthon with a reactive function via alkylation, acylation, amidation of specific functional group. This indirect multistep procedure often requires an intermediate purification of ^{18}F-labelled synthon using HPLC, SPE, or distillation; entire process is difficult to adapt to the automated modules. Recently “click” chemistry (Huisgen 1,3-dipolar cycloaddition) reaction which proceeds under mild aqueous conditions has been suggested for the synthesis ^{18}F-fluoropeptides. The newest attempts to label peptides in a single-step via ^{18}F-labelling of silicon based modification of the peptides or direct labelling of chelate-attached-peptide with aluminum-fluoride (Al^{18}F) represent a great challenge in ^{18}F-chemistry.

L-14

RECENT DEVELOPMENTS IN THE CHEMISTRY OF THE SF_5 GROUP. SYNTHESES AND APPLICATIONS

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The pentafluoro-λ^6-sulfanyl (SF_5) group is one of the fluorine-containing substituents having attracted interest because of providing compounds low surface energy, high chemical resistance, thermal stability, high electronegativity and lipophilicity and of being significant important especially for agrochemical and pharmaceutical chemistry.[1]

Here we describe our contributions in SF_5 group chemistry using SF_5Cl, SF_5Br, S_2F_{10} and SF_6 as respective sources to generate new building blocks.

[1] Kirsch, P.; Röschenthaler, G.-V. In *Current Fluoroorganic Chemistry – New Synthetic Directions, Technologies, Materials, and Biological Applications*, Soloshonok, V. A.; Mikami, K.; Yamazaki, T.; Welch, J. T.; Honek, J. F., Eds.; ACS Press, Washington 949, **2007,** 221.

Parts of the research was supported financially by the German Science Foundation (DFG 436 UKR 113/99/0-1).

L-15

[2,3]-SYGMATROPIC REARRANGEMENT OF CF_3-CONTAINING NITROGEN AND SULFUR YLIDES

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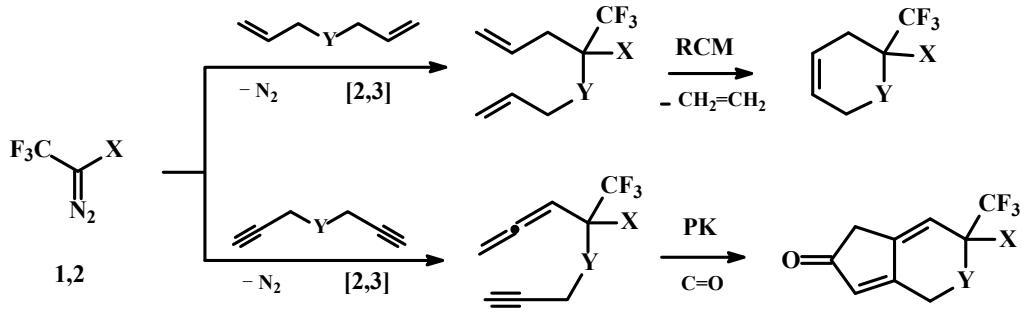
α-Trifluorometyl-substituted α-diazocarboxylate **1** and α-diazophosphonate **2** are unique reagents for simultaneous introduction of trifluoromethyl and carboxylic and phosphonic functionalities into organic molecules.[1-4]



We have developed an efficient approach to multifunctional CF_3-heterocyclic compounds, including cyclic amino carboxylic and amino phosphonic acids, based on two successive metal-catalyzed processes: ylide generation/rearrangement and carbocyclization. The synthetic sequence includes Cu(II)-catalyzed tandem ylide formation/[2,3]-sigmatropic rearrangement between acceptor/acceptor carbenoids and allyl- or/and propargyl-containing amines or sulfides to afford, in one step, unique unsaturated molecules that can be used as diversification points by means of subsequent metal-catalyzed intramolecular carbocylizations (*e.g.* such as Ru-catalyzed RCM and Co-mediated Pauson-Khand reaction).

[1] S.N. Osipov, N. Sewald, K. Burger, A.F. Kolomiets, A.V. Fokin, *Tetrahedron Lett*. **1996**, *37*, 615.
[2] I.D. Titanyuk, D.V.Vorobjeva, S.N. Osipov, I.P. Beletskaya, *Synlett* **2006**, *9*, 1355.
[3] D.V. Vorobyeva, I.D.Titanyuk, I.P.Beletskaya, S.N.Osipov, *Mendeleev Commun*. **2005**, *6*, 222.
[4] I.D. Titanyuk, I.P. Beletskaya, A.S. Peregudov, S.N. Osipov, *J. Fluorine Chem.* **2007**, *128*, 723.

Acknowledgements - *This work was financially supported by Russian Foundation for Basic Research (Projects Nos. 07-03-92171, 08-03-92504).*

L-16

β-ALKOXYVINYL POLYFLUOROALKYL KETONES – VERSATILE SYNTHONS IN FLUOROORGANIC CHEMISTRY

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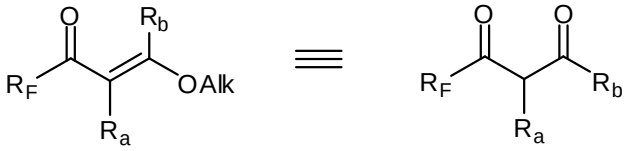
The introduction of fluorine atoms and fluorinated groups into organic molecules often confers significant and useful changes in their chemical and physical properties. Though direct fluorinating or polyfluoroalkylating methods are the most attractive and powerful new tools for constructing fluorinated compounds, the fluoro-containing building blocks are often the more convenient starting reagents.

Readily available β-alkoxyvinyl polyfluoroalkyl ketones **1** may be considered as chemical equivalent of 1,3-diketones (R_b =Alk, Ar) or 1,3-ketoaldehydes (R_b = H). The enones **1** are widely used in organic synthesis as reactive and useful polyfluoroalkyl-containing building blocks for the obtaining various fluorinated aliphatic and aromatic compounds: enaminones, hydroxy and amino acids, heterocycles, anilines and *etc*. Also the enone **1** (R_F = CF_3, R_a = R_b = H) was used as perspective reagent for amino group protection in peptide synthesis.



1

R_F = CF_3, CHF_2, $CClF_2$, C_2F_5, C_3F_7 etc.

R_a, R_b, = H, Alk, Ar

Retrospective and perspective points of view on the chemistry of the enones **1** as useful fluorinated building blocks will be presented.

L-17

ELECTROPHILIC REACTIONS OF POLYFLUOROOLEFINS

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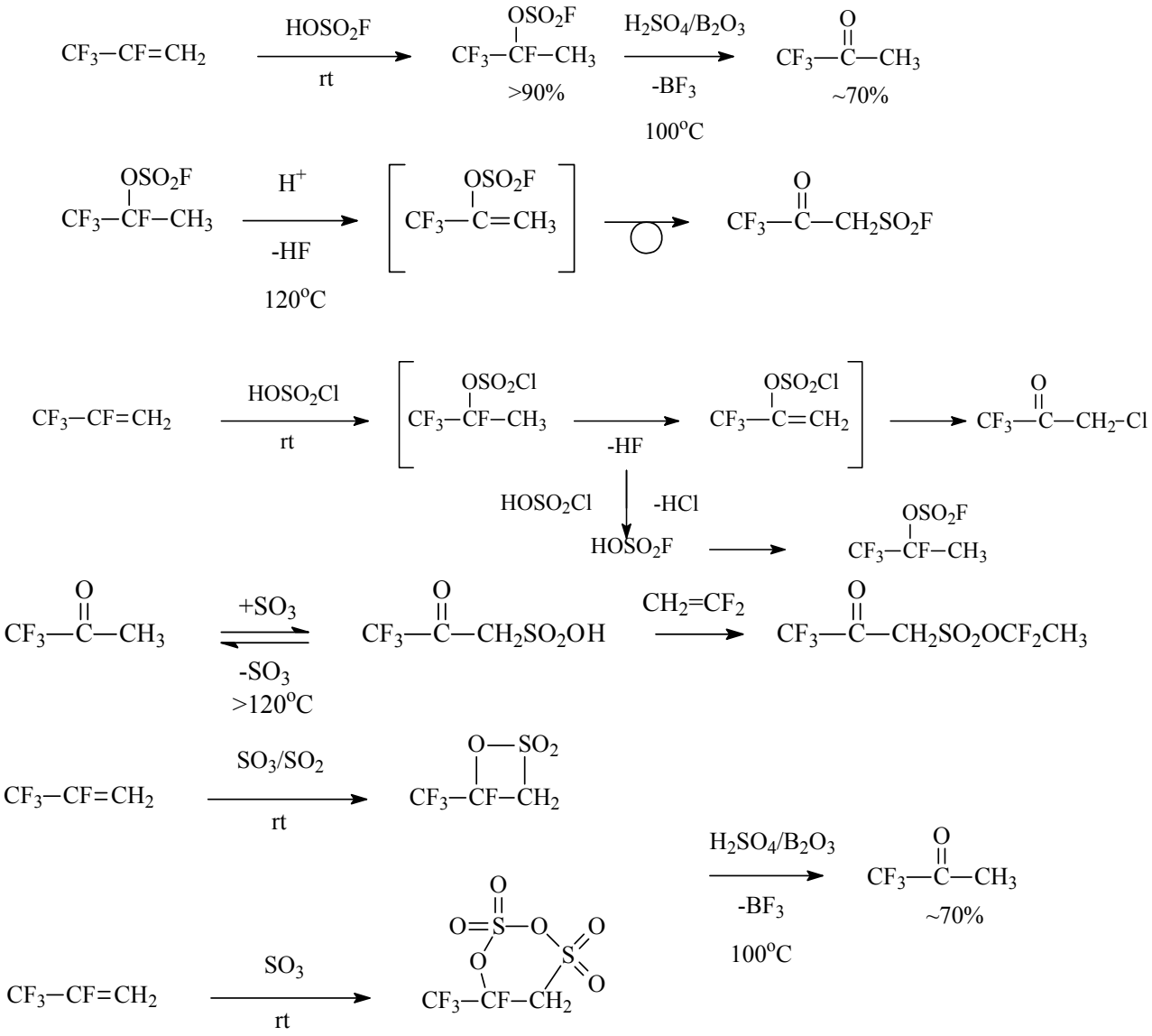
Nowadays poloyfluoroolefins known from the middle of the 20th century have become commercially available reagents as refrigerants and solvents of new generation (Freon substitutes). The chemical behavior of polyfluoroalkenes is practically unknown.

We have developed some new convenient methods for preparation of polyfluoropropenes and studied their reactions with some electrophilic reagents such as fluoro- and chlorosulfuric acids, antimony pentafluoride, sulfur trioxide *etc.*

The following scheme represents some reactions of 2,3,3,3-tetrafluoropropene:



L-18

POLYFLUORINATED β-DIIMINES IN SYNTHESES OF HETEROCYCLIC COMPOUNDS

Kurykin M.A., Vebritsky D.Yu, Petrova O.E, Keshtov M.L.

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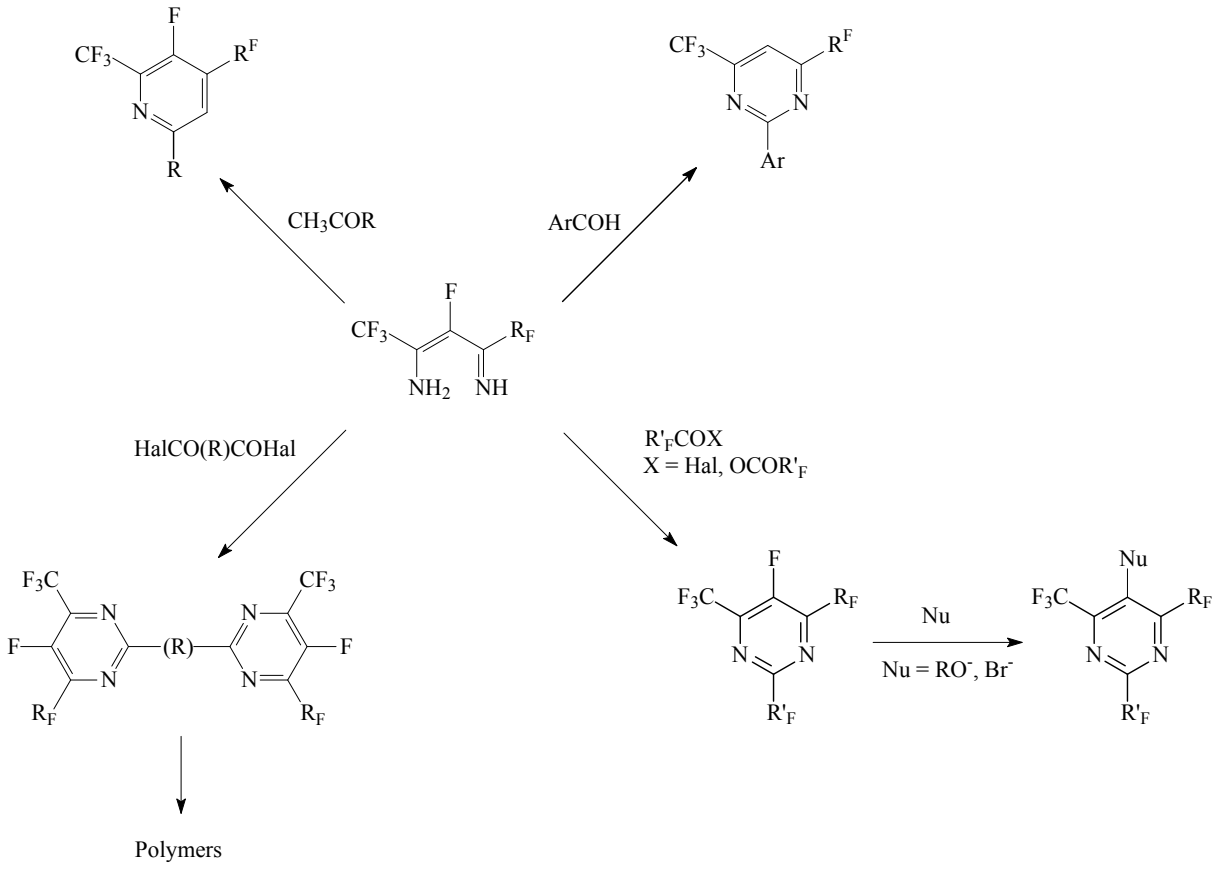
Polyfluorinated β-diimines proved to be very convenient precursors of N-heterocycles such as pyridines and pyrimidines.

We have studied reactions of the diimines with ketones, aldehydes, and acid halides.

The experimental details, physicochemical and spectral characteristics of the compounds obtained are considered.



L-19

C–F ACTIVATION OF FLUORINATED MOLECULES AT TRANSITION METALS: FROM MODEL REACTIONS TO CATALYSIS

T. Braun, M. Ahijado-Salomon, D. Breyer, A.L. Raza, A. Steffen, M. Teltewskoi, F. Wehmeier

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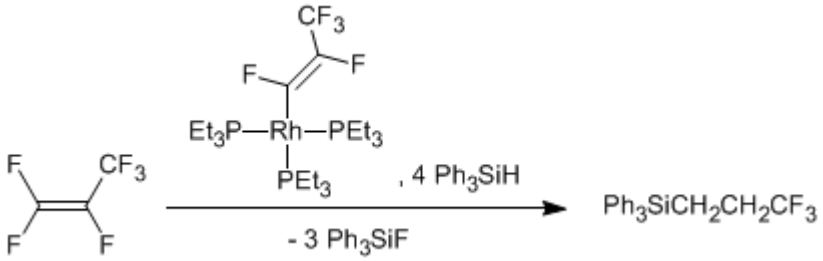
One interesting tool for the derivatization of fluorinated molecules is based on the C–F activation of a carbon-fluorine bond at a transition metal center. The strategy often involves the selective removal of a fluorine atom from highly fluorinated precursors, followed by functionalization reactions in the coordination sphere of the metal.[11]

We will report on the C–F-activation and the stoichiometric or catalytic derivatization of fluorinated pyridines and alkenes at rhodium.[2] Hexafluoropropene can be activated, and be selectively converted into 1,1,1-trifluoropropane in the presence of H_2.[3] Investigations on the reactivity of the fluoro complex $[Rh(F)(PEt_3)_3]$, which is also produced, led to the development of a cyclic process for the formation of 1,1,1-trifluoropropane from perfluoropropene, $HSiPh_3$ and H_2 (Scheme).[4] We also describe studies on the catalytic derivatization of hexafluoropropene to give silyl derivatives by transition metal mediated cleavage reactions of carbon-fluorine bonds.[5] Finally, borylation reactions which are based on C-F activation steps will be discussed.[6]



(1) T. Braun, R. N. Perutz, *Chem. Commun.* **2002**, 2749; W. D. Jones, *Dalton Trans*, **2003**, 399. (2) T. Braun, D. Noveski, M. Ahijado, F. Wehmeier, *Dalton Trans.* **2007**, 3820-3825. (3) T. Braun, D. Noveski, B. Neumann, H.-G. Stammler, *Angew. Chem. Int. Ed.* **2002**, *41*, 2745. (4) D. Noveski, T. Braun, M. Schulte, B. Neumann, H.-G. Stammler, *Dalton Trans.* **2003**, 4075; (5) T. Braun, K. Altenhöner, F. Wehmeier, *Angew. Chem. Int. Ed.* **2007**, *46*, 5321. (6) T. Braun, M. Ahijado-Salomon, K. Altenhöner, M. Teltewskoi, S. Hinze, *Angew. Chem.Int. Ed.* **2009**, *47*, 1818; M. Teltewskoi, J. A. Panetier, S. A. Macgregor, T. Braun, *Angew. Chem. Int. Ed.* **2010,** *48*, 3947-3951.

L-20

CATALYTIC OLEFINATION REACTION – A NEW APROACH TO FLUORINATED COMPOUNDS

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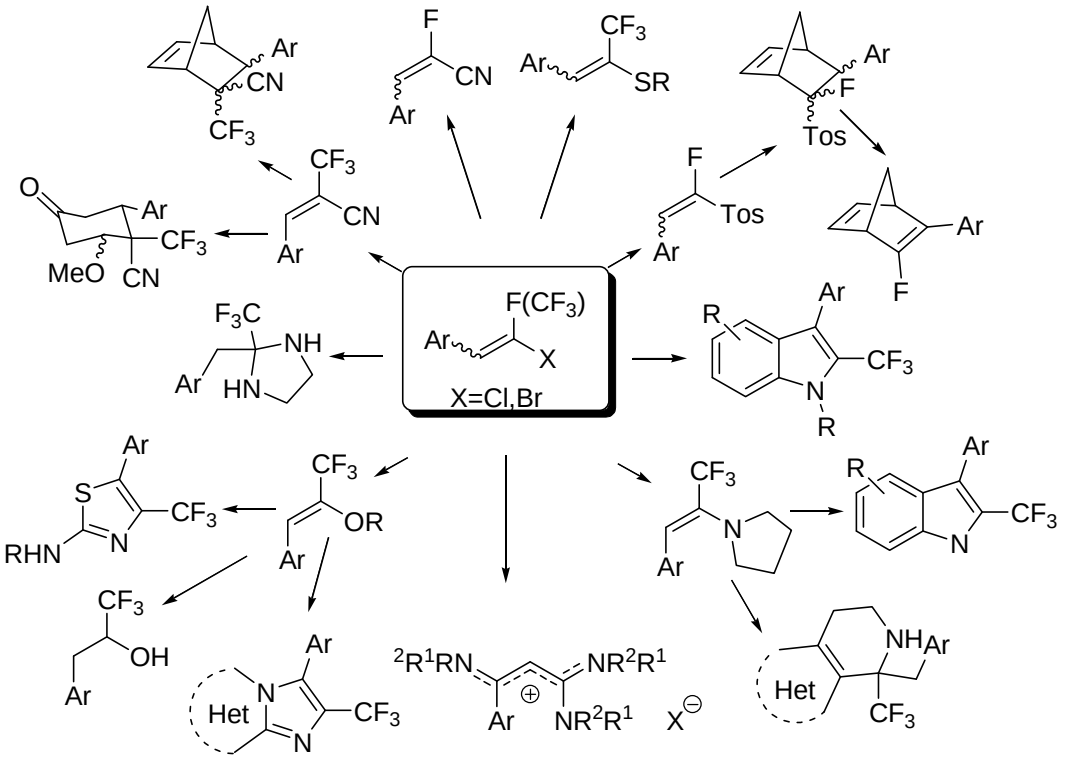
Organofluorine compounds are intensively investigated in recent decades. The remarkable interest on these compounds is due to their unique physical and biological properties caused by the presence of fluorine.

About a decade ago, a novel synthesis of alkenes has been discovered by our research group. It was found that *N*-unsubstituted hydrazones of carbonyl compounds can be smoothly transformed into various substituted alkenes by treatment with polyhalogenalkanes in the presence of catalytic amounts of CuCl. This reaction was found to be a new general approach for the construction of carbon-carbon double bonds. A number of convenient and simple methods for the synthesis of various alkenes including fluorinated ones were developed.

Fluorinated β-halogenstyrenes easily synthesized by this method are of special interest because of the possibility of their modification by nucleophilic vinylic substitution. We demonstrated, that β-halogen atoms in fluoro- and CF_3-styrenes can be easily substituted by *C*-, *S*-, *N*- and *O*-nucleophiles providing simple and general pathway to useful fluorinated building blocks. The latter compounds were successfully used in the synthesis of various carbo- and heterocyclic compounds as shown in the chart.



L-21

WEAKLY COORDINATING ANIONS. FROM ACADEMIC CURIOSITY TO INDUSTRIAL IMPORTANCE.

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First investigations of weakly coordinating anions were performed by M. H. Klaproth, who studied the reaction of sulfur, selenium or tellurium in conc. sulfuric acid 200 years ago. Chalcogen cations formed in this manner as well as other non-metal cations and cationic coordination compounds were selectively synthesised and characterised in detail during the last 50 years. In the related field of carbocations G. A. Olah was an important contributor. For the stabilisation of all these strongly electrophilic cations mainly the halo anions $[BF_4]^-$, $[AlCl_4]^-$, $[AsF_6]^-$, $[Sb_2F_{11}]^-$ have been used.

Beside these more academic applications of the above mentioned anions, in recent years an increasing interest emerged in chemically robust weakly coordinating anions. They should exhibit low charge density, high stability against acids and bases, reducing and oxidizing agents, high thermal stability and should be soluble in weakly coordinating solvents. There is a need for such anions in salts of cationic catalysts, in electrochemical applications (Li ion batteries, fuel cells, cyclovoltammetry, galvanic etc.) and ionic liquids (solvent with low vapour pressure, photovoltaic, super capacitors, extraction, sensors, ion turbojet etc.).

Based on fluorinated borates, aluminates and phosphates many weakly coordinating anions were developed that meet in part the mentioned demands. Examples are $[B(C_6F_5)_4]^-$, $[B(CF_3)_4]^-$, $[FB(C_2F_5)_3]^-$, $[RCB_{11}F_{11}]^-$, $[B_{21}F_{18}]^-$, $[Al(OR_F)_4]^-$, and $[(C_2F_5)_3PF_3]^-$. Their synthesis, properties and applications will be reported here.

L-22

FLUORIDE TECHNOLOGIES OF RARE AND RARE-EARTH ELEMENTS

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[b]Tomsk State University, Lenina Prosp., 36, Tomsk, Russian Federation

Fluoride metallurgy for getting metals and alloys is perspective. Therefore with common processes of getting metal U, Pu and reduction other fluorides, fluoride metallurgy is used for getting individual REM, Zr, Ti and other metals and alloys on their base. Expansion of using fluorides is explained by their small tendency to hydrolyse and large thermal effects during metalothermal reduction in comparison with other halogenides, which allows making reduction in SHSregime.

It has developed dry fluorous technology in getting magnet materials on Nd-Fe-B basics: alloys, high energy magnets (HEPM).

The principle of technology is based on the following operations: fluorinations of oxides and other kind of raw materials with elemental fluorine, furnace charge preparation of the base of REM fluorides and other transitional metals mixture, their metallothermal reduction outside kiln in the Regime of Selfspread-Hightemperature Synthesis (SHS), getting magnets by different methods and wastes processing in order to utilize fluorine and other valuable compounds, REM first of all.

The technology has the following advantages:

– the piculiarity of fluorinating gas; it consist in the possibility to use it for processing any kind of raw materials: oxide, metals, concentrates, wastes;

– high level of process intensity;

– the pirculiarity of psysico-chemical properties of the obtained fluorides. For example, they are less sensitive for hydrolysis in compransion with chlorides. It permits to process them in atmosherical conditions. Another important property is their thermal effect of metallothermal reduction that is bigger by 2-4 times than one of the elements. Thix property permits to process them out-of-kiln and ger compect alloys;

– the possibility to use in the given technology the gained scientific and industrial expirience, tecnological equipment, eborated in high nuclear technology;

– ecological advantures; they are the following: the usage of shortered schemes, the absence of liquid wastes and the possibility to regenerate fluorine.

Studies of fluorine technology improvement to get magnet materials and HEPM have been carried out in the following directions:

– theoretical possibility evaluation of getting metal fluorides by gaseous fluorine technology;

– equipment improvement and development of new devices to get REM fluorides and transitional metals;

– condition analysis of the reduction outside kiln of metal fluoride mixture and alloying additions on SHS;

– equipment development for different stages of HEMP productions by powder metallurgy and from fast tempered magnet alloys;

– theoretical ground and experimental development of different magnet production wastes processing technology.

L-23

FLUORINE IN THE PERIPHERY: ENABLING CHEMISTRY WITH WEAKLY COORDINATING ANIONS

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If the surface of a larger, chemically robust anion is terminated by fluorine, its performance as a weakly coordinating anion (WCA) usually get better. This is mainly due to the low polarizability of element-fluorine bonds and the capability of fluorine to effectively delocalize the negative charges (Figure 1).

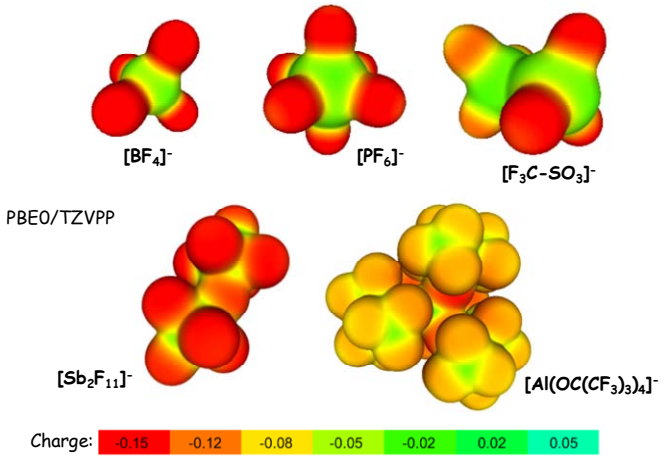

Figure 1: Calculated electrostatic potential projected on the 0.005 e^-/B^3 isodensity surface (PBE0/TZVPP).

The lecture will focus on the chemistry of the $[Al(OR^F)_4]^-$ (R^F = fluorinated alkoxide) and related types of WCAs and their underlying strong Lewis Acids. New types of anions and a new fluorination approach will be included.

The research was supported financially by DFG, the FCI and the University of Freiburg.

L-24

NEW METHODS FOR SYNTHESIS OF BASIC ORGANOFLUORINE COMPOUNDS

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I. The first line of basic organofluorine products for manufacturing a large range of fluoroaliphatic compounds includes tetrafluoroethylene and perfluoropropylene. The only scheme for manufacturing these products that was realized by all worldwide manufacturers, is as follows:

$$CHF_2Cl \xrightarrow{700^0C} CF_2 = CF_2 + CF_2 = CFCF_3$$

We proposed a new scheme for manufacturing these products:

$$CH_2 = CHCO_2CH_3 \xrightarrow[HF]{ECF} CF_3CF_2COF + COF_2 \xrightarrow[300^0C]{cat.} CF_2 = CF_2 + 2COF_2$$

$$CH_2 = C(CH_3)CO_2CH_3 \longrightarrow CF_3CF(CF_3)COF + COF_2 \xrightarrow{\triangle} CF_2 = CFCF_3 + 2COF_2$$

II. The next group of large-tonnage products includes oligomers of perfluoropropylene oxide and perfluorovinyl ethers. We have developed and applied a new technology for manufacturing these products:

$$n\text{CF}_3\text{CF}\underset{}{\overset{O}{\diagup\diagdown}}\text{CF}_2 \xrightarrow[\text{solvent } 0^0C]{R_2NCH_2NR_2\ (cat.)} C_8F_7[CF(CF_3)CF_2O]_{n-2}CF(CF_3)COF$$

$$2COF_2 + R_2NCH_2NR_2 \longrightarrow FCONR_2 + \underset{cat.}{[\ CF_3O^-CH_2^+NR_2\ ]} \xrightarrow[-10^0C,\ solvent,\ 3bar]{COF_2 + CF_3CF\overset{O}{\diagup\diagdown}CF_2}$$

$$CF_3OCF(CF_3)COF \longrightarrow CF_3OCF = CF_2$$

III. Another line of manufacturing fluorine-containing compounds is based on products of addition of perfluoroalkyliodides to alkenes. This process is realized as a thermal chain radical reaction of addition initiated either by peroxides (benzoyl peroxide) or azobisisobutyronitrile.

We have developed a redox system that made it possible to carry out a similar process under very mild conditions

$$R_F - I + CH_2 = CH_2 \xrightarrow[15\%\ Cu^{2+},\ 20^0C,\ ROH]{15\%\ N_2H_4 \cdot H_2O} R_F - CH_2CH_2I$$

IV. The third class of basic organofluorine products includes fluoroaromatic compounds. We managed to develop a number of available and cheap catalysts based on aminoethanamidine salts that allow one to carry out the “calex” process at moderate temperature and atmosphere pressure.

$$C_6Cl_6 + KF \xrightarrow[150 - 180^0C]{(R_2N)_3C^+N^-} C_6F_xCl_{6-x} + KCl$$

L-25

SYNTHESES AND CHEMICAL PROPERTIES OF AZOLES WITH N-POLYFLUORINATED SUBSTITUENTS

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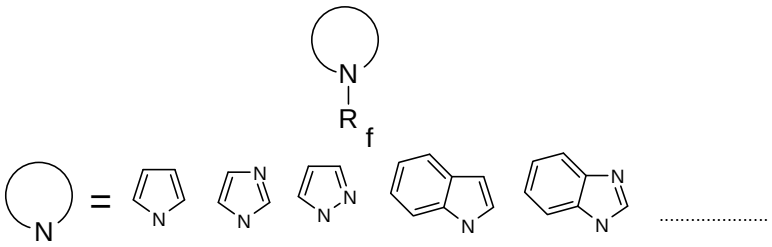
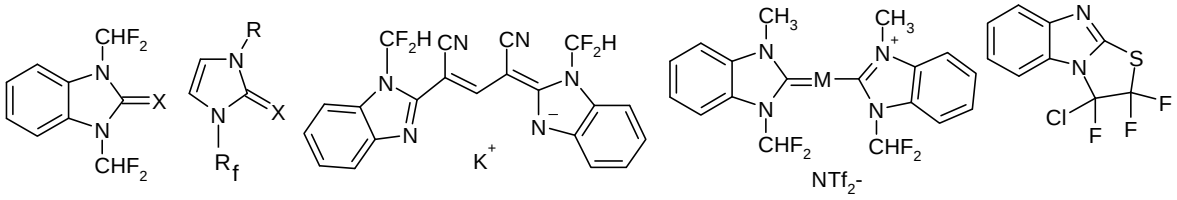
The report is devoted to obtaining and chemical behavior investigation of the nitrogen-containing heterocycles with CF_2H, CF_2CF_2H[1], CF_2CF_2Hal[2,3], $CF{=}CFCl$[4] and some others fluorinated groups near the nitrogen atom. The ways of functionalization of the fluorine containing fragment were shown. The corresponding silanes, sulfides, sulfones, sulfonic and carboxylic acids, ketones, and secondary alcohols were obtained[4]. The quaternary salts from the corresponding N-polyfluoroalkyl imidazoles were synthesized. The last were converted into the corresponding thiones, selenones, dithocarboxylates and transition metals complexes (Ag, Ni, Pd, Hg) through the intermediate imidazole-2-carbene formation.

The reaction of some Freons with heterocyclic ambident systems (N-C-S, N-C-N, N-C-C) were studied[5]. The products formed by interaction with different reaction centers were isolated, in some cases the reaction conditions were optimized to obtain the desired product. The new anionic fluorine-containing dyes were obtained in the case of 2-cyanomethylbenzimidazole[6] and new fluorinated tricyclic systems were isolated in the case of 2-mercaptobezimidazole.



R_f = CF_2H, CF_3, CF_2CF_2H, CF_2CF_2Br, CF_2CFCl_2, CF_2CF_2I, CF_2CFClI, $CF_2CFClBr$, $CFClCFCl_2$, C_2F_5, $CF_2CF_2SiMe_3$, $CF_2CF_2C(O)Ar$, $CF_2CF_2CH(OH)Ar$, $CF_2CF_2C(O)OH$, $CF_2CF_2SO_2Na$, $CF_2CF_2C(S)SCH_3$, CF_2CF_2Ar, $CF{=}CFCl$, $CF{=}CFSAr$, $CF{=}CFHt$



X = O, S, Se

M = Ag, Ni. Hg, Pd

[1] L.M. Yagupolskii, T.M Sokolenko. K.I Petko, *Russ. Chem . Bull*. 2005, (3), 781-787.
[2] L.M. Yagupolskii, K.I. Petko, T.M. Sokolenko, *J. Fluor. Chem.* 2005, **126** (9), 1342-1346.
[3] K.I. Petko, S.Yu. Kot, L.M. Yagupolskii, *J. Fluor. Chem.* 2008, **129** (11), 1119-1123.
[4] K.I. Petko, S.Yu. Kot, L.M. Yagupolskii, *Zhurn. Org. Khim.* 2010, **46** (4), 555-559.
[5] K.I. Petko, S.Yu. Kot, L.M. Yagupolskii, *J. Fluor. Chem.* 2008, **129** (4), 301-306.
[6] K.I. Petko, L.M. Yagupolskii, *J. Fluor. Chem.* 2001, **106** (2), 211-214.
[7] L.M. Yagupolskii, T.M Sokolenko. K.I Petko, *Zhurn. Org. Khim.* 2005, **41** (3), 437-440.

L-26

FUNCTIONALIZED FLUORINATED CARBA-CLOSO-DODECABORATES − M[1-R-closo-1-$CB_{11}F_{11}$] (R = NC, H_2N, PhHg, M = K, Cs, [Et_4N]) −

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The properties of the carba-*closo*-dodecaborate anion strongly depend on the substituents bonded to the {*closo*-1-CB_{11}} cluster.[12, 13] Especially undecafluorinated {*closo*-1-CB_{11}} clusters with a functional group bonded to the cluster carbon atom exhibit unusual reactivities. One example is the anion [1-H_2N-*closo*-1-$CB_{11}F_{11}$]$^-$ [14] that reacts with strong non-nucleophilic bases to result in the dianion [3-NC-*closo*-$B_{11}F_{10}$]$^{2-}$,[15] and a second example is the anion [1-NC-*closo*-1-$CB_{11}F_{11}$]$^-$ [16] that readily reacts with water (Fig. 1).

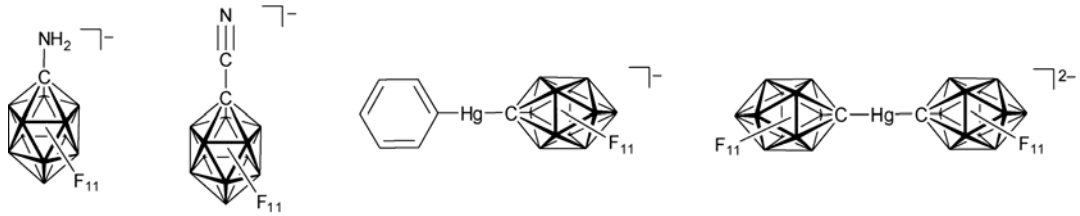

Fig. 1. Undecafluorinated carba-*closo*-dodecaborate anions with an amino or cyano group or Hg(II) bonded to the cluster carbon atom.

[Et_4N]$^+$ salts of the anionic Hg(II) complexes [1-PhHg-*closo*-1-$CB_{11}F_{11}$]$^-$ and [Hg(*closo*-1-$CB_{11}F_{11}$)$_2$]$^{2-}$ are accessible by the reaction of [*closo*-1-$CB_{11}F_{11}$]$^{2-}$ with PhHgCl and $HgCl_2$, respectively. The Hg(II) atom in the dianion [Hg(*closo*-1-$CB_{11}F_{11}$)$_2$]$^{2-}$ is coordinated by a solvent molecule, e.g. in [Hg(*closo*-1-$CB_{11}F_{11}$)$_2$(NCMe)]$^{2-}$ and [Hg(*closo*-1-$CB_{11}F_{11}$)$_2$(H_2O)]$^{2-}$. In contrast, the Hg(II) atom of [1-PhHg-*closo*-1-$CB_{11}F_{11}$]$^-$ is not coordinated by a further ligand (Fig. 2). The spectroscopic and structural properties of these complexes will be compared to data of related mercury(II) complexes.

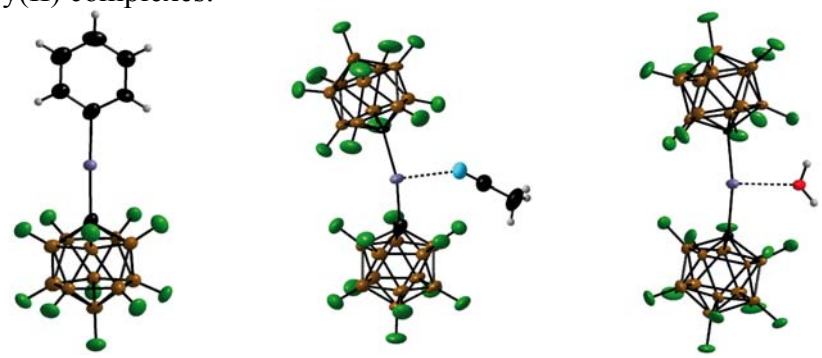

Fig. 2. The anionic Hg(II) complexes [1-PhHg-*closo*-1-$CB_{11}F_{11}$]$^-$, [Hg(*closo*-1-$CB_{11}F_{11}$)$_2$(NCMe)]$^{2-}$, and [Hg(*closo*-1-$CB_{11}F_{11}$)$_2$(H_2O)]$^{2-}$ in their [Et_4N]$^+$ salts.

This research project was supported by the Deutsche Forschungsgemeinschaft (DFG).

[1] S. Körbe *et al. Chem. Rev.* 2006, **106**(12), 5208-5249.
[2] S.V. Ivanov *et al. J. Am. Chem. Soc.* 1998, **120**(17), 4224-4225.
[3] M. Finze *et al. Inorg. Chem.* 2007, **46**(23), 9873-9883.
[4] M. Finze *Angew. Chem. Int. Ed.* 2007, **46**(46), 8880-8882.
[5] J.A. Sprenger *et al. Dalton Trans.* 2010, **39**(10), 2708-2716.

L-27

SYNTHESIS AND PROPERTIES OF PERFLUOROALKYL BORON DERIVATIVES

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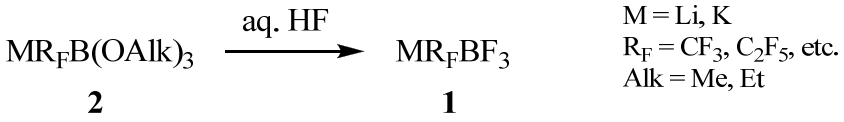
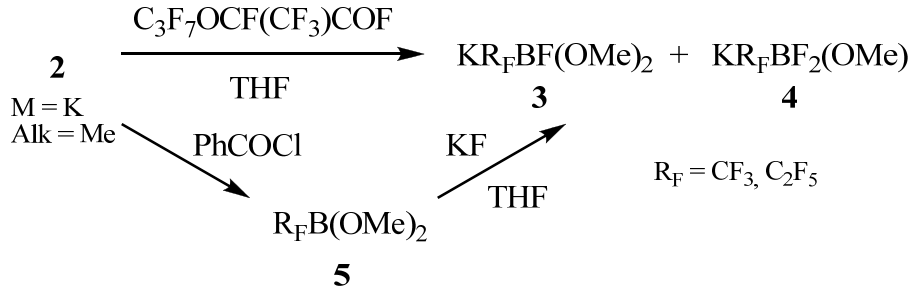
The fluoroalkyltrifluoroborates (**1**) are undoubtedly of practical interest being applied as fluoroalkylating agents [1], ionic liquids and electrolytes [2]. These compounds can be obtained by the reaction of aq. HF with fluoroalkyltrialkoxyborates **2** [3-4].

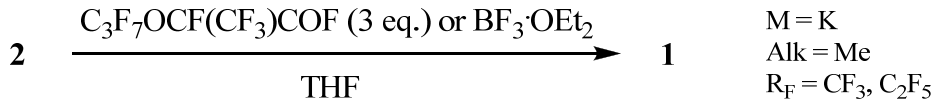


We have found that the reaction of **2** with perfluoroacyl fluorides leads to the formation of a mixture of salts **3-4**:



that is a result of the reaction of an intermediate ester **5** [5] with KF, generated in the course of the reaction.

In the presence of three equivalents of fluoroacyl fluoride, perfluoroalkyltrifluoroborate **1** is the only reaction product. Trifluoroborates **1** can be also obtained from **2** under the action of $BF_3 \cdot OEt_2$.



The reactions of salts **2** with other electrophiles are discussed.

1. S. Darses, J.-P. Genet. *Chem. Rev.* **2008**, 108, 288-325.
2. Z.-B. Zhou, M. Takeda, M. Ue. *JFC*. **2003**, 123, 127-131.
3. H.-J. Frohn, V. V. Bardin. *ZAAC*. **2001**, 627, 15-16.
4. G. A. Molander. *Organometallics*. **2003**, 22, 3313-3315
5. A. A. Kolomeitsev et al. *TL*. **2003**, 44, 8273-8277.

L-28

OXIDATION OF PERHALOGENATED DODECABORATES $[B_{12}X_{12}]^{2-}$ (X = F, Cl, Br, I) WITH ARSENIC PENTAFLUORIDE

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Perhalogenated dodecaborates $[B_{12}X_{12}]^{2-}$ (X = F, Cl, Br, I) are of fundamental interest as weakly coordinating dianions for the stabilization of unusual cations and dications in the solid state [1-3] and as anions for lithium ion batteries. The first solid diprotic super acid $H_2B_{12}Cl_{12}$ [4] and the strong methylating agent $Me_2B_{12}Cl_{12}$ [5] have been successfully prepared utilizing the perchloronated dodecaborate $[B_{12}Cl_{12}]^{2-}$.

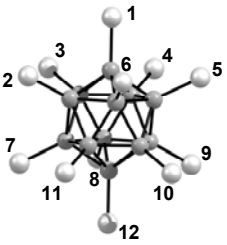

Fig. 1. PBE0/def2-TZVPP calculated structure of $[B_{12}Cl_{12}]^{2-}$ and numbering scheme.

Oxidation of halogenated dodecaborates was previously believed to be highly irreversible.[6] However, in the course of our investigations we discovered that the reaction of $Na_2[B_{12}X_{12}]$ with the strong oxidizing agent AsF_5 in liquid sulfur dioxide gives the corresponding radical anion $[B_{12}X_{12}]^{\bullet-}$ (X = Cl, Br) as a blue solid in high yield. The oxidation is reversible and the radical anion $[B_{12}X_{12}]^{\bullet-}$ itself is a strong oxidizer, which may be used to oxidize other substrates. EPR and NMR experiments in liquid SO_2 solution and the solid state and CV and UV/Vis measurements in SO_2 solution together with quantum chemical calculations confirm the formation of the radical anion $[B_{12}X_{12}]^{\bullet-}$ (X = F, Cl, Br, I).

[1] C. Knapp, C. Schulz, *Chem. Commun.,* 2009, 4991-4993.
[2] M. Keßler, C. Knapp, V. Sagawe, H. Scherer and R. Uzun, *Inorg. Chem.*, 2010, DOI: 10.1021/ic100337k
[3] V. Geis, K. Guttsche, C. Knapp, H. Scherer and R. Uzun, *Dalton Trans.*, 2009, 2687-2694.
[4] A. Avelar, F. S. Tham and C. A. Reed, *Angew. Chem. Int. Ed.*, 2009, **48**, 3491-3493.
[5] C. Bolli, J. Derendorf , M. Keßler, C. Knapp, H. Scherer, C. Schulz and J. Warneke, *Angew. Chem. Int. Ed.*, 2010, **49**, 3536-3538.
[6] W. Kaim, N. S. Hosmane, S. Záliš, J. A. Maguire and W. N. Lipscomb, *Angew. Chem. Int. Ed.*, 2009, **48**, 5082-5091.

L-29

FLUOROALKYL SUBSTITUTED THIOPYRAN DERIVATIVES

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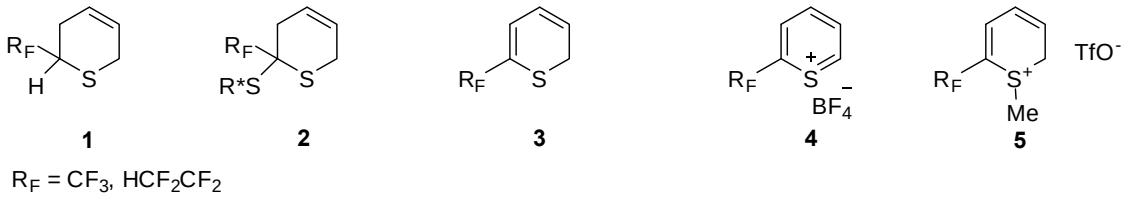
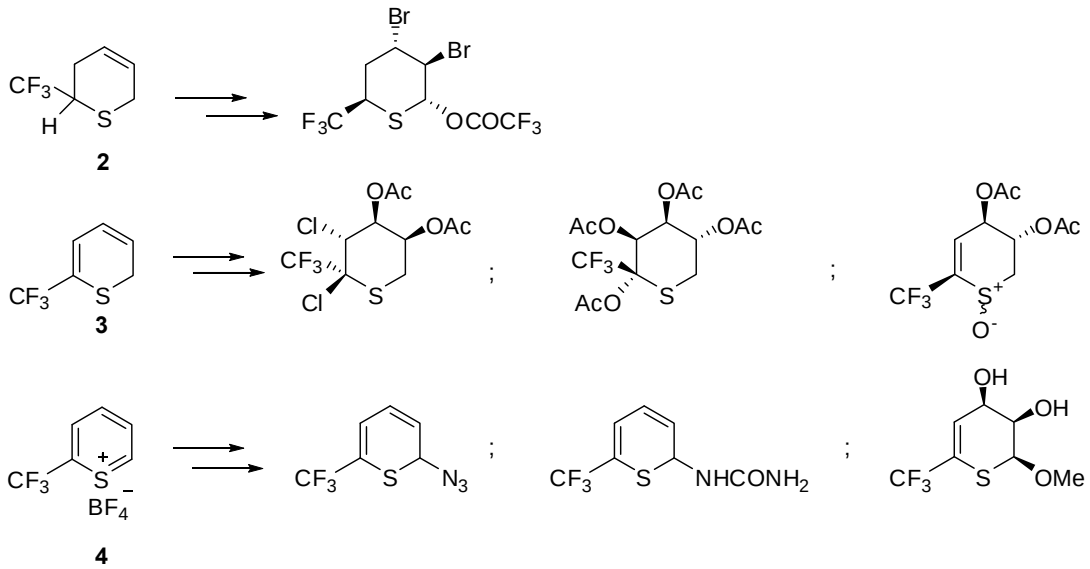
Thiopyran derivatives are a subject of considerable interest due to their potentially useful properties. In particular, numerous syntheses of sugar analogues with endocyclic sulfur as well as thionucleozides were developed because of their diverse biological activity and importance for carbohydrate chemistry and biochemistry[17,18]. Thiopyran derivatives bearing polyfluoroalkyl substituents are only briefly studied to date due to their low synthetic availability. Using of recently published convenient methods of polyfluorothiocarbonyl synthesis followed by their utilising as dienophiles in hetero-Diels-Alder reactions with 1,3-dienes[19,20] we developed simple procedures for preparing polyfluoroalkyl substituted sulfur-containing heterocycles (**1–5**, fig. 1).



R_F = CF_3, HCF_2CF_2

Fig. 1

Chemical transformations of **1–5** open a way to a number of highly substituted fluorinated thiopyran derivatives including unknown polyfluoroalkyl-containing thiosugar analogues (Scheme 1).



Scheme 1

[1] Z.J. Witczak *et al. Appl. Microbiol. Biotechnol*. 2005, **69**, 237–244.
[2] J.G. Fernandez-Bolanos *et al. Carbohydr. Chem. Biochem*. 2001, **57**, 21–29.
[3] A. Yu. Sizov *et al. Russ. Chem. Bull*., 2006, **55**, 1156–1163.
[4] V.M. Timoshenko *et al. J. Fluorine Chem.* 2010, **131,** 172–183.

L-30

SYNTHESIS AND TRANSFORMATIONS OF 3-FLUOROALKYL-2-(HET)ARYLHYDRAZON-1,3-DICARBONYL COMPOUNDS

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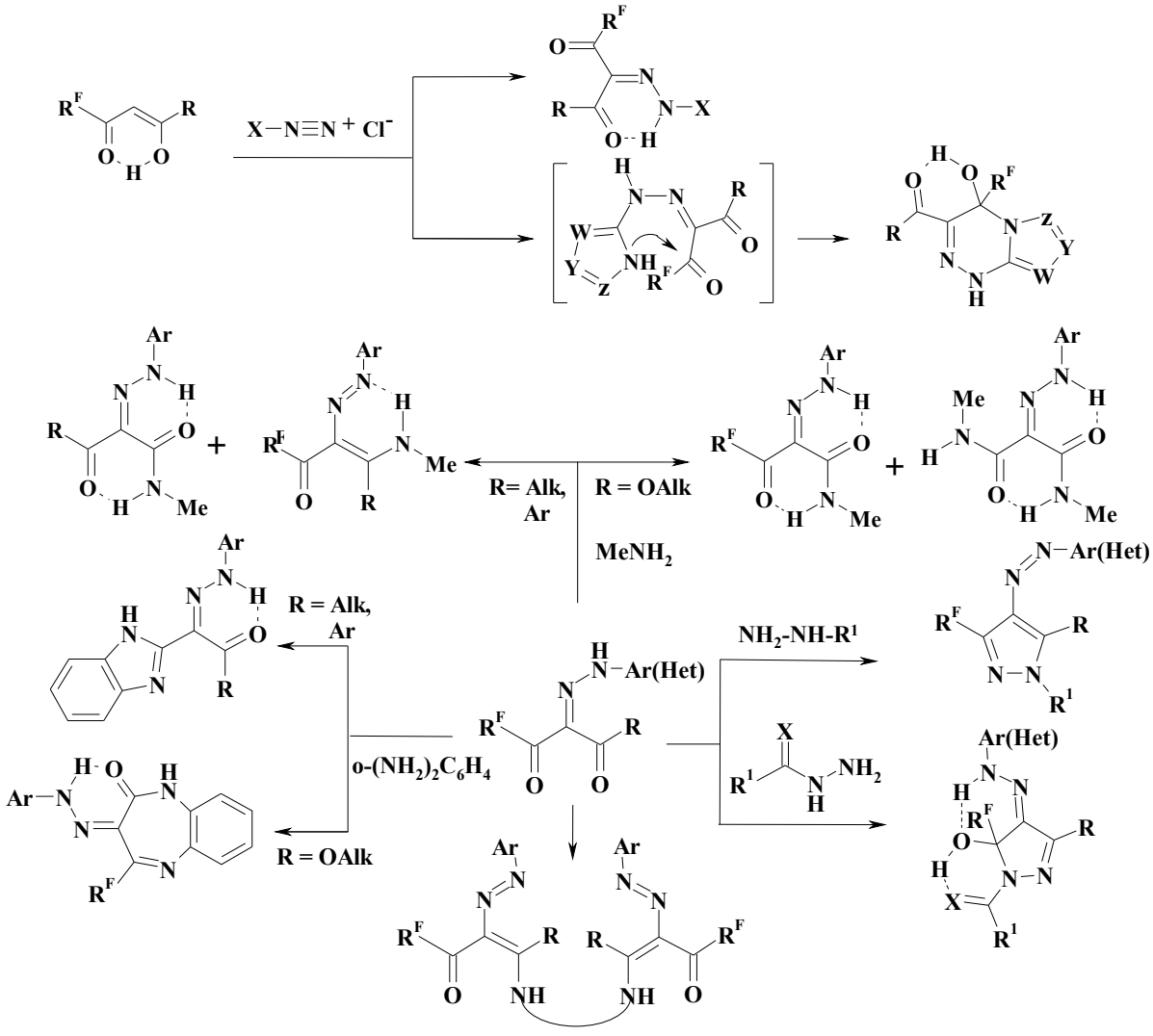
In this report we discuss the development of synthesis procedure of fluoroalkyl-containing 2-(het)arylhydrazono-1,3-dicarbonyl compounds and their derivatives. We have been studied their structure and chemical transformations to obtain new polydentate ligands and heterocyclic systems as the potential biologically active substances.



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L-31

STABLE *gem*-TRIFLUOROMETHYL ANIONIC σ-COMPLEXES BASED ON 1,3,5-TRIS(SULFONYL)BENZENE DERIVATIVES AND THEIR TRANSFORMATIONS

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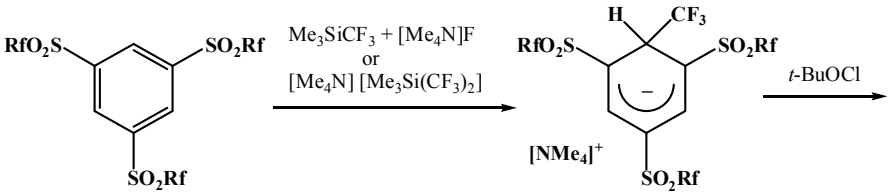
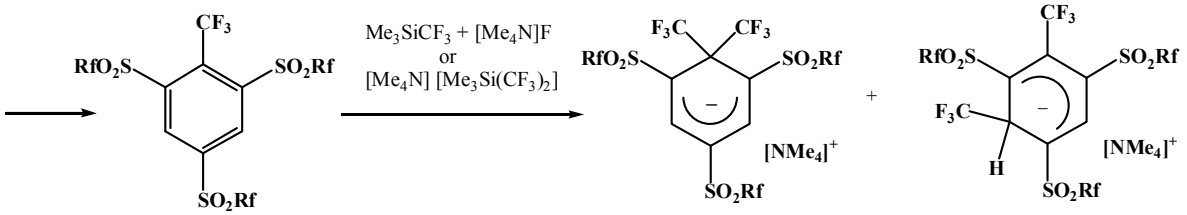
Trifluoromethyl-substituted compounds show significantly interesting features in field of medicine, agricultural chemicals and functional materials. Therefore, the methods for introducing a CF_3 group into an organic compound are investigated actively. The σ-complexes containing trifluoromethyl group at the sp^3-carbon atom could provide an original approach to the synthesis of the trifluoromethyl-containing aromatic products. Up to now the only one stable CF_3 – containing anionic σ-complex is described in literature[1].

We found that the reactions of 1,3,5-tris(sulfonyl)derivatives of benzene with Me_3SiCF_3/F^- or with silicate $[Me_4N][Me_3Si(CF_3)_2]$ lead to the formation of anionic σ-complexes. Most of adducts were isolated and fully characterized. But alongside with complexation, by-reactions at the sulfonyl center were observed in the case of sulfonyl fluoride (Rf = F) and trifluoromethylsulfone (Rf = CF_3). Stable anionic σ-complexes were successfully oxidized into benzotrifluorides which occurred to be able to interact with $[CF_3^-]$ forming mixtures of new stable anionic σ-complexes.



Rf = F; OCH_2CF_3 ; CF_3



Rf = OCH_2CF_3	9	:	1
Rf = F	3	:	7

[1] A.A. Kolomeitsev *et al. Tetrahedron Lett.* 1992, **33**, 6191.

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FLUOROALIPHATIC SULFOCHLORINE DERIVATIVES OBTAINED BY A METHOD OF THE PHOTOCHEMICAL SULFOCHLORINATION

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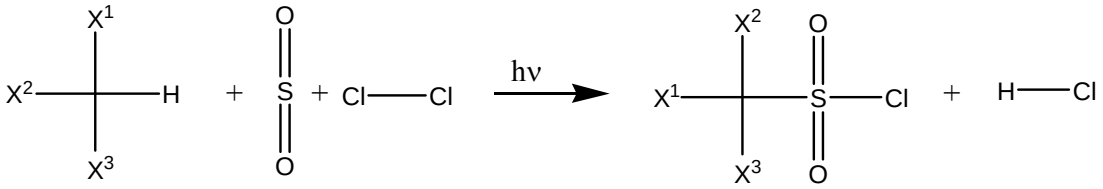
The fluorinated aliphatic sulphoacids and their derivatives use at the synthesis of medicinal substances, pesticides [1], and, also, as acid catalysts of various organic reactions [2]. However, existing now, methods of synthesis of these molecules connections possess a number of essential lacks, such as, low yields, synthesis severe constraints, complexity of allocation that causes high cost of the products in the world market and considerably are limited by their production. Usually one of route for difluoromethanesulphoacids reception is sulphonation of Freon-22 by sodium sulphite. Reaction is carried out in an autoclave within 20h at temperatures 120-150°C and high pressure from 80 to 150 atm., provided that the main product yields is no more than 50 % [2]. Therefore the research of essentially new synthesis route of the fluorinated aliphatic sulphoacids is an actual scientific and technical task.

The purpose of this work consisted in creation of a new synthesis route for fluoroalkansulphochlorides obtaining. We had been investigated reaction of sulphochlorination fluorine-substitute aliphatic hydrocarbons under the scheme 1.



$X^1X^2X^3 \equiv$ Cl,F ore H

Scheme. 1

Sulphochlorination carried out by photochemical method, at an irradiation of the fluorine-hydrocarbon, Cl_2 and SO_2 mixture by UV-radiation. As radiation sources UV-lamps (λ_{max} = 254, 310 nm) was served. Reaction was carried out in the flowing quartz photochemical reactor equipped with a jacket, connected to a thermostat. Reaction made in isothermal conditions at various temperatures in a range from -20 to +50°C. Pressure in system was supported close to the atmospheric. Sulphochlorination carried out both in gas, and in a liquid phase. Reaction made at equimolecular parities of fluorine-substitute hydrocarbon and Cl2, and at 1.5 - 5 multiple surplus of SO_2. As a result, the yielded method had been obtained a number of fluoroalkansulphochlorides with various yields. For the considered reaction thermodynamic estimations which are made are in the good consent with received experimental results. Structures of the all derivates were proved by means of NMR spectroscopy ^1H, ^{13}C and mass spectrometry.

The research was supported financially by ADTP "Development of scientific potential of the higher school (2009-2010)" (Project № 2.1.1/2430) and by FTP «Scientific and scientific and pedagogical shots of innovative Russia» for 2009-2013 (Projects № №02.740.11.0257 and № П74).

[1]Zili Chen, Wennan Xiong and Biao Jiang. Zn(ODf)2: preparation and application in asymmetric alkynylation of aldehydes// CHEM. COMMUN., 2002, 2098–2099.

[2]Schmeisser, M.; Sartori, P.; Lippsmeier, B.; Chemische Berichte; Chemische Berichte; vol. 102; (1969); p. 2150 - 2152

L-33

DIELS-ALDER REACTION OF 3-ACYLAMINO-6-POLYFLUOROALKYL-2*H*-PYRAN-2-ONE

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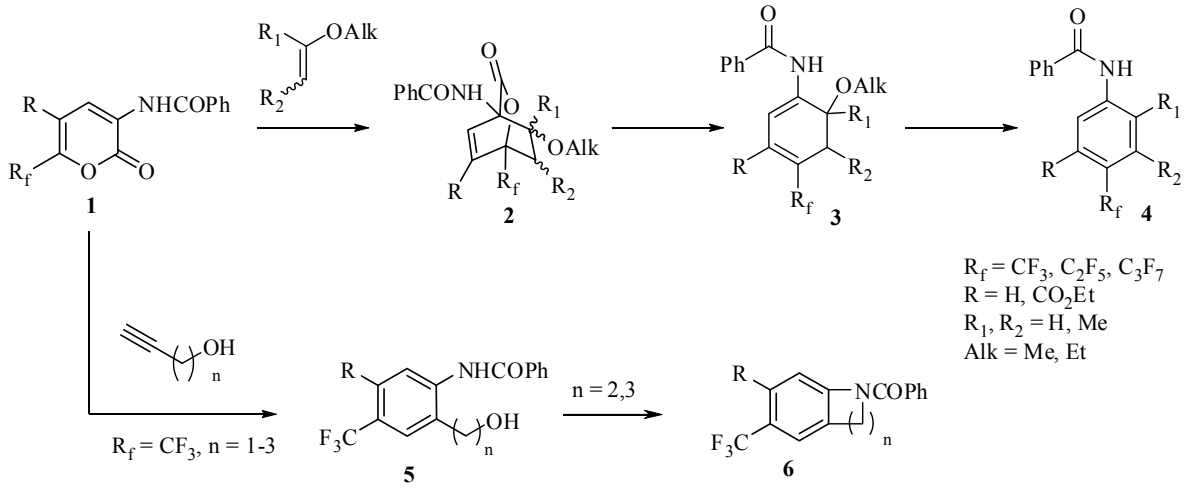
2*H*-Pyran-2-ones are widely used in organic synthesis as reactive synthons. Especially they are convenient substrates for Diels-Alder reaction which usually gives aromatic compounds after CO_2-elimination. However there are just few papers[1,2] which consider Diels-Alder reaction with polyfluoroalkyl containing pyrones though the reaction can be convenient method for the preparation of new polyfluoroalkyl containing aromatic compounds. Earlier[1] we described some examples of Diels-Alder reaction of 3-benzamido-6-(trifluoromethyl)-2*H*-pyran-2-one **1a** (R = H, R_f = CF_3). Now we report on broadened scope of the reaction using various both 6-polyfluoroalkyl pyrones and dienophyles.

In the cases of the Diels-Alder reaction of pyrones **1** with alkoxyalkenes under mild conditions stable intermediates **2** and/or **3** were isolated and characterized. Forced conditions led to the formation of 4-polyfluoroalkyl-*N*-benzoyl anilines **4**.

The reaction of CF_3-pyrones **1** with propargyl alcohol and its homologs led to the compounds **5** which were used for further cyclization giving heterocyclic products **6**.



Particularities of the synthesis as well as perspectivity of compounds synthesized as new fluorinated building blocks will be presented.

The research was supported financially by Deutsche Forschungsgemeinschaft (Az: Ha 2145/9-1; AOBJ:560896).

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[1] N. A. Tolmachova *et al. Eur. J. Org. Chem.* 2006, 4704-4709.
[2] B. I. Usachev *et al. Org. Lett.* 2008, **10**, 2857-2859.

L-34

INVESTIGATION OF HIGH-VALENT/HIGH-OXIDIZED COMPOUNDS BY COMBINATION OF FLUORINE CHEMISTRY WITH MATRIX-ISOLATION SPECTROSCOPY

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The discovery of novel high-valent inorganic species helps to enhance and expand our chemical understanding of the behavior of the elements and their compounds. Matrix-isolation spectroscopy in combination with quantum-chemical calculations represents an excellent combination for this kind of investigations. This was shown in our recent publications of HgF_4[1], IrO_4[2] and $[F_3]^-$[3]. Thus we like to report examples of our last research projects which have lead into a deeper understanding of novel high-valent compounds.

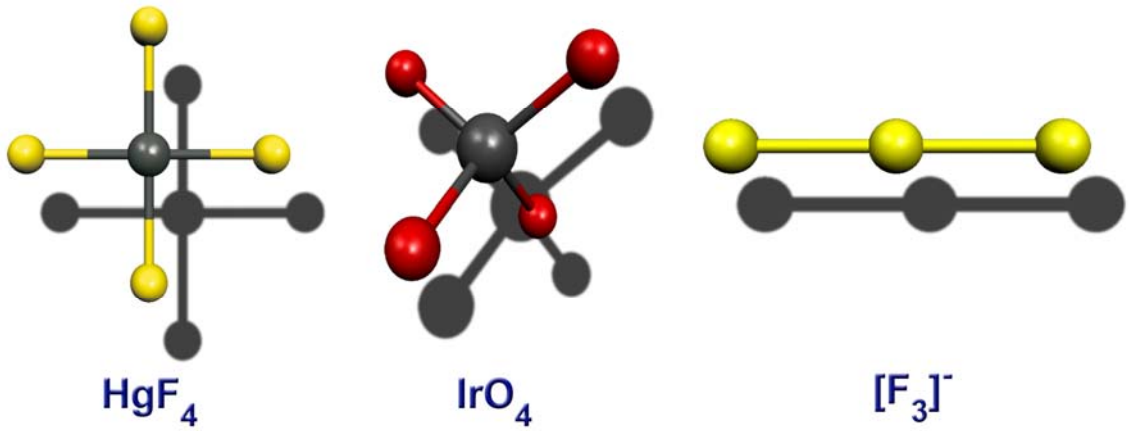

Figure 1. Compounds synthesized by matrix-isolation technique

The research was supported financially by Fonds der Chemischen Industrie, Deutschen Forschungsgemeinschaft (DFG) and Alexander von Humboldt Foundation.

[1] X. Wang, L. Andrews, S. Riedel, M. Kaupp, *Angew. Chem. Int. Ed.* **2007**, *46*, 8371.
[2] Y. Gong, M. Zhou, M. Kaupp, S. Riedel, *Angew Chem Int. Ed.* **2009**, *48*, 7879.
[3] S. Riedel, T. Köchner, X. Wang, L. Andrews, *Inorg. Chem.* **2010** *submitted.*

L-35

POLYFLUORINATED CHROMANES AND CHROMENES BASED ON NATURAL COMPOUNDS

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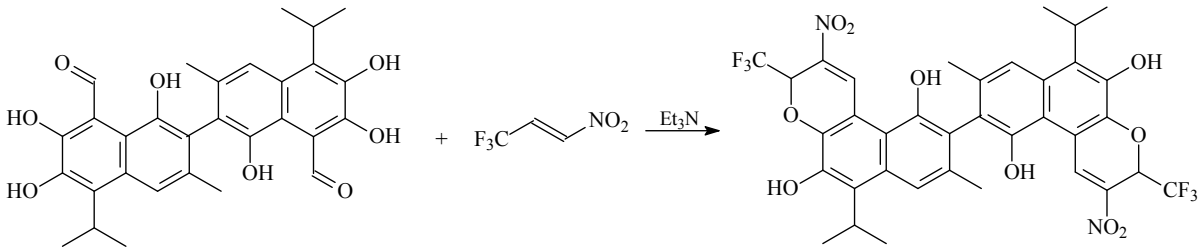
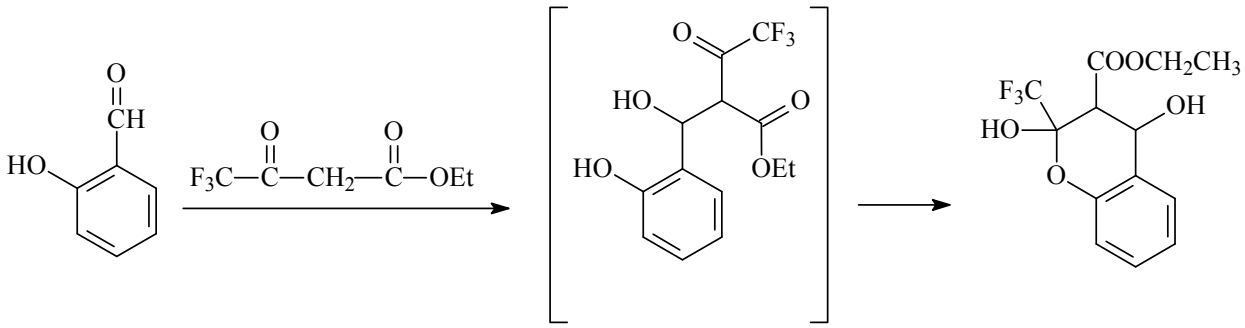
A new fluorinated polycyclic nitrochromene 6,6'-Diisopropyl-8,8'-dimethyl-2,2'-dinitro-3,3'-bistri-trifluoromethyl-3H,3'H-[9,9']di[benzo(f)chromenyl]-5,10,5',10'-tetraol was synthesized by the reaction between gossypol and its acetate with 3,3,3-trifluoro-1-nitropropene:



The structure of the derived compound was determined by means of PMR, NMR ^{19}F and ^{13}C including the use of COSY-NOEZY method. Crystals of the derivative were grown in order to determine the absolute configuration using X-ray structure analysis. The synthesized fluorinated nitrochromene shows significant antitumor activity.

It was discovered that the interaction of salicylic aldehyde as gossypol simulative compound with ethyltrifluoromethylacetoacetate results on the first stage in formation of 4,4,4-trifluoro-2-[hydroxy-(2-hydroxyphenyl)-methyl]-3-oleic acid ethyl ester which by intramolecular cyclization transforms into 3-ethylaceto-2,4-dioxy-2-trifluoro-methylchromen with good yield.



The chromane was defined by all of the available methods of physicochemical analysis including X-ray structure analysis.

The interaction of salicylic aldehyde and gossypol with other fluorinated electrophiles was studied as well.

The work is done with the financial support of the Federal Agency of Science and Innovations. State Contract № 02.512.11.2164.

L-36

SYNTHESIS OF MULTIFUNCTIONAL ALPHA-CF_3-ALPHA-AMINOCARBOXYLATES AND PHOSPHONATES VIA COPPER-CATALYZED 1,3-DIPOLAR CYCLOADDITION

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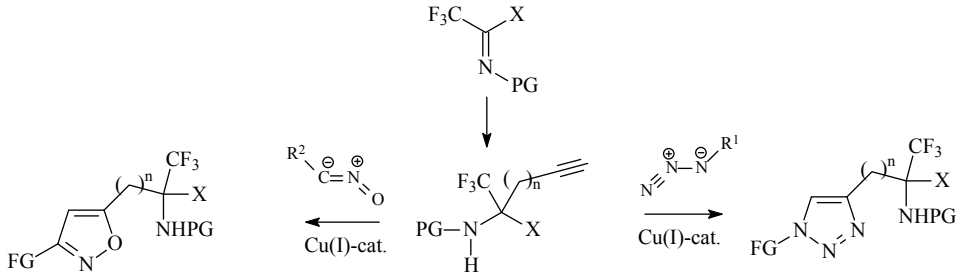
The development of new methods for the synthesis of five-membered heterocyclic compounds is an ever-expanding area in bioorganic and medicinal chemistry. Moreover the modern drug discovery requires the identification and the optimization of synthetic routes to specifically acting low molecular weight molecules. That is why simple methods that can quickly and easily generate large libraries of compounds have become more and more used[21]. The copper-catalyzed 1,3-dipolar cycloaddition[22] is one of these methods based on reactions which are of wide scope, give high yields, and use highly energetic reactants to form irreversible carbon–heteroatom bonds. Thus, we have investigated the ligation of 1,3-dipols such as azides or nitrile oxides and terminal alkynes to give the corresponding 1,2,3-triazole and 1,2-isoxazole derivatives[23]. Therefore, the proposed synthesis of new fluorinated α-aminocarboxylates and α-aminophosphonates bearing functionalized triazole and isoxazole moieties as additional pharmacophore groups is highly motivated both from synthetic and bioactivity point of view.

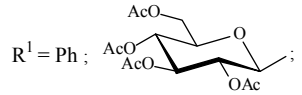


n = 0,1 X = CO_2Me, $P(O)(OEt)_2$

PG = Cbz, Boc; R^2 = Aryl

n = 0,1 X = $P(O)(OEt)_2$ PG = Cbz

R^1 = Ph ;



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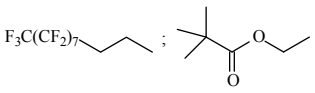

The research was supported financially by Deutsche Forschungsgemeinschaft (№. RO 362/37-1; № RO 362/42-1)and Russian Foundation for Basic Research (№ 06-03-04003).

[21] K. H. Bleicher *et al. Nat. Rev. Drug Discovery*, 2003, **2**, 369-378; (*b*) J. F. Pritchard, *et al. Nat. Rev. Drug Discovery*, 2003, **2**, 542-553.
[22] R. Huisgen, in: *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley, New York, 1984.
[23] D. V. Vorobyeva *et.al. J. Fluor.Chem,* 2010, **131** (3), 378-383.

L-37

STUDY OF PERFLUOROKETENE DITHIOACETALS AND PERFLUOROKETENE-N,S-ACETALS IN THE SYNTHESIS OF NEW FLUORINATED ACYCLIC AND HETEROCYCLIC COMPOUNDS

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E-mail: misergey@yahoo.com, sherm@ioch.kiev.ua
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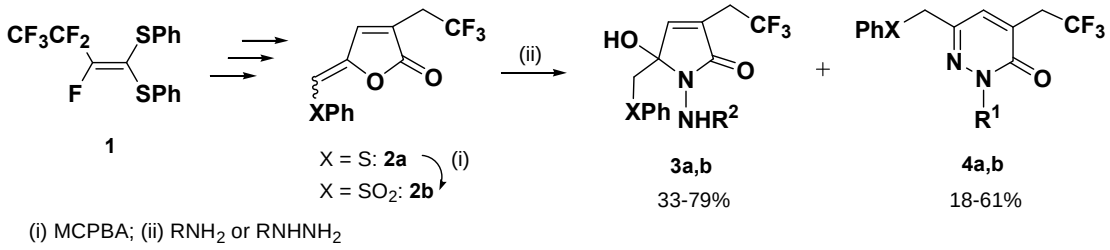
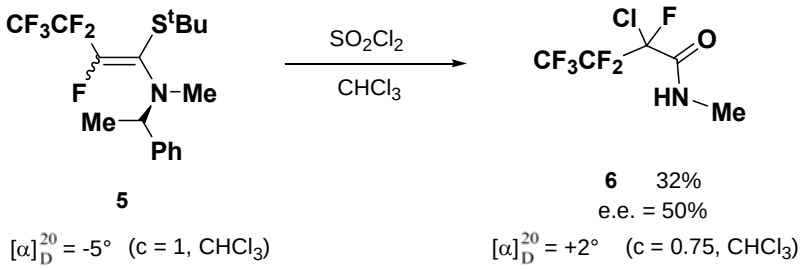
Perfluoroketene dithioacetals are versatile building blocks for the synthesis of a wide variety of fluorinated nitrogen-containing heterocycles [1]. γ-Lactone 2a was obtained from perfluoroketene dithioacetal 1 according to reported procedures [2]. Here we report on the reactions of 2a and 2b with various substituted amines and hydrazines to give the new γ-lactams 3a,b and pyridazin-3(*2H*)-ones 4a,b [3a,b] (Scheme 1).



Scheme 1

Also we have investigated hydrolysis, oxidation and chlorination reactions of perfluoroketene-N,S-acetals as a new type of fluorinated compounds [4]. We have found that chlorination of chiral N,S-acetal 5 with sulfuryl chloride led to optically active α-chloro perfluoroamide 6 as a result of asymmetric induction.



Scheme 2

Compound **6** is the first example of optically active α-chloro perfluoroalkane carboxylic acid derivatives.

[1] C. Portella *et al. ACS Symposium Series # 911*, Soloshonok, V. A. Ed., Oxford University Press, American Chemical Society, Washington D.C., 2005, Chapter 12, 232-247.
[2] J.P. Bouillon *et al. Synthesis* 2006, 1050-1056.
[3] (a) J.P. Bouillon *et al. J. Fluorine Chem.* 2007, **128** (8), 931-937. (b) S.S. Mykhaylychenko *et al. Journal of Fluorine Chem.* 2009, **130** (4), 418-427.
[4] S.S. Mykhaylychenko *et al. Journal of Fluorine Chem.* 2009, **130** (10), 878-885.

L-38

UNUSUAL REACTIONS OF TRIFLUOROMETHYL(BROMO)ENONES WITH NUCLEOPHILES

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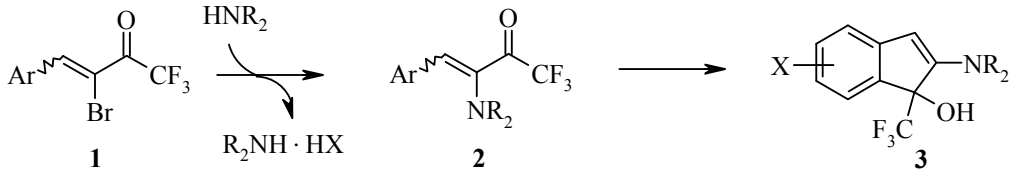
The fluorinated polyfunctional building blocks as starting materials for the *de novo* preparation of a wide ring of bioactive compounds attract an increasing interest. The use of α,β-unsaturated trifluoromethylketones in the modern organic synthesis is well established.[24] At the same time the chemistry of the corresponding halogen- and amino derivatives which could be versatile building blocks in the synthesis of various biologically important carbo- and heterocycles remains till now *terra incognita*.

We have developed an elegant one-pot synthesis of trifluoromethylated indenols starting from α-bromo-α,β-unsaturated trifluoromethylketones. To our surprise, the treatment of 4-aryl-3-bromo-1,1,1-trifluorobut-3-en-2-ones **1** with secondary amines (two equiv.) does not give the expected captodative carbonyl-bearing aminoalkenes **2**[25] but leads easily to the corresponding indenols **3** under very mild conditions (room temperature, ether, without catalyst). When the reaction of secondary amines is performed with *meta*-substituted bromoenones **1**, the mixture of two isomeric indenols is always formed.[26]



Scheme 1. Synthesis of trifluoromethylated indenols 3.

From a mechanistic point of view, the formation of indenols 3 can be explained in terms of a multistep process. The key steps of these domino transformations seem to be: i) aza-Michael addition of amine to the double bond of bromoenone 1 followed by nucleophilic substitution of the halogen atom at the sp^3-carbon atom and β-elimination of an amine molecule forming the captodative carbonyl-containing aminoalkene. In the case of the strong electron-withdrawing group $C(O)CF_3$, the following hydroxyalkylation reaction of intermediates **2** gives readily indenols **3**. In some cases aminoenone **2** can be isolated or detected by the NMR spectroscopy. During the monitoring of the reaction the intensity of the aminoenone signals decreases while the signals of target indenol increase. These facts demonstrate clearly that ketones 2 are really direct precursor of indenols **3**.[27]

Non-trivial reactions of the same bromoenones **1** with both N,N- and N,O-binucleophiles will be discussed together with recent results on the action of binucleophiles (aminoalcohols and diamines) on similar non-fluorinated enones.

The research was supported financially by Russian Foundation for Basic Research (Project No. 08-03-00067a).

[1]S.V. Druzhinin *et al. Tetrahedron* 2007, **63** (33), 7753-7808.
[2]A.Yu. Rulev. *Russ.Chem. Rev*. 2002, **71** (3), 195-221.
[3]A.Yu. Rulev *et al*. *Tetrahedron,* 2008, **64** (35), 8073-8077.
[4]A.Yu. Rulev *et al*. *Eur. J. Org. Chem.*, 2007, 6039-6045.

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