P-01

MOLECULAR STRUCTURE OF 1-AMINOPYRAZONIUM CATIONS

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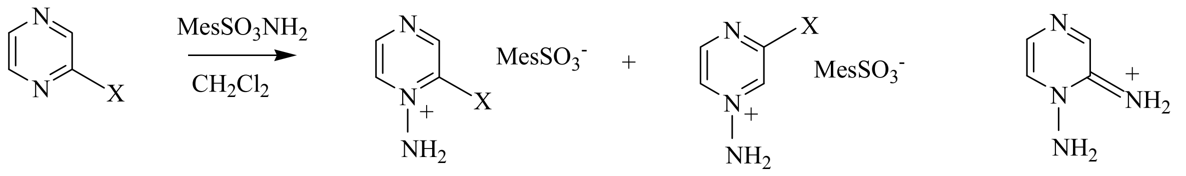
X-ray data for the structure of N-amine salts of nitrogen-based heterocyclic compounds are few in number, and they are absent for N-amine salts of diazines (see [1]).

Our objective was to study the structure peculiarities of 1-amine-2-X-pyrazonium cations by the means of X-ray analysis, and to check for adequacy the quantum-chemical forecast of those cations geometry.

Those cation salt crystals **1a-e** were prepared through the interaction between 2-X-pyrazines (**2a-e)** and O-mesitylsulfonylhydroxylamine.



2A-D **1A, B** **1C, D, E** **A**

X = H(a), NH_2(b), NHAc(c), MeO(d), Cl(e)

According to X-ray data the skeleton of **1a-e** cations is virtually plane and, reasoning from their valence angles, the hybridization of C and N atoms is close to sp^2. For all those cations the valence angle at nitrogen belonging to NH_2 ($C^2N^1C^6$) exceeds considerably $C^3N^4C^5$ valence angle. Judging from the H–N–H and H–N–N angle values in cations **1a-c**, the hybridization of nitrogen in the amine group is close to sp^3, while in **1d** and **1e** ions it is close to sp^2. N^1–NH_2 bond length in **1b** cation is close to that of N–N single bond, while C^2–NH_2 bond length is shorter being close to that of usual $C_{sp}{}^2$=N double bond. This points to the significant contribution of imine **A** structure to the resonance hybrid.

For all **1a-e** cations the corresponding quantum chemical computations [AM1, PM3, HF/6-31G+(d,p), DFT/3z, B3LYP/6-31G++(2d,p)] result in geometry close to experimental one, the hybridization of nitrogen in amine group being sp^3.

The paper deals with the peculiar features of pyrazine amine cations discussed in comparison with similar cations of some other nitrogen-containing heterocycles.

This study was financially supported by Russian Fund of Fundamental Research (Project № 06-03-32406) and Chemicals and Materials Department of Russian Academy of Sciences (Program № 5.1.9).

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[1] Р.В. Андреев, Г.И. Бородкин, Ю.В. Гатилов, М.М. Шакиров, В.Г. Шубин. *Ж. орг. хим*. **2004**, *40,* 595.

P-02

REGIOSELECTIVITY OF AMINATION OF PYRAZINES

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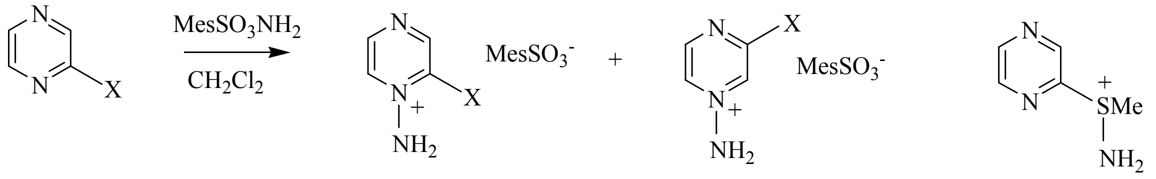
Azine N-amine salts are widely applied in the synthesis of heterocyclic compounds. When an azine cycle contains either variously surrounded nitrogens or a substituent capable of interacting with some aminating reactant, the question arises of regioselectivity of the amination process [1, 2]. Mono-substituted pyrazines offer an interesting model for the question solving.

Interaction between O-mesitylsulfonylhydroxylamine and X-pyrazines (**1a-i, k-m**) in CH_2Cl_2 resulted in a number of cations (**2a-d, f, g**) and (**3a-i, k-m**). We failed to observe **2h** cation because at the reaction conditions it underwent cyclization to give 2-methyl-[1,2,4] triazole [1,5-*a*] pyrazine. Amination does not occur when the pyrazine contains substituents that exhibit considerable M-effect (X = Ac, CN, COOMe, σ_R = 0.20, 0.08 and 0.11 correspondingly), and in the case of pyrazine **1j** MeS group is drawn into interaction to give cation **4**. The structure of amine cations was recognized by NMR ^1H and ^{13}C method.



1A-M **2A-D,F-H** **3A-I, K-M** **4**

X = H(a), Me(b), Et(c), *i*-Pr(d), *t*-Bu(e), CH(OH)Me(f), NH_2(g), NHAc(h), MeO(i), MeS (j), Cl(k), I (l), $CONH_2$(m), Ac(n), CN(o), COOMe(p)

The cation **2a-d,f-h** to cation **2a-d,f-h** ratio is described by the correlation as follows:

$$\lg [\mathbf{2}]/[\mathbf{3}] = (-0.29\pm0.07) - (1.52\pm0.28)\cdot\sigma_R^0 + (0.95\pm0.11)\cdot E_s^0,\quad r = 0.977,\ s = 0.12,\ n = 7$$

The relation does not work for pyrazines with the substituents that contain non-conjugated unshared electron pairs (X = MeO, Cl, I), and we interpreted the fact within the framework of quantum-chemical computation by DFT method.

This study was financially supported by Russian Fund of Fundamental Research (Project № 06-03-32406) and Chemicals and Materials Department of Russian Academy of Sciences (Program № 5.1.9).

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[2] Р.В. Андреев, Г.И. Бородкин, М.М. Шакиров, В.Г. Шубин. *Ж. орг. хим.*, **2004**, *40,* 1426.

P-03

X-RAY DIFFRACTION AND QUANTUM-TOPOLOGICAL STUDY OF INTERMOLECULAR INTERACTIONS IN HOMOCRYSTALS OF PARTIALLY FLUORINATED QUINOLINES.

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Non-valence π-stacking interactions between aromatic and polyfluoroaromatic nuclei are of considerable interest for crystal engineering. In this connection recently large attention was also given to accompanying π-stacking weak intermolecular interactions C-H…F-C, C-F…p and F…F. However, their role in crystal formation is not studied completely by now. A possible approach to the problem solving would be the research on homocrystals of fluorinated substances that contain condensed benzene and heterocycle rings.

We undertook X-ray study of homocrystals of 5,6,7,8-tetrafluoroquinoline (1), 5,6,8-trifluoroquinoline (2), 5,7-difluoroquinoline (3), 2-phenyl-5,7,8-trifluoroquinoline (4)*, 5,7,8-trifluoro-6-trifluoromethylquinoline (5). It was shown that the main types of interactions in stack motives of those systems were π…π polyfluoroarene..polyfluoroarene, polyfluoroarene..heteroarene, heteroarene..heteroarene interactions. Besides of that it was found that C-F…π interactions were of considerable importance for substances 1, 2, and 5. In all those cases the molecules that belong to different stacks are mainly connected via F…H, F…F and H…N interactions. Those results were confirmed by topological investigation of electronic density distribution in crystal fragments of substances 1-5 and 1,3,4-trifluoroisoquinoline, computed with DFT/B3LYP with basic set 6-311G (d,p), using also AIM theory. We found the critical points (3, -1) of electron density that determine intermolecular bonding in the systems under study. We applied Chioslovsky-Mikson approach to calculate the order of intermolecular bonds in the obtained critical points. We also determined the atom pairs the contacts of which contribute at most to the molecular bonding at the crystal formation. It was shown that initiation of polyfluoroarene…polyfluoroarene, polyfluoroarene…heteroarene и heteroarene…heteroarene contacts depend mainly on intermolecular bonding of carbons belonging to their aromatic rings. Usually those bond orders are 0.013-0.015. C..F bonds with orders 0.010-0.012 contribute the greatest possible share to C-F…π interactions. As to F…H, F…F and H…N bonds between molecules belonging to different stacks their bonding order is widely variable, ranging from 0.009 to 0.034.

This study was financially supported by Russian Fund of Fundamental Research (№ 06-03-32229, № 07-03-96041-р).

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* E.V. Panteleeva, V.D. Shteingarts, J. Grobe, B. Krebs, M.U. Triller, H. Rabeneck, Z. Anorg. Allg. Chem. 2003, *629*, 71.

P-04

INTERMOLECULAR INTERACTIONS AND PACKING EFFECTS IN BENZODITHIADIAZINES DERIVATIVES CRYSTALS

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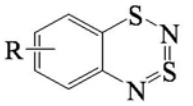
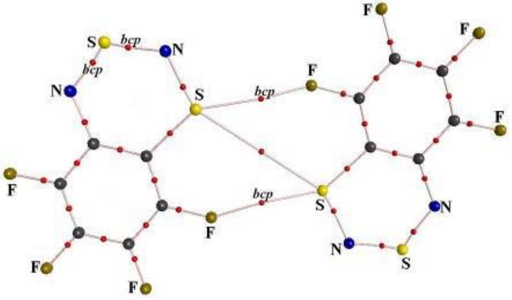
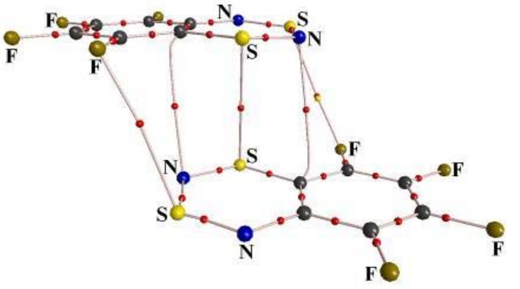
A number of benzodithiazines with various substituents in their carbocycles are hyperelectron compounds, their molecular structure being nearly planar. According to X-ray data in the event of R = H; 6-F; 5,6,8-F_3; 5,6,7-F_3; 5-CF_3; 7-OCH_3; 7-Br those molecules are virtually flat, while in the case of R = 5-OCH_3; 6-CH_3; 5,7-t-Bu, 6,8-F_2 the molecule is bent along its S1…N4 axe by 10.8(2)°, 6.9(1)°, or 25.2(2)° correspondingly. In the case when R = 5,6,7,8-F_4; 5-Br; 6-Br; 8-Br the bending angle of dithiadiazine cycle ranges between 3.1° to 8.3°.



For the above structures we calculated their molecular geometry within the isolated molecule approximation (6-31G(d,p)). Electronic properties were calculated for benzodithiazine dimers those being pairs of neighbouring molecules in the crystal, considerably connected through intermolecular bonding. The properties of molecular interactions between the pairs of neighbouring molecules were obtained through the use of topological analysis of electron density ρ(r) and corresponding Laplacian within the software package AIMPAC.





It was established that the molecule polarity (t- criterion 2.6) is among the factors governing their classification either with planar or non-planar structures. The polarity of non-planar structures is much higher. Yet, in average, much higher localization of electron density within the covalent bonding area is intrinsic for planar structures. Certain peculiarities of S=N bonds were revealed in dithiadiazine cycles. For those bonds their critical points of electronic density have got high positive Laplacian values $\nabla^2\rho$=0.60÷0.79. So dramatic decay of electronic density within the bonding area, as to compare with adjacent neighbourhood, is indicative of the non-covalent bonding. In the area of both lateral and stacking molecular interactions S…S, S…N, S…Hal there are critical points of electronic density that correspond to bonding (*bcp* – bond critical point).

The above approach made it possible to establish that the tendency to non-planarity of the corresponding dithiadiazine cycles is provided both by the electron properties of their structure, and by their packing factors.

P-05

FLUOROCONTAINING GLYCIDYL ETHERS. SYNTHESIS AND REDUCTIVE REACTIONS

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Fluorinated glycidyl ethers (FGE) are important intermediates in the synthesis of various polymer materials known for their unique physico-chemical properties [1]. The search for FGE manufacture processes and studies on FGE reactivity are issue of the day.

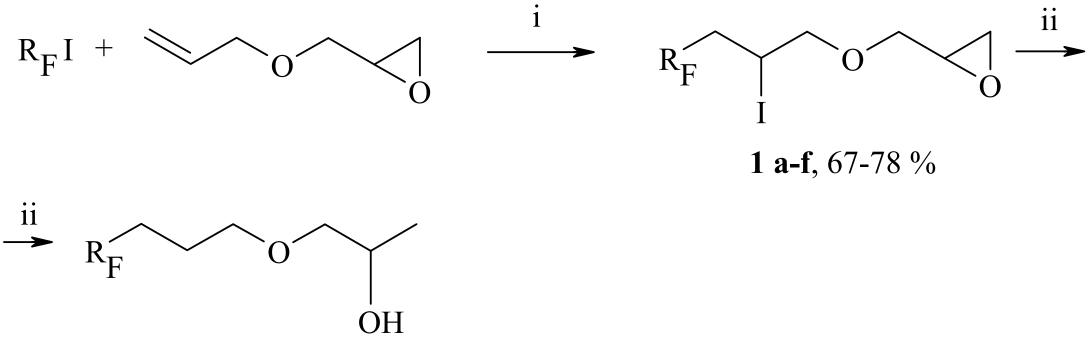
It is well known that FGE synthesis may be conducted through three main routs: epoxidation of allyl ethers prepared from fluorinated alcohols and allyl halogenides [2], addition of glycidol to polyfluoroalkene [3], and interaction between fluorinated alcohols and epichlorhydrin [1].

In this our study the reaction between polyfluoroalkyl iodides (R_FI) and allylglycidyl ether at radical conditions resulted in FGE **1 a-f** synthesized with high yield (see Diagram). None of other products were identified in the reaction media.

We found that the usage of Bz_2O_2 in radical addition of R_FI to allylglycidyl ether resulted in by rather low yield of FGE **1 a-f** (30-40 %) and formation of hydrogenated products (R_FH)**.**

Under the action of $LiAlH_4$ bifunctional FGE **1 a-f** undergoes reduction by its oxirane ring and C-I group, resulting in corresponding hydroxy ethers **2 a-f**.

Diagram



1 a-f, 67-78 %

2 a-f, 83-89 %

R_F= $F(CF_2)_6$ (a), $H(CF_2)_6$ (b), $Cl(CF_2)_6$ (c), $F(CF_2)_3$ (d), $F(CF_2)_4$ (f)

i : $Na_2S_2O_4/NaHCO_3$, $CH_3CN:H_2O$; ii : $LiAlH_4$, Et_2O

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P-06

FLUOROBENZENE RADICAL ANIONS: STRUCTURE FLEXIBILITY AND MONOMOLECULAR FRAGMENTATION

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One of the fundamental problems of modern chemistry is that of the search for connections between the chemical structure and reactivity of active organic intermediates that are very important with reference to synthesis reactions of reduction dehalogenation of arenes and nucleophilic substitution of $S_{RN}1$ type occur via formation of intermediate anion-radicals (AR) followed with their fragmentation. The structure of the potential energy surface (PES) is the key to detailed understanding of the AR fragmentation mechanism.

We undertook (CIS/6-31G*) computation of anionic states of various symmetry, that arise when electrons are captured by fluorosubstituted benzene derivatives. Depending on the number and mutual location of fluorines, and also on the presence of other substituents known for their donor or acceptor properties, the AR thus formed differ in the type of their ground electron state and distribution of their electron density. However, in any case, the existence of low lying excited states call forth complicated structure of PES.

The single theoretical approach (B3LYP/6-31+G*) is used here to investigate AR PES of multitude of fluorosubstituted benzene derivatives. It was found that structural flexibility is an inherent characteristic of all particles under study. Their PES are pseudo-rotation surfaces that account for Yahn-Teller structure of PES of the parent benzene AR. The pseudo-rotation cycle is formed by a various number of stationary structures, divided by comparatively low energy barriers. Typical out-of-plane distortions manifest themselves mainly through fluorine distortions out of the cycle plane. Transitions between stationary structures occur with considerable re-distribution of electron density. The rout of pseudo-rotation is at the same time that of inversion of non-planar structures.

The presence of a polyatomic substituent complicates PES structure thanks to possible superposition of the pseudo-rotation coordinate and characteristic movements of the substituent, those being internal rotation or inversion. For instance, possible inversion of amine group results in doubling of pseudo-rotation cycles for perfluoroaniline AR, $C_6F_5NH_2^{-}$.

The correlation between the PES structure and the anion F^{-} detachment capability is considered using monomolecular decomposition of fluorobenzene and isomeric difluorobenzene AR as an example. The loss in the yield of fluorine-anions, observed by [1] for AR *para*-difluorobenzene as to compare with AR fluorobenzene, is the only known and experimentally verified case when there is a violation of the general rule that the AR capability to decomposition grows with the number of fluorines in its aromatic ring; the said violation is due to the deceleration of the step of electron density transfer to the breaking bond due to the growth of the pseudo-rotation barrier.

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P-07

STRUCTURE CLUSTERING OF SPECTRAL SEARCH RESULT AS A METHOD OF STRUCTURE ELUCIDATION

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One of the steps in the recognition of organic substances structure with the help of spectral information retrieval systems is construction of hypothetical structural formulas of the unknown substance using the available set of structural fragments found during the spectral search. It is impractical to apply any structure formula generators for this job, if there is no information about large parts of molecular graphs. Preliminary determination of large structural fragments cuts down considerably the list of possible structures for the unknown substance. In case that in the search result (SR) we succeed to consolidate structurally similar compounds into corresponding groups, the probability of the large fragment determination increases.

In this work to form the most probable hypothesis concerning the structure of the compound under study were applied a structure formula generator GENM [1] and the large fragments found through the search in the IR spectra data base. To reveal the said fragments we conducted preliminary consolidation of SR-selected compounds into groups belonging to certain chemical classes (clustering structure). The structure formula analysis of the cluster compounds makes it possible to recognize a large related fragment in the compound under study. To describe the compound structure they are presented as an exhaustive set of related non-isomorphous fragments with 2 to 7 vertexes.

The proposed method was tested using a sample of 100 entries taken from the IR spectra data base involving ~32000 IR spectra and organic substances structures. Each SR selected 30 spectral analogues that were the most similar to the substance under study. Those 30 SR-selected items formed in average 5 clusters, each incorporating in average three structures to be further analyzed in order to choose a large structural fragment [2]. If not considering fragments with elemental compositions that do not agree with that of the substance under study, (the structure formula generator is only applicable when the molecular formula of the substance under study has been determined) then in the average the number of structures for the fragments selected from the taxons are half as many as in the sample as whole.

Introduction of the method in 17 cases enabled to select a singular and the only correct structure for the compound under study. In 25 cases the usage of the large fragment selected from the cluster resulted in the development of a reasonable number of hypotheses (2 to 20) about the structure of the unknown substance.

This study in part was financially supported by Russian Fund of Fundamental Research (Project Grant № 07-07-00113).

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P-08

NEW APPROACH TO THE SYNTHESIS OF CHIRAL α-AMINOPHOSPHONATES

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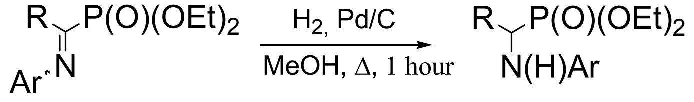
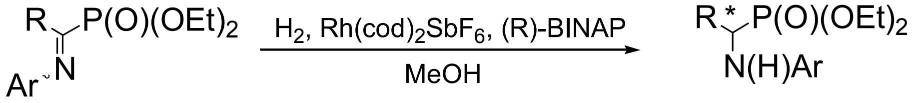
A new method is developed for the manufacture of racemic and optically active esters of α-aminephosphono acids, based on catalyzed reduction of the related α-iminophophonates.

Racemic α-aminephosphonates are prepared through heterogenic hydrogenation of unsaturated precursors (synthesized by Arbusov reaction through the action of triethylphosphite on the corresponding imidoylchlorides) by hydrogen in the presence of catalytic amounts of carbon-supported palladium:



R = Ph, n-MeC_6H_4, n-FC_6H_4, t-Bu, CF_3 YIeld: 93-100%
Ar = Ph, n-$MeOC_6H_4$

To obtain optically active α- aminephosphonates enantioface differentiating hydrogenation of α- iminophophonates was carried out in the presence of chiral rhodium catalysts.



ee: 75-94%

P-09

FLUORINATION OF AROMATIC COMPOUNDS WITH F-TEDA-BF$_4$ IN SOLID STATE

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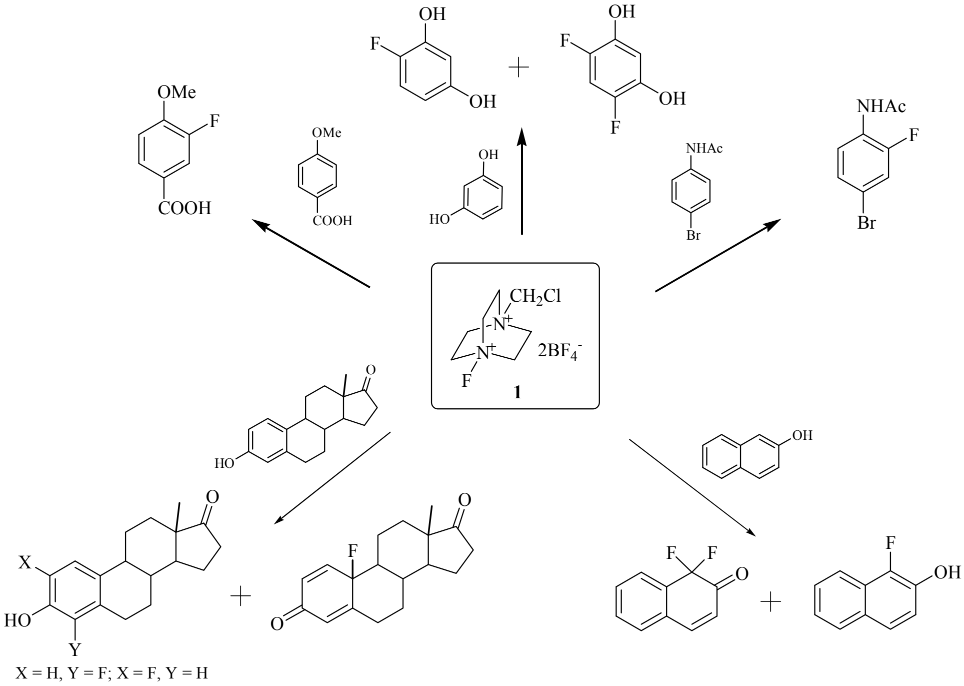
Development of environmental friendly processes for fluorination of aromatic compounds is an urgent issue [1]. In recent twenty years NF reagents are widely applied as fluorine sources in soft and selective fluorination of organic substances [2].

We proved that electrophylic fluorination of aromatic amines, phenols and the related ethers is realizable with the help of bis(tetrafluoroborate) 1-fluoro-4-chloromethyl-1,4-diazonium bicyclo[2.2.2]octane (F-TEDA-BF$_4$, **1**) in solid phase. The main reaction products are shown in the diagram below:



The structures of the obtained substances were confirmed by NMR ^{1}H, ^{19}F and chromato-mass-spectrometry.

The paper discusses both the reaction mechanism and peculiar features of phenol behaviour during their electrophylic fluorination in solid phase.

This study was financially supported by Russian Fund of Fundamental Research (Project № 06-03-32406, 07-03-00475-a) and by Chemicals and Materials Department of Russian Academy of Sciences (Program № 5.1.9).

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[1] P. Kirsch. *Modern Fluoroorganic Chemistry. Synthesis, Reactivity, Applications*. Weinheim: Wiley-VCH, **2004**.

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P-10

FLUORINATION OF AROMATIC AND *N*-HETEROAROMATIC COMPOUNDS WITH F-TEDA-BF$_4$ IN WATER

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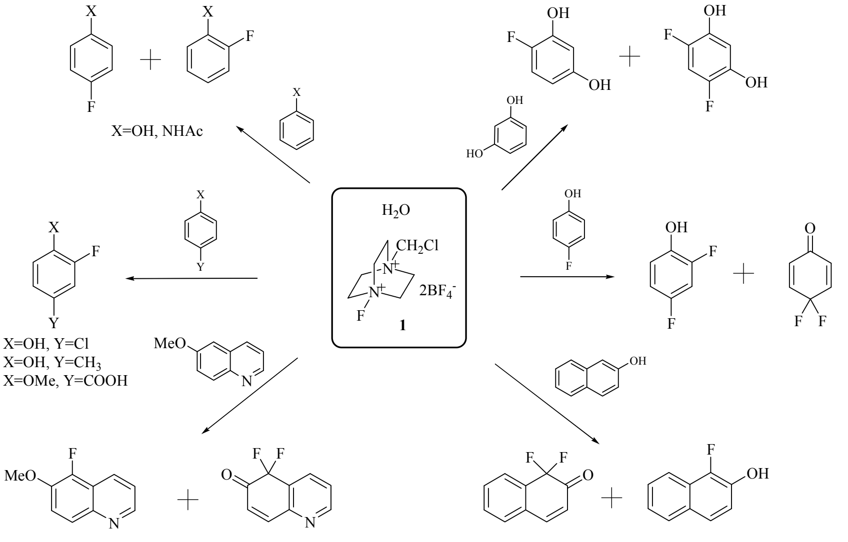
The growing interest in fluorinated aromatics stimulated by their wide usage for drugs, pesticides, dyes, liquid crystals and polymers [1] requires the development of environment friendly and economically feasible fluorination methods. In recent years water is often considered for an alternative to usual organic solvents [2]. This «live solvent» is non-toxic and incombustible, it stands high temperature, and its high polarity and ability to form hydrogen bonds provide its efficiency in heterolytic reactions.

We proved that electrophylic fluorination of aromatic amines, phenols and the related ethers is realizable with the help of bis(tetrafluoroborate) 1-fluoro-4-chloromethyl-1,4-diazonium bicyclo[2.2.2]octane (F-TEDA-BF$_4$, **1**) in water. The main reaction products are shown in the diagram below:



The structures of the obtained substances were confirmed by NMR ^{1}H, ^{19}F and chromato-mass-spectrometry.

The paper discusses both the reaction mechanism and regioselectivity of electrophylic fluorination of aromatics in water as to compare with usual organic solvents.

This study was financially supported by Russian Fund of Fundamental Research (Project № 06-03-32406, 07-03-00475-a) and by Chemicals and Materials Department of Russian Academy of Sciences (Program № 5.1.9).

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[1] P. Kirsch. *Modern Fluoroorganic Chemistry. Synthesis, Reactivity, Applications.* Weinheim: Wiley-VCH, **2004**.
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P-11

PENDULAR REARRANGEMENT OF EPIMERIC 3b,4,4a,5-TETRAMETHYL-3b,4,4a,5-TETRAHYDRO-4*H*-CYCLOPROPA-[*a*]PHENALEN-5-YL CATIONS

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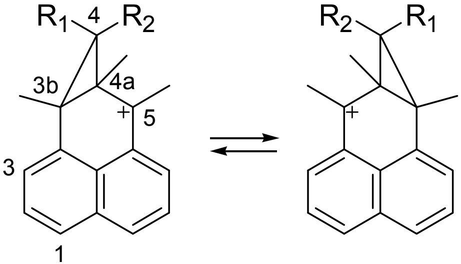
Earlier (see [1]) it was found that there is degenerated rearrangement of 3b,4-*exo*,4a,5-tetra-methyl-3b,4,4f,5-tetrahydro-4*H*-cyclopropa[*a*]phenalene-5-nyl cation (Ia) and its *endo*-epimer (Iб) generated under "long-life" conditions of carbocations. Typically, such rearrangement results in preserving of C^4-C^{4a} bond while C^{3b}–C^4 bond moves nearer to C^5 that is to the carbocation centre. By analogy with «rotary» carbocation rearrangement [2, 3] one may assume that the mechanism for ions rearrangement (Ia,б) involves one-step reversible shift of C^{3b}–C^4 bond similar to the swing of a pendulum, i.e. the diagram shows not only the original and final states of those cations (Ia,б) but also their rearrangement mechanism.



Ia,б I'a,б

$R_1 = CH_3, R_2 = H$ (a)
$R_1 = H, R_2 = CH_3$ (б)

Indeed, our quantum chemical computations using DFT method (NATURE software [4]) demonstrated that alternative rearrangement mechanisms are unlikely to work as corresponding energy thresholds exceed considerably that of one-step rearrangement.

Our dynamic NMR study on cation «pendulum» rearrangement (Ia,б) in acidic system CF_3SO_3H-$CHCl_3$ resulted in : $k^{25\ єC}$(Ia) = 2500 s^{-1}, $DG^{\#}$ 53.6 kJ/mole; $k^{25\ єC}$(Iб) = 40 s^{-1}, $DG^{\#}$ 64.0 kJ/mole. The decrease in velocity of the cation (Iб) rearrangement as to compare with (Ia) is probably attributable to unfavourable space interactions between *endo*-CH_3 and skeleton carbons in transient state.

This study was financially supported by Russian Fund of Fundamental Research (Project № 06-03-32406) and Chemicals and Materials Department of Russian Academy of Sciences (Program № 5.1.9).

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[3] F.-G. Klörner, *Top. Stereochem.* **1984**, *15*, 1.

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P-12

ON KINETIC STABILITY OF PLANAR “TRIANGULAR” BENZENE DICATION

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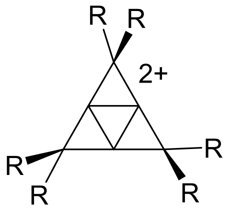
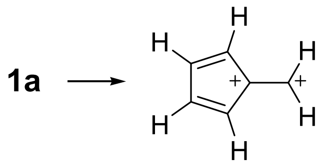
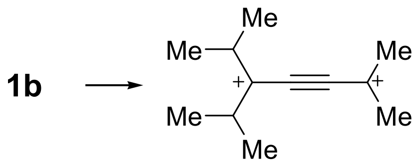


1 (**a**. R=H, **b**. R=Me)

Particles known for their unusual, non-classic structures occur widely in the chemistry of carbocations [1]. Among them «triangular» dication $C_6H_6^{2+}$ (**1a**) described by Indian researchers [2] is the most exciting subject in the mind's eye. The cation’s important peculiarity is the presence of planar tetracoordinated carbons in its structure. Both *ab initio* and DFT (B3LYP) calculations evidence that a minimum on the potential energy surface corresponds to dication **1a** [2].

We estimated the dication kinetic stability using DFT method (NATURE software, PBE potential) [3]. The energy barrier for its isomerization is 9.1 kcal/mole (estimated half reaction time period is about 4 min. at –140 °C), while the isomerization energy barrier for its hexamethylsubstituted analogue (**1b**) is even lower: 1.9 kcal/mole.





Therefore, kinetic stability of dication **1a** and its methylated derivative **1b** is low. That is why we doubt that those dications can be generated at the conditions of «long life» carbocations.

This study was financially supported by Russian Fund of Fundamental Research (Project № 06-03-32406) and Chemicals and Materials Department of Russian Academy of Sciences (Program № 5.1.9).

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P-13

REARRANGEMENTS OF 6b,7,8,8a-TETRAMETHYL-6b,8a-DIHYDRO-CYCLOBUTA[*a*]ACENAPHTHYLENE IN ACIDS: VARIATION OF ACIDIC MEDIUM – EFFECTIVE MEANS TO CONTROL CARBOCATION REARRANGEMENTS

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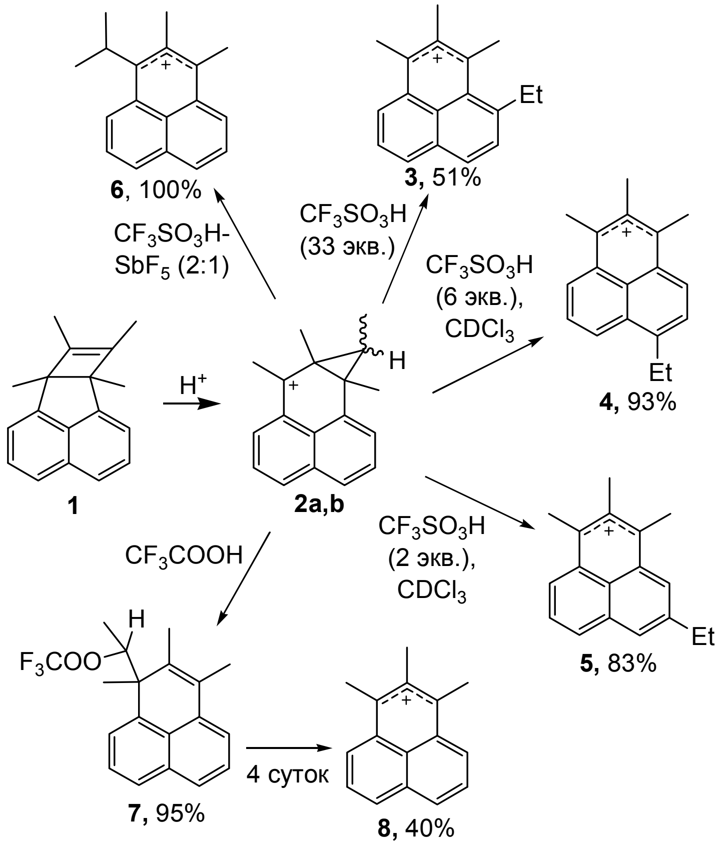
NMR is applied to study rearrangements of 6b,7,8,8a-tetramethyl-6b,8a-dihydrocyclobuta[*a*]acenaphtylene (**1**) in acids. It is shown that firstly formed 3b,4-*exo*,4a,5-tetramethyl-3b,4,4a,5-tetrahydro-4*H*-cyclopropa[*a*]phenalene-5-yl cation (**2a**) and its *endo*-epimer (**2b**)[1] in CF_3SO_3H regroupe to result in phenalene-type carbocations **3**-**5**. Those cations' formation in CF_3SO_3H- SbF_5 system is completely suppressed, cation **6** being the only product of rearrangement. It points out the intermolecular mechanism of cations **3**-**5** formation.



Under action of CF_3COOH olefine **1** converts to give trifluoroacetate **7**, that turns into cation **8** after long storage in solution.

Unexpectedly, those transformations sharply depend on even comparatively small variation in the medium acidity, while it is possible to direct the reaction so that it would in fact completely result in only one or another chosen product.

This study was financially supported by Russian Fund of Fundamental Research (Project № 06-03-32406) and Chemicals and Materials Department of Russian Academy of Sciences (Program № 5.1.9).

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P-14

HOMOPHENALENIUM CATIONS – NEW REPRESENTATIVES OF HOMOAROMATIC SYSTEMS, THEIR STRUCTURE FLEXIBILITY AND TEMPERATURE DEPENDENCE OF NMR CHEMICAL SHIFTS

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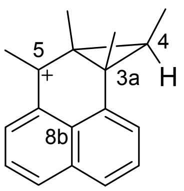
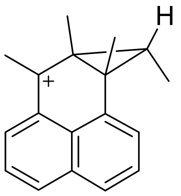
Assignement is completed for signals in NMR spectra of 3b,4-*exo*,4a,5-tetramethyl-3b,4,4a,5-tetrahydro-4*H*-cyclopropa[*a*]phenalene-5-yl cation **1a** and its *endo*-epimer **1b** [1]. Those particles are shown to represent a new type of homoaromatic systems, those being homophenalene carbocations. In the same manner as for phenalene ions they demonstrate strong-field offset for C^{8b} chemical shifts (d 124.5 m.d. in **1a** and 126.2 m.d. in **1b**). Besides of that, the position of C^4 signal (d 63.7 m.d. in **1a** and 73.3 m.d. in **1b**) is typical for homoaromatic cations (such as cyclobutenyl and homotropyl) and differs considerably from that of corresponding atoms in structurally related cyclopropylcarbinyl ions without homoaromaticity at all.

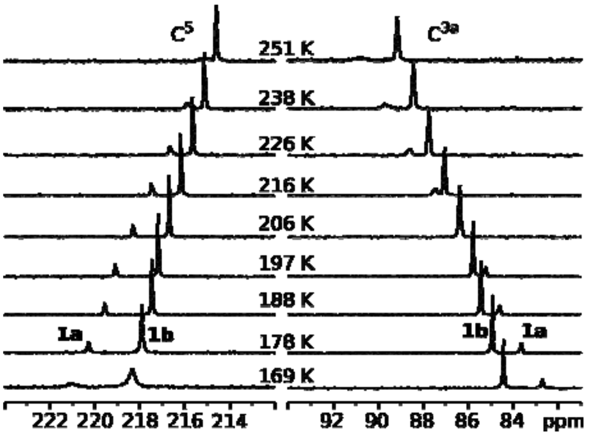


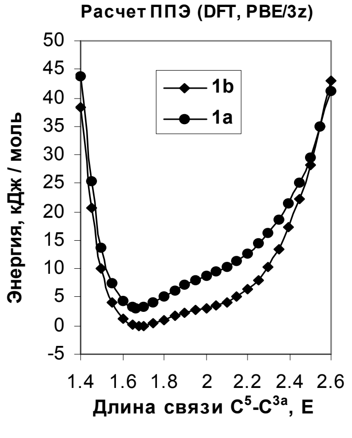
1a



1b

An essential feature of cations **1a** and **1b** is their structural non-rigidity. According to quantum chemical computations for those cations their potential energy surface section along the coordinate related to their C^5–C^{3a}, interatomic distance has the form of asymmetric wide potential wells with flat sloping bottom. The said peculiarity manifests itself in very strong temperature dependence of some chemical shifts (see [2]).





This study was financially supported by Russian Fund of Fundamental Research (Project № 06-03-32406) and Chemicals and Materials Department of Russian Academy of Sciences (Program № 5.1.9).

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[1] Осадчий С.А., Микушова Н.В., Шубин В.Г. *ЖОрХ.* **1999**, *35*, 1813.

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P-15

THE CLEMMENSEN REACTION WITH NON-AMALGAMATED ZINC: REDUCTION OF ALIPHATIC ALDEHYDES

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The most well known method for the reduction of carbonyl groups in organics to methylene groups is the Clemmensen reaction [1-3] that occurs through the action of amalgamated zinc and muriatic acid on initial carbonyl substances. The method was applied to reduce a number of aromatic aldehydes to related methylsubstituted benzenes, but if speaking about aliphatic aldehydes it was only enantal that was reduced to heptane [1]. Earlier we have already shown that the reduction of aromatic aldehydes to methylsubstituted benzenes is also realizable using non-amalgamated zinc dust and muriatic acid [4].

Here we are reporting a method for reduction of aliphatic aldehydes to hydrocarbons using zinc metal and muriatic acid:

$$\mathrm{AlkCHO + Zn + 2HCl = AlkCH_3 + ZnCl_2 + H_2O}$$

The reaction was conducted while boiling aldehyde, zinc dust and aqueous muriatic acid. Apparently, lower aldehydes are non-applicable for reduction at such conditions due to their insufficiently high boiling points, and besides of that their reduction products being gaseous at room temperature their isolation is rather difficult. Reduction of valerianic aldehydes occurs with considerable loss of target volatile hydrocarbons. Kapron and other higher aldehydes, up to decanal, both normal and iso-structured, react with efficient to high yields of the target hydrocarbons.

Starting AlkCHO	B. p., (°C)	Product, AlkCH$_3$	B. p., (°C)	Yield, %
$CH_3(CH_2)_3CHO$	102-103	$CH_3(CH_2)_3CH_3$	35-36	45
$(CH_3)_2CHCH_2CHO$	93-95	$(CH_3)_2CHCH_2CH_3$	30	40
$CH_3(CH_2)_4CHO$	130-131	$CH_3(CH_2)_4CH_3$	68-69	60
$CH_3(CH_2)_2CH(CH_3)CHO$	119-120	$(CH_3)_2CH(CH_2)_2CH_3$	61-62	59
$(CH_3)_2CH(CH_2)_2CHO$	118-120	$(CH_3)_2CH(CH_2)_2CH_3$	61-62	58
$CH_3(CH_2)_5CHO$	152-154	$CH_3(CH_2)_5CH_3$	97-99	73
$CH_3(CH_2)_6CHO$	169-171	$CH_3(CH_2)_6CH_3$	125-126	76
$(CH_3)_2CH(CH_2)_4CHO$	160-163	$(CH_3)_2CH(CH_2)_4CH_3$	115-117	75
$CH_3(CH_2)_7CHO$	190-192	$CH_3(CH_2)_7CH_3$	150-152	77
$CH_3(CH_2)_8CHO$	208-209	$CH_3(CH_2)_8CH_3$	173-175	76

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P-16

THE REACTIONS OF 9,10-ANTHRAQUINONES DERIVATIVES WITH UNSATURATED COMPOUNDS

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Arylation of unsaturated substances with arenediazonium salts (Meerwein reaction) is only studied insufficiently as far as it concerns anthraquinonyldiazonium salts (AD). Having in mind to determine the bounds of the reaction applicability we studied interactions between hydrosulphates, tetrafluoroborates, tetrachlorocuprates AD and unsaturated substances, containing both activated (acrylamide, methyl-methacrylate, methylacrylate, maleic anhydride, benzoquinone) and non-activated multiple bonds (styrene, phenylacetylene). It is established that formation of arylation or anionarylation products results only from the usage of activated unsaturated substances and typically followed by the substitution of diazogroup AD by на hydrogen, hydroxyl or halogen (in the case of tetrachlorocuprates). 1-AD salts are more active than 2-AD salts. The nature of solvent is of great importance. When conducting the reaction in aqueous acetonee we found that tetrafluoroborate 1-AD enters a side-reaction (azo-addition) with acetone to give 1-acetonylazoanthraquinone that exists in its tutomeric hydrosone form. Similarly phenylacetylene, that does not undergo Meerwein arylation, interacts with tetrafluoroborate to give 1-AD phenylglyoxal anthraquinoneylhydrasone. In the presence of zero-valent palladium complex both 1- and 2-iodine-anthraquinone react with ethylene derivatives to form products, where iodine is substituted by alkenyl group. We also have revealed that in the presence of triphenyl-phospine (TPHPH) complexation agent bromine-substituted anthraquinones are also able to condense. Taking into account that iodine in the anthraquinone nucleus may be replaced by alklenyl group in the absence of TPHPH, while bromine is only replaced only in the presence of TPHPH, we succeeded to synthesize iodo-bromo-substituted anthraquinones, differing in mutual location of their halogens, and to involve them into ethylene condensation, particularly it concerned 1-bromo-2-iodo- and 1-iodo-2-bromoanthraquinones. Depending on the presence or absence of TPHPH in our reaction blend we observed substitution either of iodine alone, or both of iodine and bromine. Thanks to that it is possible to introduce consecutively various alkenyl groups into iodobromanthraquinone molecule. Though nucleophilic substitution of halogens by ethynyl group in anthraquinone nucleus is under long study already the behavior of aminohalogenanthraquinones in the reaction is virtually not understood by now. We found that iodine in position “1” of 1,3-di-iodo-2-amineanthraquinone molecule (DAA) is easily exchanged to phenylethynyl group during its interaction with copper phenylacetylenide in pyridine even at room temperature. At 75°C the process leads to the closure of angularly condensed pyrrole cycle due to the addition of amine group to triple carbon-carbon bond. Nucleophilic substitution followed by the closure of pyrrole cycle occurs as in the reaction of copper phenylacetylenide with 1,3-dibromo- or 1-bromo-3-chloro-2-amino-anthraquinones, 1-iodo-2,3-diamino-anthraquinones in pyridine medium. If the latter is the case one amine group remains that may further undergo nitriding and convertions typical for aromatic diazosubstances. Thus resulting heterocyclic derivatives of anthraquinone are of potential interest as biologically active substances.

P-17

AMINATION OF 3,5-DI-*TERT*-BUTYL-*O*-BENZOQUINONE

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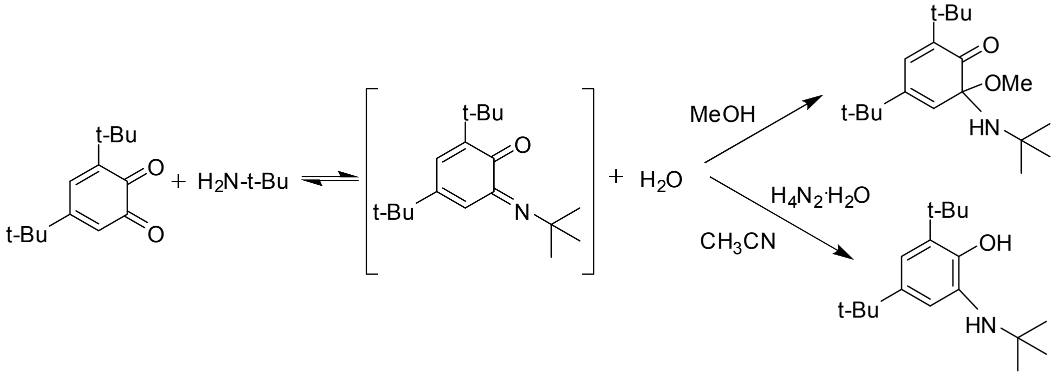
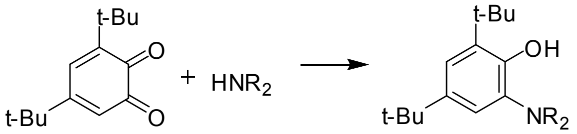
For 3,5-di-*tert*-butyl-*o*-benzoquinone 1,2-addition of nucleophilic agents by less stereo-hindered carbonyl group is quite typical. The interaction is reversible with primary aliphatic amines used for nucleophilic agents. Surplus amine shifts the balance to *o*-quinonimine. Reduction of acetonitrile solution by hydrazinehydrate results in the formation of aminephenols, while in methanol the same reaction allows isolation of a product of the solvent addition to thus formed quinonimine.

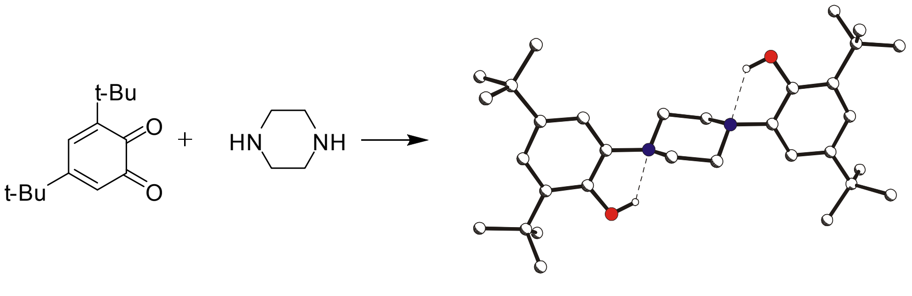


Our study on the interaction between 3,5-di-tert-butyl-*o*-benzoquinone and a number of secondary amines (Me_2NH, Et_2NH, piperidine, morpholine, N-substituted piperazines) proved related aminophenols to be the principal reaction products (their yields being at least 50%):



Those reactions occur in polar media (methanol, acetonitrile), and as well in non-solvating solvents (benzene, heptane) and are always followed with minor products formation: those being substances of benzoxyazol or phenoxyazine structures.

Piperazine reacts with 3,5-di-*tert*-butyl-*o*-benzoquinone in the same manner. Their interaction product is bis-*o*-aminephenol bonded by a piperazine bridge:



This study was financially supported by Russian Fund of Fundamental Research (Project № 04-03-2413, № 04-03-2409) and by Grant of the President of Russian Federation for support of Leading Scientific Schools (NS – 4947.2006.3).

P-18

NUCLEOPHILIC ADDITION OF SECONDARY PHOSPHINE CHALCOGENIDES TO ACYLACETYLENES

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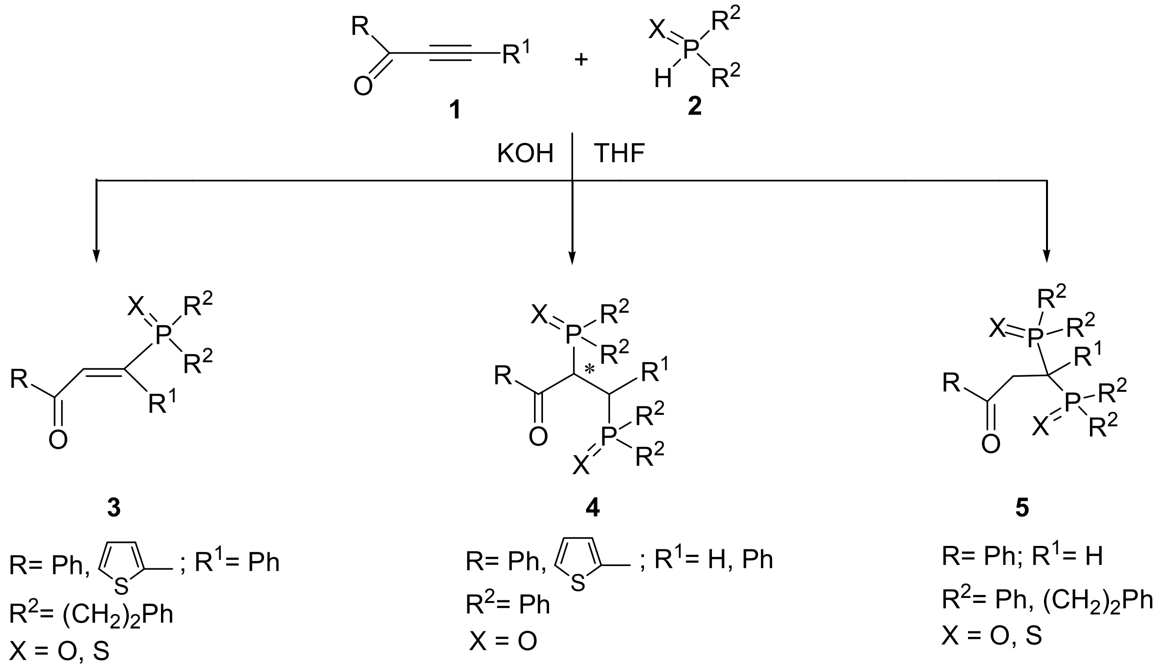
Recent developments of a new conception for the method of H-phosphines and H-phosphinechalcogenides manufacture from elemental phosphorus [1] organylhalogenides and aryl- or hetero-arylalkenes in the presence of strong bases opened wide possibilities for those key substances further application in organophosphorus synthesis [2].

We found that secondary phosphinechalcogenides react with acylacetylenes at soft conditions (KOH-THF, 20-65°C) and, depending on the reagents nature, selectively produce either mono-adducts **3**, or products **4, 5** resulting from double *б,в*- and *в,в*- addition.



Therefore, nucleophilic addition of PH-addends to triple bond in acylacetylene molecules is a convenient general approach to atom-saving synthesis of functional tertiary phosphinechalcogenides those being promising polydental ligands in contemporary design of catalysts, coordinating solvents and intermediates, used in the manufacture of conductive nano-materials and reactive construction blocks for organic synthesis.

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P-19

SYNTHESIS AND PROPERTIES OF HYDROXYARYLALKYLAMINES AND ITS DERIVATIVES

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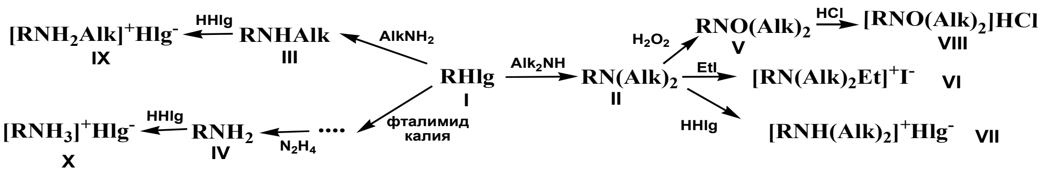
Alkylphenol derivatives with alkylamine groups in *para*-position and the corresponding ammonium salts are known for their evident anti-oxidation activity and they are of specific interest not only as stabilizers of polymer materials, rubbers, fuels and oils, but also as biologically active substances, e.g., as resolvents or antitumor agents.

In this connection we undertook the present investigation starting with ω-(4-hydroxyaryl)haloalkanes (I), conducted the synthesis of structurally interconnected amines (II-IV) and their water-soluble derivatives (V-X), and studied their antioxidant activity (AOA) in various model systems and hepato-protection properties of substances (II-X). We made halogenides (I) to react with dialkylamines or alkylamines resulting in tertiary amines (II) and secondary amines (III), and we conducted Gabriel phtalimide synthesis to produce primary amines (IV). Amines (IV) interaction with H_2O_2 resulted in their oxidation products those being N-oxides (V). Staring with amines (II-IV) and their N-oxides (V) we produced wide range of ammonium salts (VI-X).



Here R= *o*-(3,5-dialkyl-, 3-alkyl-4-hydroxyphenyl)alkyl; Hlg=Cl, Br; Alk=Me, Et, Pr.

For those synthesized amines (II-IV) we determined rate constants for their interaction with cumene or methyloleate (MO) peroxide radicals, and studied as well gross inhibition activity of substances (II-IV) in model reactions of thermal autooxidation of lard and hexadecane (HD).

It is established that amines (II-IV) are highly reactive with respect to cumene peroxide radicals and MO and they have inhibitory action on lard and HD oxidation processes 3.4-30 times increasing thermo-oxidation stability of both substrates. We revealed the regularities in alteration of amines (II-IV) OAO that depend on both structure and properties of the substrate oxidation.

Hepato-protection performance of amines (II-IV) and their water-soluble analogues (V-X) was studied using CCl_4-induced mouse hepatitis for model. The fact that most of those substances when the dose was $0{,}1LD_{50}$ decreased toxic action of CCl_4 was evidenced by reliable loss in activity of alanineaminetransferase in blood serum and decrease in malone dialdehyde content in animal liver.

The obtained data prove advisability of further investigation into the applicability of a range of synthesized substances as antioxidants and hepato-protectors.

P-20

METHOD OF SYNTHESIS OF POLYFLUOROARENESULPHONYL BROMIDES

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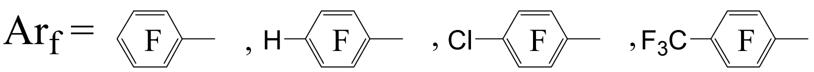
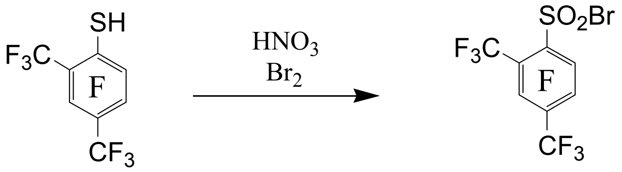
Polyfluoroarenesulfonyl bromides represent virtually unstudied class of chemical substances. The only earlier described synthesis is that of pentafluorobenzenesulfonyl bromide from chloropentafluorobenzene via Greniard reagent. When so doing bis(pentafluorophenyl)sulfone is by-produced in considerable amount [1].

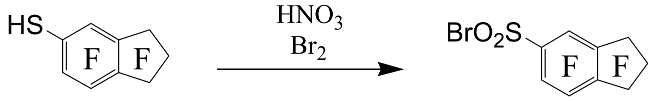
We have shown that pentafluorobenzenesulfonyl bromide and 4-substituted tetrafluorobenzenesulfonyl bromides result from the treatment of polyfluoroarene thiols with bromine/fuming nitric acid produced according to the method described in [2].

$$Ar_fSH \xrightarrow{Br_2 + HNO_3} Ar_fSO_2Br$$

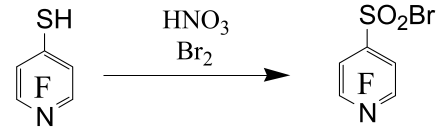


2,4-bis(trifluoromethyl)trifluorobenzene thiol and 5-nonafluoroindan thiol undergo similar transformations.





With the help of bromine and nitric acid we succeeded to realize a similar reaction with 2,3,5,6-tetrafluoropyridine thiol.



Ar_fSO_2Br is also formed in reactions between polyfluoroarenethiols and concentrated nitric acid/sulphuric acid/bromine blends.

The avenues for the formation of polyfluoroarenesulfonyl bromide are discussed.

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P-21

INTERACTION OF BENZOPOLYFLUORINATED QUINOLINES WITH NITROGEN NUCLEOPHILES

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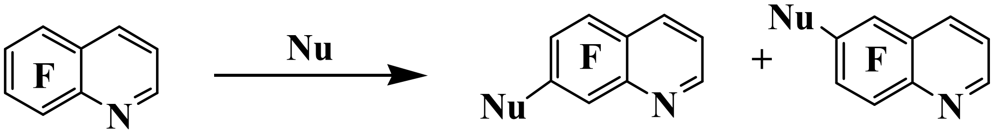
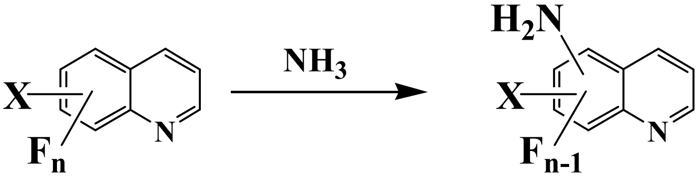
Fluorinated quinoline derivatives are of increased interest as perspective biologically active substances [1]. Therefore the development of novel direct pathways for their synthesis is an important issue. Nucleophilic fluorine substitution is a general approach to the modification of polyfluorinated quinolines [2]. As far as it concerns nitrogen-centered nucleophils with quinolines fluorinated by their benzene rings only ammonolysis of 5,6,7,8-tetrafluoroquinoline is well known [3].

We have shown that interaction of ammonia, piperidine, hydrazine-hydrate (in dioxane medium) or sodium amide (in liquid ammonia) with 5,6,7,8-tetrafluoroquinoline result in the products where fluorines are substituted in 7 and 6 positions (the ratio being from 5 : 1 to 3 : 1, correspondingly).



Nu = NH_3 aq., NH_3 liq., NH_2NH_2-H_2O, piperidine, $NaNH_2$

Ammonolysis of less-fluorinated quinolines, or quinolines containing substituents other than fluorine, result in monoaminequinoline blends. In aminegroups insertion their orientation is defined by the substrate structure.



n = 2 5,7-difluoro; 5,7- difluoro -8-chloro
n = 3 5,7,8- trifluoro; 5,7,8- trifluoro X=CF_3

The end products of the transformation were isolated as individual substances, their yields being 30-70% of their content in the blend.

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[3] Brooke G. M., Musgrave W.K.R., Rutherford R. J. D. *J. Chem. Soc.* **1966**, 215.

P-22

REDOX PROPERTIES OF 1-SUBSTITUTED NAPHTHALENES

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The method of cyclic voltamperometry is applied to study electrochemical behavior of a series of 1-substituted naphthalene (X = Me, OMe, CO_2Me, $CONH_2$, $CONMe_2$, CN, COPh, COMe, CHO, NO_2) in MeCN at a stationary platinum electrode. One or two reduction peaks are observed in the cathode branch of the voltamperometric diagram depending on the substituent. For the most of substances under study the first reduction peak (E_p^{1K}) is found to be single-electron, reversible (E_p^{1A} - E_p^{1K} = 0.06 B, $E_{p/2}^{1K}$ - E_p^{1K} = 0.06 B) and diffusion-controlled. For the studied naphthalene series E_p^{1K} varied between –1.12V and –2.71 V (sat.c.e.).

Experimental E_p^{1K} potential values correlate very well with adiabatic electron affinity values (r = 0.980) and HBMO energy for 1-X-naphtalenes (r = 0.986) calculated using DFT/BLYP method.

EPR spectra are registered in DMFA for electrochemically generated AP with X = Me, OMe, CO_2Me, $CONMe_2$, CN, COMe, CHO, NO_2. CTB constants calculated by DFT/BLYP method for AP 1-X-naphtalenes are in good agreement with experimental values. According to calculations the AP naphthalene skeleton is flat and the substituents (X = NO_2, CHO, COMe, COPh, CO_2Me) are located in the plane of naphthalene ring thus favoring delocalization both of negative charge and spin density. Half-periods are estimated for $ф_{1/2}$ AP conversion at T=295 K (from 30 s for AP (X=CHO) to 730 s for AP (X=CN)).

The second electrochemical reduction peak, tentatively attributable to AP reduction to dianions, is observed for X = NO_2, COPh, COMe, and also for CHO in DMFA. We failed to register peak 2K reversibility for the said substances, and this is the evidence of instability of the related dianions.

Electrochemical oxidation of the above 1-substituted naphthalene is also studied using CVA method. Within the series the first oxidation peak potential varies from 1.33 V (X=OMe) to 2.13 V (X=NO_2) depending on the substituent. For the naphthalene under study their first oxidation peaks are diffusion-controlled and responsible for two or more electrons transfer ($I_p^{1Oк} \geq 2.8\ I_p^{1K}$). We failed to observe single-electron reversible oxidation peaks for 1-substituted naphthalene, including those with donor substituents, even at high rates of electrode polarization (v = 50 h 100 V/s) this being the evidence of extreme instability of cation-radicals produced through the single-electron oxidation of 1-X-naphtalenes.

P-23

PENTAFLUOROPHENYLSUBSTITUTED PYRILIUM SALTS: REACTIONS WITH HYDROXYLAMINE

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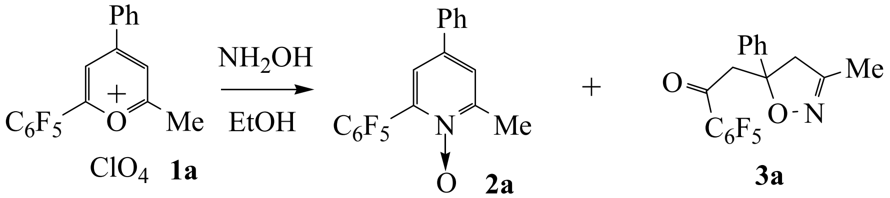
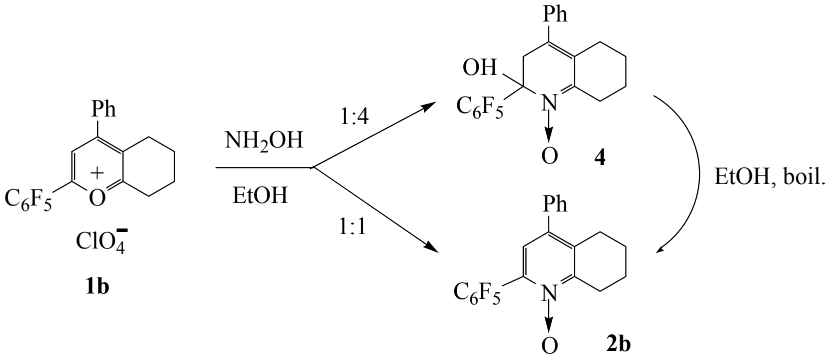
Reactions between pyrylium salts and nitrogen-containing nucleophilic, particularly bi-nucleophilic, reagents such as hydrazine and hydroxylamine result in various, often rarely available nitrogen-containing heterocyclic compounds. The use of pentafluorophenyl-substituted pyrylium salts in those reactions allows synthesis of previously unknown polyfluorinated heterocycles, those being promising bioactive substances. The reactions between pyrylium salts and hydroxylamine are known to result in related pyridine N-oxides and/or in phenacyl-substituted isoxazolines depending on the original pyrylium salt structure.

We studied the interaction between hydroxylamine and two 2-pentafluorophenyl-substituted pyrylium salts that contain active methyl- or methylene- groups in position 6 of their pyrylium cycles. The reaction was conducted in ethanol at 20°C, the reagents being used either in equimolar amounts or in fourfold excess of NH_2OH. Under both conditions pyrylium salt **1a** reacts to give a mixture of N-oxide **2a** and pentafluorophenacyl-substituted isoxazoline **3a** in approximately equal portions, however, the reaction velocity is much lower when there is excess of NH_2OH.



Salt **1b** reacts with equimolar quantity of hydroxylamine to result in high yield of N-oxide **2b**. When the reagent was in excess a stable intermediate **4** was formed, its structure being confirmed by X-ray structure analysis. The intermediate **4** stability may be attributed to C_6F_5-group stabilizing effect on sp^3-hybrid reaction centre under conditions of the reaction medium elevated basicity. Boiling of substance **4** in ethanol brings about the formation of N-oxide **2b**.



The study is supported by Integrated Projects of SB RAS № 15, 33, 65.

P-24

INVESTIGATION OF GLYCYRRHIZINIC ACID ASSOCIATIONS IN SOLUTIONS BY ^{1}H NMR AND CIDNP METHODS

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Glycirrhizic acid (GA) attracts the attention of numerous researchers due to its high biological activity [1] and its ability to increase the effect of other drugs when involved in a medicine formulation [2]. It is commonly supposed that the ability of GA to exert influence upon the performance of some other drugs [3] is complexation-related, however, until recently, no physicochemical evidence of the associates nature were available. That is our issue was to investigate possible association in GA solutions, and also GA association with organic molecules, including those biologically active. To study GA association we applied the method of chemical nuclear polarization (CNP) that had proved to be effective and, as well, NMR spectroscopy that is the most widely applied in experimental study of supramolecular entities. All conclusions about the newly formed GA associates' nature and its influence on the reactivity of substances under study were also based on the comparison between GA and other organized media (micelle) effects on the same process. The chosen substances were as follows: lappaconitin (LC) and methyl ester of N-acylanthranilic acid (MENA) that is an anthranilic fragment of lappaconitin (medical drug).

Using NMR data (particularly, with the help of Carr-Purcell-Melboom-Gill pulse sequence (CPMG)) we determined the time dependence of echo signal integral intensity both for GA individual solutions and for GA/MENA/LC mixture. It was found that in all instances GA associates were micelles with small number of aggregates [4]. Further to the determination of GA associates we studied GA effects on MENA and LC reactivity. The presence of GA produced a change both in MENA and LC (proton) NMR spectra and in MENA and LC reactivity. It was proved, just as in the case of well known micelles, that MENA and LC solubilization in GA solution transfer molecules from hydrophilic environment in homogenous solution to hydrophobic environment within micelle, thus altering (decreasing) the CNP intensity for MENA and LC when GA concentration grows. Therefore, the influence of natural GA associates on MENA and LC behavior correlates very well with micelle formation as to compare with well known organized media (micelle).

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[2] EUROPEAN COMMISSION; HEALTH & CONSUMER PROTECTION; Scientific Committee on Food "Opinion of the scientific committee on food on glycyrrhizinic acid and its ammonium salt" SCF/CS/ADD/EDUL/225, Brussel, 10 April 2003
[3] D.N. Dalimov, Yu.T. Isaev, and A.M. Saiitkulov: Chemistry of Natural Compounds **37(2)**, 151 (2001).
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NUCLEOPHILIC ADDITION OF SECONDARY AMINES TO 3,6-DI-*TERT*-BUTYL-*O*-BENZOQUINONE

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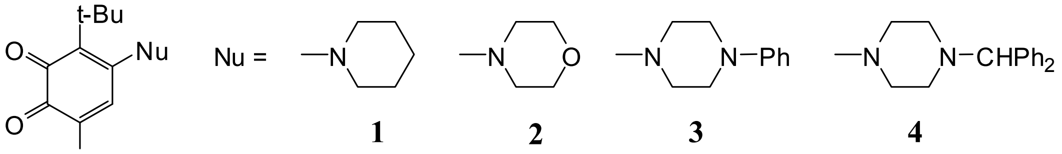
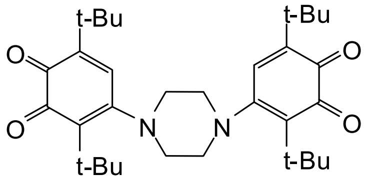
The approaches are developed to the synthesis of new stereo-hindered 3,6-di-tert-butyl-o-benzoquinones containing amine groups in position 4 in their rings (**1-4**) through the nucleophilic addition of secondary cycle amines to 3,6-di-tert-butyl-o- quinone:



1 **2** **3** **4**

The interactions with piperazine under various conditions resulted in di-o-quinone (**5**) in which molecule quinone fragments are connected by piperazine bridge, and 5,8-di-*tert*-butyl-2,3-dihydro-1,4-ethanequinoxalene-6,7-dione (**6**), the latter being a product of intermolecular cycling of intermediate 4-amine-substituted *o*-quinone. Treating of (**6**) with concentrated muriatic acid, besides of reduction to pyrocatechine, resulted in *tert*-butyl group replacement by chlorine, and further oxidation resulted in a novel *o*-quinone (**7**).



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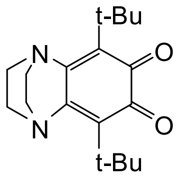

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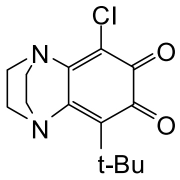

7

The structures of all those newly synthesized substances were confirmed by elemental analysis, IR-, H^1 and C^{13} NMR-spectroscopy. For (**2**), (**5**) and (**6**) their molecular structures were established through the X-ray diffraction analysis.

Both *o*-semiquinone anion-radicals formed through single-electron reduction with metal potassium and chelate o-semiquinone complexes of (**1-7**) with manganese carbonyl were studied by EPR in solutions. For diquinone (**5**) further to its monoanion-radical the signal of a bi-radical particle was detected. Judging by its zero-field resolution parameters the average distance between its paramagnetic centers was – 9.2 E.

This study was supported by Russian Fund of Fundamental Research (Project № 04-03-2413) and Grant of The President of Russian Federation for the Support of Leading Scientific Schools (ScSch–4947.2006.3).

P-26

ALKYLAMINATION OF JUGLONE

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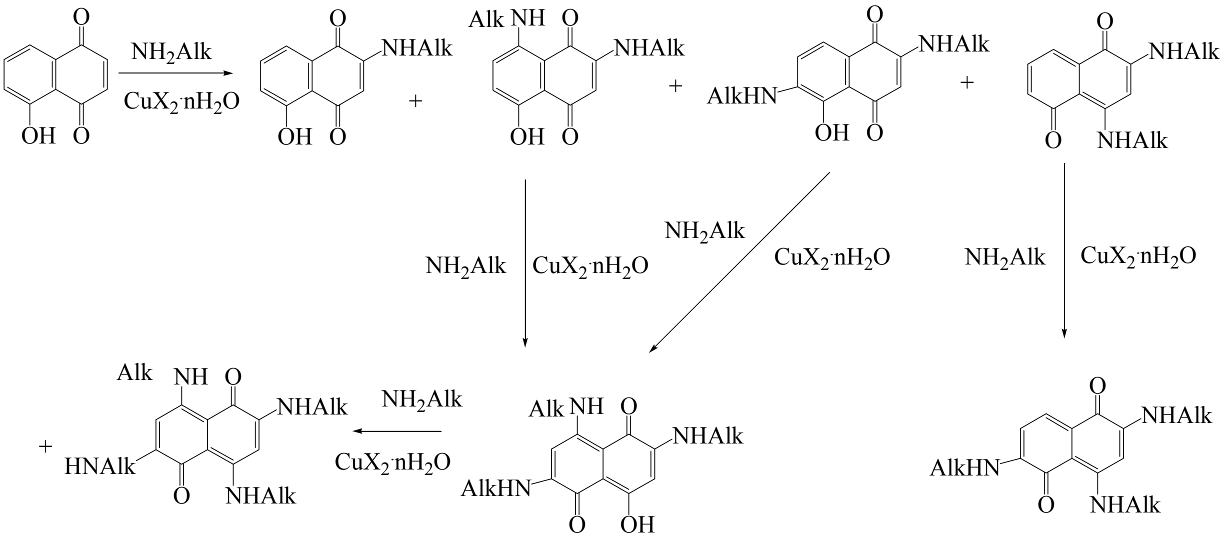
The interaction of juglone (I) (5-hydroxy-1,4-naphtoquinone) with amines is known to result in juglone 2- and 3-amine-derivatives, the 2nd isomer being prevailing [1].

We revealed that juglone reacts with primary alkylamines in the presence of divalent copper salts ($CuCl_2 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$) in amine media to form the products of hydrogen substitution for alkylamine groups, both in quinoid and aromatic rings of naphtoquinone, resulting in a blend of di-, tri- and tetra-alkyl amine naphtoquinones:



Further to it the formation of 4-amine derivatives existing as tautomeric 4-alkylamine-1,5-naphtoquinones is also observed.

[1] Methoden der Organischen Chemie (Houben-Weyl) Stuttgart, 1977, Bd VII 3a, Chinone.

P-27

SYNTHESIS OF THE SALICYLALDEHYDES BEARING BULK SUBSTITUENTS IN THE POSITIONS 3 AND 5

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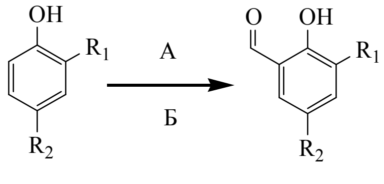
Chelate complexes of group IV transient metals with salicyl aldehyde arylimines named «phenoxy imine complexes» demonstrate high activity in olefin polymerization [1]. Variation in the ligand structure alters both steric hindrance and electronic density at the catalyst active centre, thus influencing the catalytic system activity and, possibly, altering the mechanism of polymerization [2].

Here we describe the production of a wide set of salicyl aldehydes with different combinations of bulk substituents in positions 3 and 5 having in mind to make them available for the synthesis of related group IV transient metals complexes with arylimine ligands.

It is shown that salicyl aldehydes containing *tert*-butyl, 1-phenylethyl, 1-(4-*tert*-butylphenyl)ethyl and cumyl groups in 3 and 5 positions are produced with good yields through formylation of corresponding phenols with para-foormaldehyde in the presence of $SnCl_4$ and 2,6-lutidine, while trityl-substituted aldehydes are produced through the treatment of trityl-substituted phenols with urotropine in trifluoroacetic acid.



1a-q **2a-q**

A: CH_2O, $SnCl_4$, 2,6-лутидин

Б: уротропин, CF_3COOH

a: R_1 = *tert*-butyl; R_2 = cumyl; b: R_1 = 1-phenylethyl; R_2 = H; c: R_1 = 1-phenylethyl; R_2 = methyl; d: R_1 = 1-phenylethyl; R_2 = *tert*-butyl; e: R_1 = 1-(4-*tert*-butylphenyl)phenylethyl; R_2 = H; f: R_1 = 1-(4-*tert*-butylphenyl)phenylethyl; R_2 = methyl; g: R_1 = 1-(4-*tert*-butylphenyl)-phenylethyl; R_2 = *tert*-butyl; h: R_1 = cumyl; R_2 = H; i: R_1 = cumyl; R_2 = methyl; j: R_1 = cumyl; R_2 = *tert*-butyl; k: R_1 = R_2 = cumyl; l: R_1 = *tert*-butyl; R_2 = trityl; m: R_1 = 1-phenylethyl; R_2 = trityl; n: R_1 = 1-(4-*tert*-butylphenyl)phenylethyl; R_2 = trityl; o: R_1 = cumyl; R_2 = trityl; p: R_1 = trityl; R_2 = methyl; q: R_1 = trityl; R_2 = *tert*-butyl;

Both compositions and structures of the produced aldehydes are determined on the basis of available analytical and spectral data.

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[1] S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano, and T. Fujita, *Chem. Lett.,* 1999, **28**, 1065;

[2] H. Makio, N. Kashiwa, and T. Fujita, *Adv. Synth. Catal*, 2002, 344; M. Mitani, J. Saito, S.-I. Ishii, Y. Nakayama, H. Makio, N. Matsukawa, S. Matsui, J.-I. Mohri, R. Furuyama, H. Terao, H. Bando, H. Tanaka, and T. Fujita, *Chem. Rec.,* 2004, **4**, 137.

P-28

SYNTHESIS OF THE NEW BIS(SALICYLALDIMINATO)TITANIUM (IV) COMPLEXES

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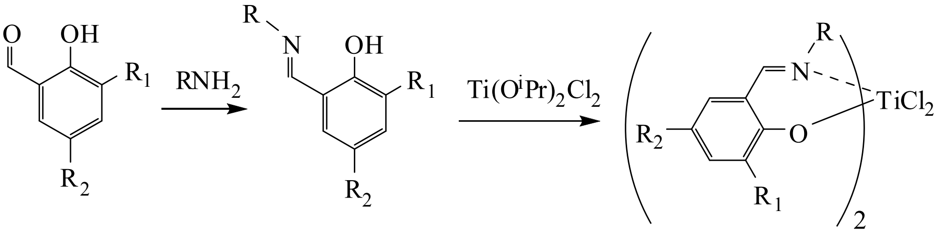
Recently discovered catalytic systems based on titanium, zirconium, and hafnium bis-phenoxyimine complexes attract much attention thanks to their high activity in olefine polymerization [1]. The researchers have already stated the general concept of substituent effects on the complex catalytic activity in polymerization process, however, it is still a topical problem to study systematically the dependence of those complexes catalytic activity on their substituents combination [2,3].

Through the interaction between salicyl aldehydes containing *tert*-butyl, phenylethyl, *tert*-butylphenylethyl, cumyl, or trityl groups in positions 3 and 5, with various amines we synthesized a wide range of phenoxyimine ligands and developed a convenient single-stage method for the synthesis of titanium (IV) bis-phenoxyimine complexes through the treatment of $Ti(O^iPr)_2Cl_2$ with salicylaldimine solution in toluene.



R_1=cumyl, R_2=methyl, R=cyclohexyl;
R_1=cumyl, R_2=tert-butyl, R=pentafluorophenyl;
R_1=cumyl; R_2=cumyl; R=phenyl;
R_1=cumyl; R_2= cumyl; R=1-adamantylethyl;
R_1=cumyl; R_2=cumyl; R=4'-tritylphenyl;
R_1= tert-butyl; R_2=trityl; R= pentafluorophenyl;
R_1=phenylethyl; R_2=H; R=cyclohexyl;
R_1=phenylethyl; R_2=H; R=pentafluorophenyl;
R_1=cumyl, R_2=methyl, R=phenyl;
R_1=tert-butyl; R_2=cumyl; R=pentafluorophenyl;
R_1=cumyl; R_2=cumyl; R=isobornyl;
R_1= tert-butyl; R_2=trityl; R=cyclohexyl;
R_1=cumyl; R_2=trityl; R=1-adamantylethyl;
R_1=phenylethyl; R_2=H; R=phenyl;
R_1=trityl; R_2=methyl; R=cyclohexyl

Both composition and structure of the prepared substances are established on the basis of analytical and spectral data.

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[1] S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano, and T. Fujita, *Chem. Lett.,* 1999, **28**, 1065;

[2] H. Makio, N. Kashiwa, and T. Fujita, *Adv. Synth. Catal*, 2002, 344;

[3] M. Mitani, J. Saito, S.-I. Ishii, Y. Nakayama, H. Makio, N. Matsukawa, S. Matsui, J.-I. Mohri, R. Furuyama, H. Terao, H. Bando, H. Tanaka, and T. Fujita, *Chem. Rec.,* 2004, **4**, 137

QUANTITATIVE ESTIMATING THE EFFICIENCY OF COMBINED USING OF IR AND MASS-SPECTRAL DATABASE FOR STRUCTURE ELUCIDATION OF ORGANIC COMPOUNDS

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Siberian Department of Russian Academy of Sciences, 9, pr. Acad.Lavrentieva;
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Both infrared spectroscopy (IR) and mass-spectrometry (MS) are widely used in practical analysis of organic compounds. For a substance under study each type of molecular spectra (IR, MS, etc.) allows revealing some structural features peculiar to the said kind of spectroscopy. In this connection combined usage of Data-Bases (DB) that cover spectra of various physical origin is of considerable interest for the determination of unknown substances structure. The greatest difficulty of such combined DB approach is their poor overlapping. Therefore, in NIOCh SD RAS the percentage of substances included both in IR Spectra DB and MS Spectra DB does not exceed 12% of the total structures number. Yet for most of substances involved in IR Spectra DB one may easily find at least one structure analogue in MS Spectra DB. [1].

Simultaneous presence of structurally related compounds in IR&MS DB search results occurs infrequently though in many cases the search chooses spectra of structural analogues.

The authors offer a structure detection algorithm based on operation not complete structures but their fragments [3,4] thus expanding applicability of various spectral DBs and enhancing the effectiveness of the search for structurally related substances.

Combined addressing to IR&MS DBs furnishes a combined search result that involves results for the search both in IR DB and in MS DB. The combined search result contains information on the selected spectra and structures of the closest spectral analogues, and a list of the mostly probable k-vertex related structural fragments assumed to be present in the substance under study. Our prime interest is in structural fragments found both in the IR DB search result and in MS DB search result. The structures of spectral analogues containing the maximal number of such fragments may perform as patterns in structure modeling of the substance under study. The examples and statistically valid performance estimations for such combined IR&MS DB usage are presented.

[1] T.A..Kornakova, B.G.Derendyaev, T.F.Bogdanova, V.N.Piottukh-Peletsky, Anal.Chem.Acta, 543 (2005) 177

[2] Б.Г.Дерендяев, В.Н.Пиоттух-Пелецкий, Т.А..Корнакова, Химия в инт. устойч. развития, 9 (2001) 17

[3] Piottukh-Peletsky V.N., Korobeinicheva I.K., Bogdanova T.F. et al., Anal. Chim. Acta, , 409 (2000) 181

[4] Б.Г.Дерендяев, В.Н.Пиоттух-Пелецкий, и др. Химия в инт. устойч. развития, **9** (2001) 405

P-30

ENTHALPY-ENTROPY RELATIONSHIPS IN THE BIMOLECULAR NUCLEOPHILIC REACTIONS

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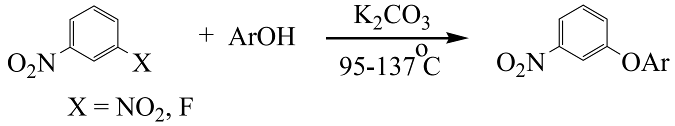
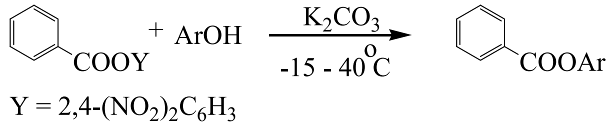
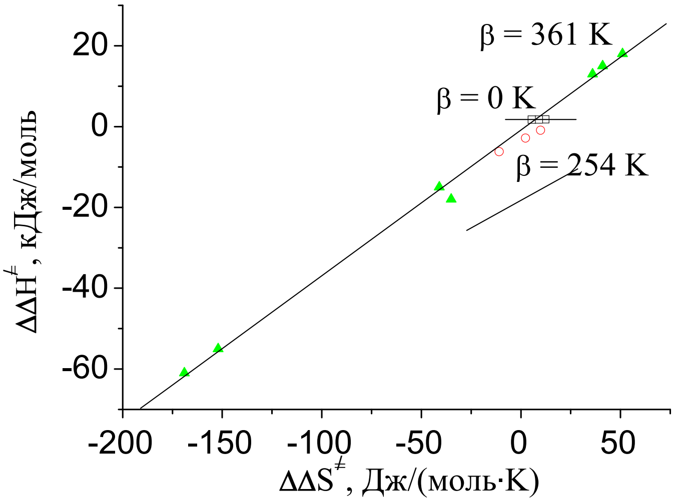
The method of competitive reactions is used to study nucleophilic substitution in 3-nitro-1-X-benzenes (X = NO_2, F) and 2,4-dinitrophenylbenzoate under the action of phenols in the presence of potassium carbonate in DMFA [1].





Correlation analysis of relative rate constants k(ArOH)/k(PhOH) and differences in the competitive reaction activation parameters ($\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$) was carried out, and it has shown that the selected reactions of aromatic nucleophilic substitution form isokinetic series with $\beta = 361$ K, while over-esterification reactions form two isokinetic series with $\beta = 0$ and 254 K correspondingly.



For each isokinetic series at the condition that $\beta < T_{exp}$ the effects of the reagent substituents are controlled by the entropy component of its free activation energy. It is shown that all substrates and reagents adhere to the same compensation dependence: $\Delta\Delta H^{\neq}$ - $\Delta\Delta S^{\neq}$. The mechanisms of the investigated reactions are discussed.

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[1] I.A. Khalfina, V.M. Vlasov, J. Phys. Org. Chem. 2007, **20**, N 2.

P-31

DIFURYLMETHANE SYNTHESIS BASED ON FURFURYL ALCOHOL IN THE PRESENCE OF ULKINSON COMPLEX

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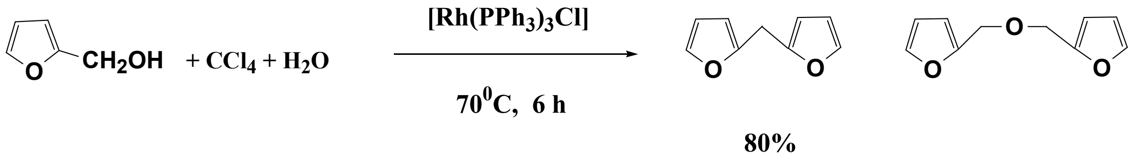
We report that furfuryl alcohol (**1**) interacts with H_2O and CCl_4 in the presence of Wilkinson complex $Rh(PPh_3)_3Cl$ to form 2,2'-difurylmethane (**2**), the yield being 80%. The reaction proceeded for 6 h at T=70°C under permanent stirring, till complete conversion of the original furfuryl alcohol. Further to (2) negligible amount of difurfuryl alcohol (3) is detected in the reaction mass, and this suggests a possible method for the synthesis of difurylmethane (**2**) through the decomposition of ether (**3**) and releasing formaldehyde.



(1) (2) (3)

The best experimentally confirmed catalyst-to-reagent ratio is as follows: $[Rh(PPh_3)_3]$: [furfuryl alcohol] : [ROH] : $[CCl_4]$ = 1 : 100 : 400 : 200.

Difurylmethane is a valuable perfume also used as a monomer in the manufacture of sensors for ion-selective chromatography; available methods for its synthesis are all difficult as regards the preparation procedures.

The study is financially supported by Russian Ministry of Education and Science (Grant NSh-7470.2006.3) and by the Fund for Assistance to National Science.

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COMPLEXES BETWEEN 18-CROWN-6 AND POLYFLUOROPHENYLENE- DIAMINES: PREPARATION, PROPERTIES, APPLICATION

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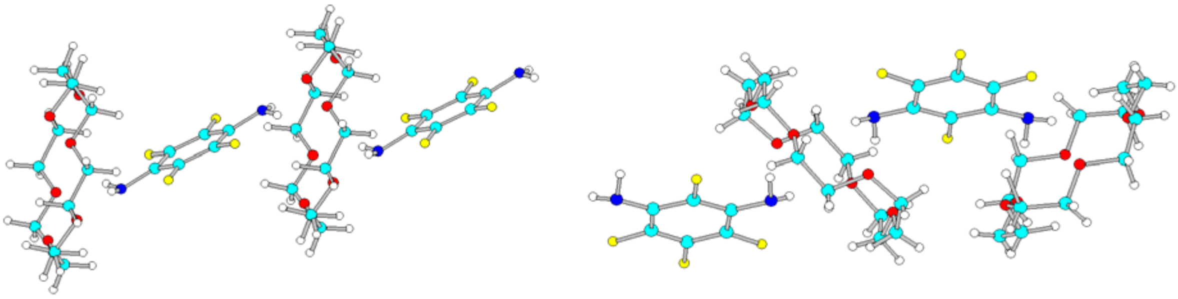
We pioneered to prepare complexes of 18-crown-6 with 2,3,5,6-tetrafluoro-1,4-phenylenediamine **1a**, 2,4,5,6-tetrafluoro-1,3-phenylenediamine **1b**, and 2,4,5-trifluoro-1,3-phenylenediamine **1c**. Those complexes precipitate when the solutions of their original individual components in non-polar solvents are mixed; under the action of water the complexes decompose quantitatively to give their original components. For all studied complexes the components stoichiometric ratio was 1:1 according both to NMR ^{1}H and X-ray structure analysis.

From X-ray structure analysis it follows that in crystal state those complexes are regular chains with alternate crown-ether and phenylenediamine units (see Figure below), their O_{crown}-$H_{diamine}$ interatomic spacing being typical for hydrogen bonding. Synchronous DSC/TGA-analysis proved that those complexes melting temperatures are reproducible in “heat-cooling” cyclic regime. Considerable difference is revealed between specific fusion heats of **1b** and **1c** (~125 *J*/g) and **1a** (~170 *J/g*) complexes.



Crystal structures of 18-crown-6 complexes with **1a** and **1b**.

We found that in a lack of 18-crown-6 its complexes’ sedimentation from polyfluorophenylenediamine **1a/1b/1c** equimolar blend solution occurs selectively in respect of **1a**: in sediment the corresponding complexes ratio is 8:1:1. Basing on the said effect we developed a simple method for the isolation of individual phenylenediamines **1a-c** (COB 97-99%, yield 70-90%) from the mixed products of hexafluorobenzene and pentafluorobenzene direct amine defluorination by aqueous ammonia. Taking into account the possibilities for quantitative regeneration of crown-ethers and for recycling and repeated complexation of non-separated polyfluorophenylenediamines the method may be of practical importance.

P-33

SYNTHESIS OF 1,4-DIHYDROXITHIOXANTHEN-9-ONE AND ITS TRANSFORMATIONS IN THIOXANTHEN-1,4,9-TRIONE DERIVATIVES

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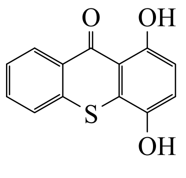
We offer using of 1,4-dihydroxythioxanthene-9-on (**I**) and its derivatives as photoinitiating agent for polymerization of unsaturated substances, bioactive agents, and analytical reagents. There are two well-known approaches to the synthesis of dihydroxythioxanthene (**I**): thiosalicylic acid (TSA)/benzoquinone condensation in organic solvents and TSA/hydroquinone condensation in acid media. The main disadvantage of the first approach is its two-step structure; the second one is attractive thanks to its simplicity, however, we think that the purifying procedure for its target product cleaning is too complicated.

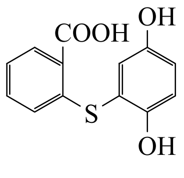
In connection with contradictions between both approaches we discuss spectral and chemical data confirming the structure of substance (**I**). In its synthesis we used the two-step method [1] that we had modified. TSA/benzoquinone condensation in diethyl ether results in $2',5'$-dihydroxy-2-carboxy-diphenylsulfide (**II**), further cyclization of (II) in thioxanthene (**I**) occurs more softly in polyphosphoric than in sulfuric acid, in which case byproducts are formed.

Under action of various oxidizers (iodic acid, cerium ammonium nitrate, hydrogen peroxide etc.) dihydroxythioxanthene (**I**) is converted to thioxanthene-1,4,9-trion (**III**). The interaction between (**I**) and thionylchloride, known for its oxidizing and chlorinating activity, oxidation occurs along with the formation of mono- and dichlorinated derivatives. Those derivatives structures are proved with the help of some model substances: 1-hydroxy-4-acetoxy (methoxy)- and 1,4-diacetoxy-thioxanthene-9-on those being produced through acetylating and methylating of (**I**).

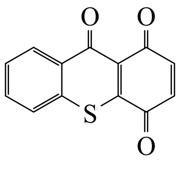
Spectral properties of thus prepared substances and assumed reaction mechanisms are discussed.



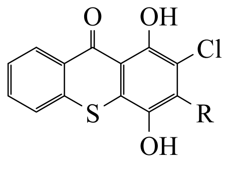
I



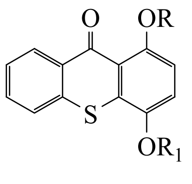
II



III



R = H, Cl



R = H, Ac
R_1 = Ac, Me

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[1] Clarke H.T., Smils S. *J. Chem. Soc.*, 1911, 1290.

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THIOXANTHEN-9-ONE DERIVATIVES AS EFFICIENT PHOTOINITIATORS FOR HOLOGRAPHY

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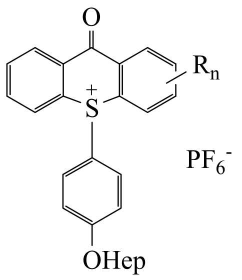
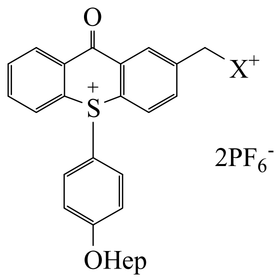
Thioxanthene-9-on derivatives are known to initiate photopolymerization of unsaturated substances applicable in holographic and photolithographic processes, in photoadhesic, etc materials.

To create thioxanthene-9-on-based universal high-performance photoinitiators we synthesized substances that contain a number of photochemically active centers that differ in their initiating mechanisms. Besides of photochemically active carbonyl oxygen available in the original thioxanthenon molecule we created cationic photochemically active centers: sulfonic (at thioxanthenon sulfur) and ammonium or phosphonium (through the introduction of corresponding substituents into the molecule). Sulfonyl-ketonic residuum is also used for additional photochemically active center, those substances distinctive feature being increased lifetime of their excited states.

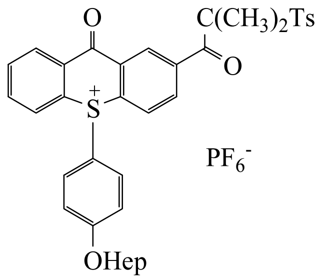
Thus synthesized polyfunctional photoinitiators (**I – III**) are studied in the process of impulse hologram recording. Photopolymerization with their participation resulted in holograms in the form of diffraction transmittance grates with diffraction efficiency about 10 %.



I



II



III

R = Alk, OAlk, Hal; X = $NAlk_3$, Alk_2NCH_2Ph, PPh_3

The study is supported by Integrated Projects of SB RAS № 15,17, 33) and RAS Programme 8-3

P-35

AMINATION OF POLYFLUORO PYRIDINES BY LIQUID AMMONIA AS A UNIVERSAL ROUTE TO THE MONOMERS FOR POLYCONDESATION

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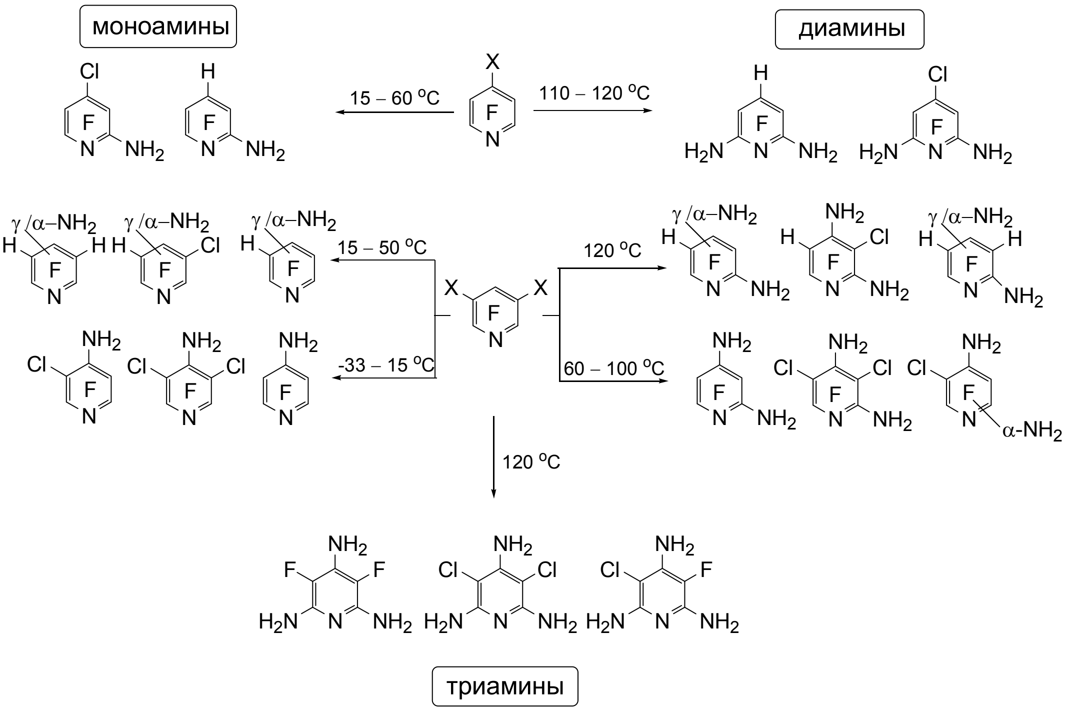
Di- and triamines of halogenated arenes are of practical interest as monomers to be used in the synthesis of polycondensed polymers. The direct rout to said substances is nucleophilic amination of polyfluorinated arenes by liquid ammonia. Using ammonia both for reagent and solvent provides rationality and excludes side-hydroxydefluorination that occurs in water ammonia solution.



It is established that in liquid ammonia at -33÷120°C ($T_{critical.}(NH_3)$=133°C) polyfluoropyridines undergo mono-, di- or even triamination (see diagram) with fluorine α- and γ-substitution. Relative substrate activity and orientation of aminedefluorination are ruled by a number of electronic effects due to substituents. Considerable difference between the regimes used for the 1st, 2nd and 3rd amine group introduction into heteroaromatic skeletons provides in most cases very high process selectivity (the purified product yields reach 60÷80%).

The universal method of direct amination of electrophilic polyfluoroarenes is applied to produce extremely pure both novel and well-known amine pyridine derivatives as required for Hi-Tech applications.

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SKELETAL TRANSFORMATIONS OF PERFLUOROALKYLPHENYLBENZOCYCLOBUTENES UNDER THE ACTION OF ANTIMONY PENTAFLUORIDE

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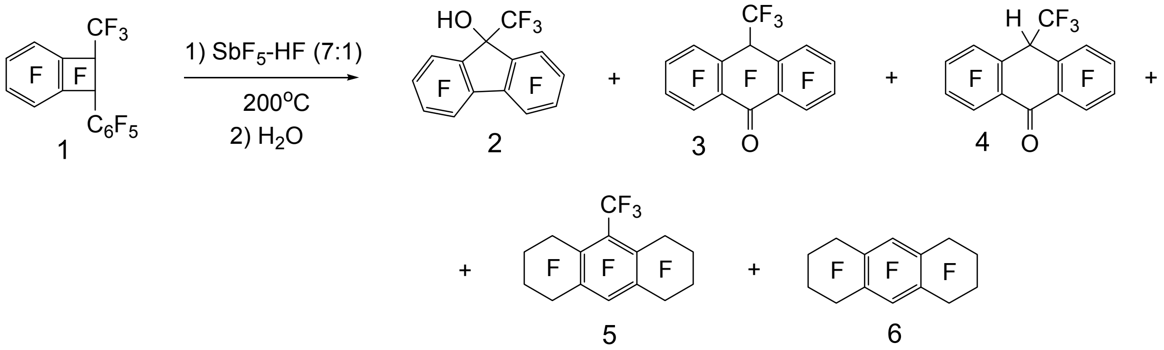
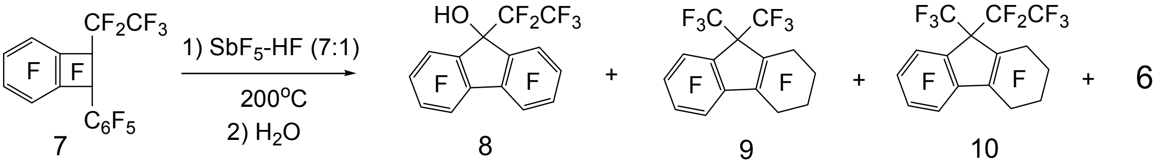
It is shown that perfluorinated methylphenyl- and ethylphenyl- benzocyclobutenes in SbF_5 environment undergo skeletal transformations resulting mainly in fluorene and anthracene derivatives. For instance, heating of perfluoro-1-methyl-2-phenylbenzocyclobutene (**1**) with SbF_5 in the presence of HF followed by hydrolysis of the reaction mixture results in the formation of fluorene **2,** anthracenes **3** and **4**, and negligible amounts of octahydroanthracenes **5** and **6**. Under similar conditions perfluoro-2-phenyl-1-ethylbenzocyclobutene (**7**) reacts to give fluorene **8**, tetrahydrofluorenes **9** and **10**, and small quantity of product **6**.





The reaction routs are discussed.

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NON-EMPIRICAL QUANTUM CHEMICAL CALCULATIONS OF HERZ CATIONS AND RADICALS AND THEIR SELENA ANALOGUES

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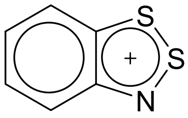
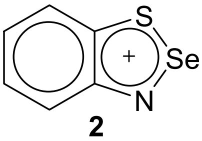
Cations (**1**-**4**), Hertz radicals (**5**-**8**) and their selenium-containing analogues are calculated by DFT and MP2 methods using different basis. Radicals **5**-**8** are of practical interest as possible components of molecular magnetic and/or conductors, cations **1**-**4** are their usual immediate synthetic precursors.



1



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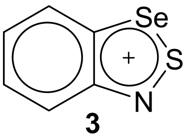

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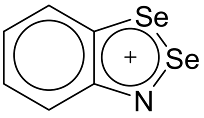

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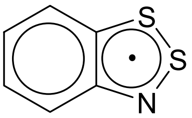

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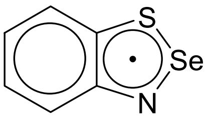

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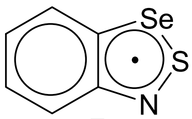

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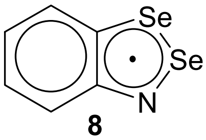

8

The convergence of 1,2,3-benzodithioazolium (**1**) cation structural parameters is achieved at the level of B1B95/cc-pVTZ, B1B95/cc-pVQZ and MP2/cc-pVTZ and in good accordance between calculated heterocyclic geometry and RSA data for its 5,7-di-*tert*-butylderivative. B1B95/cc-pVTZ method is used to calculate geometry, atomic charges and Hirshfeld[1,2] bond orders for cation **1** and its mono- and di-selenium-containing analogues (**2**-**4**), NICS(0) и NICS(1) indices are calculated for carbo- and heterocycles. Aromatic cycle π-conjugation with 40-50% charge delocalization over carbocycle is typical for the cations under study. Sulfur-to-selenium substitution results in considerable alteration of charge only for the atoms directly connected to the replaceable chalcogen and orders only of adjacent bonds.

B1B95/cc-pVTZ method is used to calculate geometry, atomic charges, spin density distribution and Hirshfeld[1,2] bond orders for 1,2,3-benzodithiazolyl radical (**5**) and its mono- and diselenium-containing analogues (**6**-**8**). Radicals **5**-**8** are slightly polarized. Unpaired electron is ~75% located at heteroatom, while sulfur-to-selenium substitution results only in small alteration of spin density distribution.

The same method is applied to calculate radical dimers **5**-**8** with all possible chalcogen-chalcogen, chalcogen-nitrogen and nitrogen-nitrogen contacts, two conformations (flat and stack) are considered for each case. Radical-to-radical interactions in the dimers proved to be weak: their dimerisation energy is small and positive in all cases, other than flat radical **6** dimer involving Se-N', N-Se' contacts, its stability exceeding that of separate radicals by ~3 kcal/mole.

The calculations are carried out at *Department of Chemistry, University of Antwerp, Belgium* using Gaussian 03 and BRABO software.

The authors appreciate very much financial support of their work provided by INTAS (Grant № 05-109-4637).

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REACTIVITY OF 5,6-BIS(DIMETHYLAMINO)ACENAPHTHYLENE

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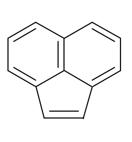
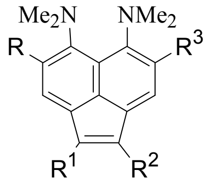
Acenaphtylene (**1**) and its derivatives are widely used in organic synthesis, particularly for syntons in various polycyclic systems (see e.g. [1,2]). Recently [3] we synthesized 5,6-bis(dimethylamino)acenaphtylene (**2**) that may be considered as a "proton sponge" and activated alkene.

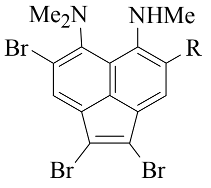


1



2 $R=R^1=R^2=R^3=H$
3 $R=R^1=R^2=H$, $R^3=Cl$
4 $R^1=R^2=H$, $R=R^3=Cl$
5 $R=R^1=R^3=H$, $R^2=Br$
6 $R=R^3=H$, $R^1=R^2=Br$
7 $R=R^1=R^3=H$, $R^2=I$
8 $R=R^3=H$, $R^1=R^2=I$
11 $R=H$, $R^1=R^2=R^3=Br$
12 $R=R^1=R^2=R^3=Br$
13 $R=R^3=Cl$, $R^1=R^2=Br$
14 $R=R^1=R^3=H$, $R^2=CCPh$
15 $R=R^3=H$, $R^1=R^2=CCPh$
16 $R=R^1=R^3=H$, $R^2=CCSiMe_3$
17 $R=R^3=H$, $R^1=R^2=CCSiMe_3$
18 $R=R^3=Cl$, $R^1=R^2=CCPh$
19 $R=R^1=R^3=H$, $R^2=CHO$
20 $R=R^3=H$, $R^1=R^2=CHO$
21 $R=R^1=H$, $R^2=R^3=CHO$

It is established that acenaphtylene **2** easily reacts with *N*-halogen succinimide resulting in **3**–**8**. The direction of halogenation is determined, first of all, by the halogen size and, secondly, by the solvent polarity. It permits regioselective production of either 1(2) or 4(7)-(di)halogenides. Introduction of the 3rd and 4th bromines is followed by competitive mono-*N*-dimethylation resulting in the formation of **9** and **10** convertible further to **11** and **12**. X-ray structure analysis is conducted for **4** and **9**.



9 R=H
10 R=Br

Due to strong rotation of NMe_2-groupes and low activation of π-system dichloride **4** is very inert relative to electron-seeking reagents. Particularly, it undergoes halogenation with the help of *N*-chlorosuccinimide (NCS) and *N*-bromosuccinimide in wide range of conditions. At the same time less hindered dibromide **6** reacts with NCS (2 equiv.) in chloroform to give mixed tetrahalogenide **13**. Bromine and iodine addition to 5,6-bis(dimethylamino)acenaphtylene results in the formation of 1(2)-dihalogenated acenaphtylenes **5**–**8**. Bromides **5**, **6** and **13** interact with phenylacetylene and trimethylsylilacetylene at Sonogashira reaction conditions to give related ethynyl derivatives **14**–**18**.

Acenaphtylene **2** formylation according to Vilsmeier leads to aldehydes **19**–**21** formation.

Therefore, we have shown that in reactions with electron-seeking reagents naphthalene nuclei and ethylene fragments of acenaphtylene **2** are strongly activated by *peri*-dimethylamine groups.

Authors are much obliged to RFFR for partial financial support (Project № 05-03-32110).

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[1] Olashi K., Kubo T., Masui T., Yamamoto K., Nakauji K., Takui T., Kai Y., Murata J., J. Am. Chem. Soc.,1998, **120**, 2018–2027

[2] Panda K., Venkatesh C., Ila H., Junjappa H., Eur. J. Org. Chem., 2005, 2045-2055

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THE STRUCTURE OF NOVEL TETRAHYDROBENZO[*e*]PYRANO-[4,3-*b*]PYRIDINE DERIVATIVES IN CRYSTAL

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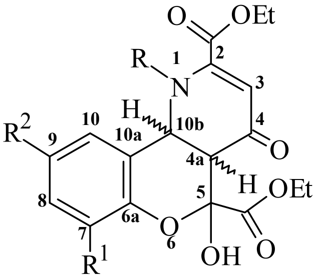
X-ray analysis is conducted for five substances belonging to tetrahydrobenzo-[*e*]pyrano[4,3-*b*]pyridine raw resulting from reactions in “diethyl ether 2,4,6-trioxoheptane dicarboxylic acid – substituted salicylic aldehyde – ammonium acetate” system. The presence of two tautomeric systems (tetrahydropyridine-4-on and 2-hydrooxypyrane) in tetrahydrobenzo[*e*]-pyrano[4,3-*b*]pyridine make one assume that those substances may exist in various tautomeric forms, including those open-chain depending on the medium phase state and polarity and also on the nature of R^1 and R^2 substituents. The study objective was to determine unambiguously those product structures.



1-5

1: R = H, R^1 = H, R^2 = H; 2: R = H, R^1 = H, R^2 = OMe; 3: R = H, R^1 = OMe, R^2 = H;
4: R = H, R^1 = Cl, R^2 = Cl; 5: R = tolyl, R^1 = H, R^2 = OMe.

X-ray analysis made it clear that substances **1-5** crystallize as tricycle isomers with three chiral centres: C(10b), C(4a), and C(5). All substances crystallize as racemates: for **1** and **3** the related chiral centre configuration being *R,S,R*, while for **2, 4, 5** it is *R,R,R*. In all five substances the conformation of the pyrane cycle is “half-chair”. For tetrahydropyridine cycles in the presence of methoxy-substituents at 7th or 9th carbons the molecule conformation changes from “twist-boat” to “half-chair”, while in the presence either of chlorine substituents at 7th or 9th carbons or tolyl substituents at nitrogen the configuration is changed to “C-envelope”. Thanks to “classic” hydrogen bonds of type N–H···O- and O–H···O the molecules of substances under study form in crystals 1D-structures, with one exception of substance **5**, where dimer associates are formed (0D-structure). C–H···O-interactions result in various types of packaging (2D and 3D) or act as “classic” hydrogen bonds. Reasoning from the chiral centre configurations in substances **2, 4, 5** hydrogens at C(10b) and C(4a) are in *cis*-positions, while in **1** and **3** they are in *trans*-positions, that is indicative of their steric structure relationship with that of natural tetrahydrocannabinols, those being physiologically active components of cannabis.

The study is carried out thanks to financial support provided by RFFR grants № 04-03-32156, 05-03-33008 and National Science Assistance Fund.

P-40

POLYSUBSTITUTED PHTHALONITRILES AND PHTHALOCYANINES FROM TETRACHLOROPHTHALONITRILE

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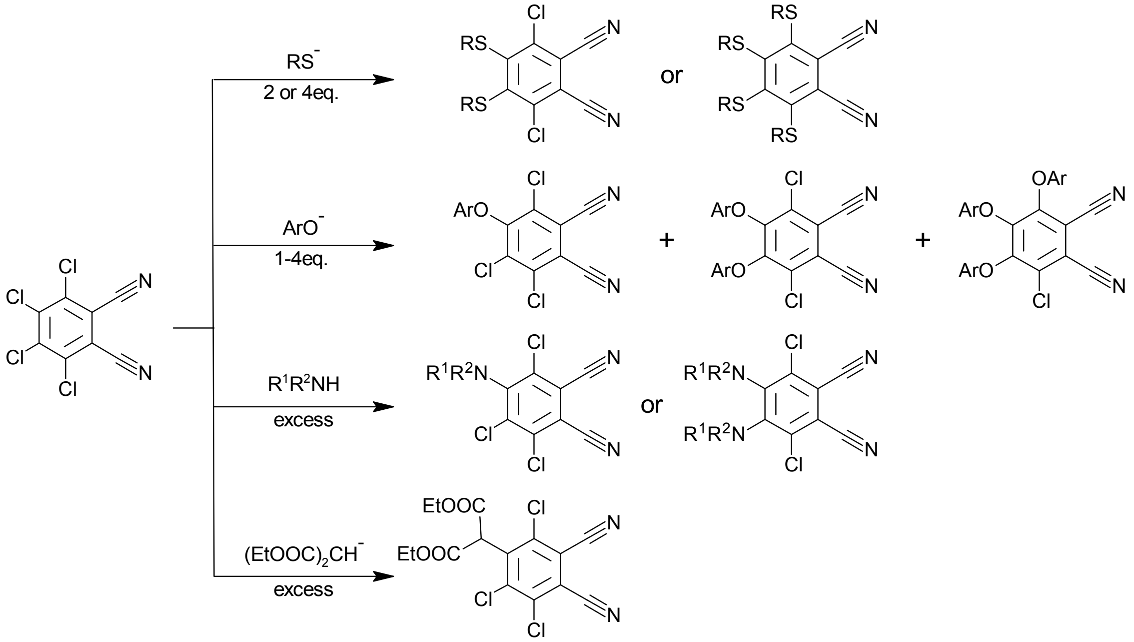
One of the most convenient methods for the manufacture of substituted phthalocyanines is cyclotetramerisation of the related phthalonitriles. The manufacture of phthalonitriles through nucleophilic substitution is a well-known routine process [1] that is only limited by the availability of original phthalonitriles with groups suitable for substitution. The latter include, e.g., 4-nitro-, 3-nitro-, 4,5-dibromo- [2], 4-bromo-5-nitrophthalonitrile [3]. On the other hand, the substitution of commercially available tetrachlorophthalonitrile has not been adequately explored.



We studied the interaction of tetrachlorophthalonitrile with nucleophilic reagents of various nature and found that substitution occurs regioselectively, and the maximal number of substituted chlorines drops from four to one within the nucleophilic sequence: $RS^- > ArO^- > R^1R^2NH > (EtO_2C)_2CH^-$. In the case of incomplete substitution the residual chlorines may be substituted by nucleophils of other type.

The prepared polysubstituted phthalonitriles are used to synthesize corresponding phthalocyanines, and the effects of different substituents on their absorption spectra were traced, particularly, their influence on the position of their long-wave band in the near IR region.

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P-41

ELECTROCHEMICAL REDUCTION AND OXIDATION OF ORGANIC COMPOUNDS. POLARIZINE EFFECT IN ANION- AND CATION-RADICALS

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Usually when investigating the effect of substituent X on the value of potential half-wave of reduction ($E_{1/2}^{Red}$) and oxidation ($E_{1/2}^{Ox}$), the researcher considers electrode process types as follows

$$X–B–R_C + e \rightarrow X–B–R_C^{\bullet-} \text{ и } X–B–R_C - e \rightarrow X–B–R_C^{\bullet+}, \qquad (1)$$

Here $X–B–R_C$ is reaction series, where R_C is unchangeable reaction centre that performs as являющийся electrochemically active group; X is substituent that influences the reaction (1), though not participating in it directly; B is a bridge between R_C and X.

Our analysis of numerous published data has shown that the mechanism of those substituent X influence on $E_{1/2}$ values is not adequately studied.

We have considered the effects of substituents X on $E_{1/2}^{Red}$ for 8 series of organic substances and on $E_{1/2}^{Ox}$ for 5 series of organic substances with R_C=const. In those series variable substituents X are: H, Me, Et, Pr, *i*-Pr, Bu, *t*-Bu, $CH_2CH=CH_2$, Ph, CH_2Ph, OMe, CHO, COOH, COMe, COPh, CH_2CN, CN, NH_2, NMe_2, NO_2, Cl, Br, CF_3.

Using the correlation analysis method we found that in the investigated ion-radical systems polarization effect is to be taken into account along with inductive and resonance effects of substituent X. The polarization effect is due to ion-dipole interaction between charge q at the reaction ion-radical centre and dipole induced by charge q in substituent X. The criteria of polarization effect existing in a reaction series is statistical significance of σ_α in Gammet-Taft relation

$$E_{1/2} = E_{1/2}^{H} + a\sigma_I + b\sigma_R\ (\sigma_R^{+}, \sigma_R^{-}) + c\sigma_\alpha, \qquad (2)$$

Here $E_{1/2}^{H}$ – value $E_{1/2}$ when X=H; σ_R, σ_R^{+} and σ_R^{-} – constants that characterize resonance effects of substituent X in the case of small and large positive or large negative charge at R_C, correspondingly; σ_α – polarization constant of substituent X as quantitative characteristics of polarization effect (*ab-initio* calculated).

The relation between inductive, resonance and polarization effects follows the equation

$$E_{1/2} = E_{1/2}^{H} + \mathrm{Ind} + \mathrm{Res} + \mathrm{Pol}, \qquad (3)$$

Here Ind = $a\sum\sigma_I$, Res = $b\sum\sigma_R(\sigma_R^{+},\sigma_R^{-})$, Pol = $c\sum\sigma_\alpha$ – are, correspondingly, inductive, resonance and polarization contributions into total change of $E_{1/2}$ under the action of substituent X. For the considered series the share of polarization effect ranges from 4 to 52% in the case of $E_{1/2}^{Red}$ and from 7 to 27% in the case of $E_{1/2}^{Ox}$.

P-42

REACTIVITIES OF *O*- AND *S*–NUCLEOPHILES IN *TRANS*-ESTERIFICATION REACTIONS OF 4-NITROPHENYLBENZOATES IN DIMETHYL FORMAMIDE

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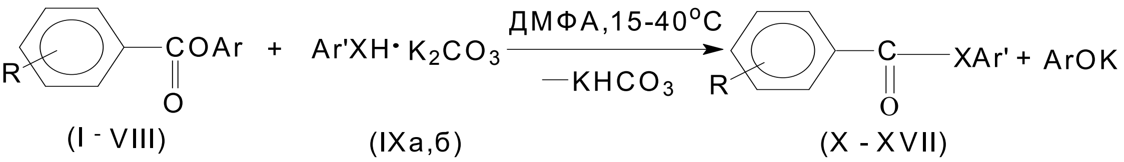
The topicality of research on acyl-transport reactions is connected both with acyl participation in biological processes and its application in chemical synthesis [1]. The nature of nucleophil is an important factor that influences both the carbonyl carbon reactivity and the mechanism of interesterification. Having in mind to estimate the effect of nucleophil nature on the regularities of interesterification in this study we applied the competitive reactions method to investigate the kinetics of interaction between *n*-nitrophenylesters of substituted benzoic acids and *S*- and *O*-nucleophils at various temperatures (15 - 40°C) in dimethylformamide.



R= 4-MeO (I,X); 4-Me (II,XI); H(III,XII); 4-Br(IV,XIII); 3-Br (V, XIV); 4-CF$_3$ (VI,XV); 3-NO$_2$ (VII, XVI); 4-NO$_2$ (VIII, XVII); Ar= 4-NO$_2$C$_6$H$_4$, Ar'X = PhS (IXa), 4-ClC$_6$H$_4$O(IXб)

Variation in free energy of activation for all reactions is predominately governed by the change in activation enthalpy. Isokinetic dependencies are revealed for reactions between phenylbenzoates and electron-seeking substituents, the isokinetic temperature values being β=318 K in the case of *S*-nucleophils and β=390 K in the case of *O*-nucleophils. Enthalpy-entropy compensation effect is observed for all reactions of benzoate series.

Interesterification of substituted 4-nitrophenylbenzoates by *S*- and *O*-nucleophils in DMFA occurs following a multi-step mechanism, when so doing it is not the step of the leaving group abstraction that governs the reaction rate. In the case of *O*-nucleophils one may assume the formation of cycle transition state, while in the case of *S*–nucleophil transition state is probably acyclic. The observed difference in reactivity of *S*- and *O*-nucleophils is discussed depending on the polarizability of nucleophil centres in *S*- and *O*-nucleophils.

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P-43

THE INTERACTION OF PHTHALONITRILE RADICAL ANION WITH ALLYL-, BENZYL- AND ω-ALKENYL BROMIDES

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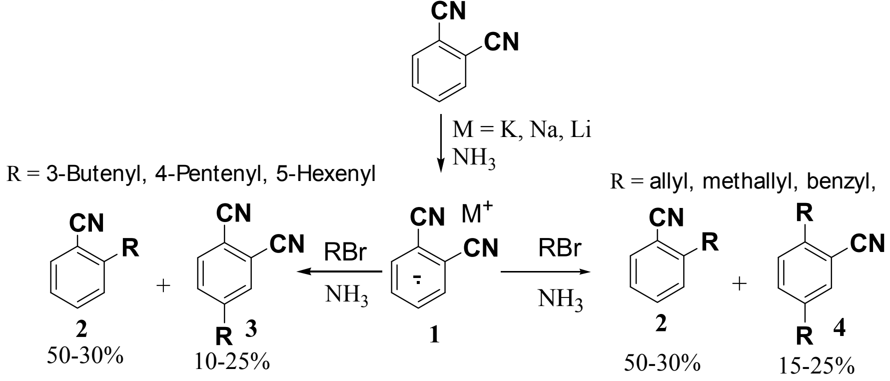
Alkenylsubstituted benzene ring provides structural base for numerous naturally occurring compounds [1]. Alkenylbenzene derivatives with functional groups easily undergoing various transformations are precious "building blocks" in the synthesis of promising biologically active compounds. Cyano group belongs to the most promising functionalities. The well-known methods for alkenylcyanarens manufacture rely predominantly on the involvement of halogenalkenes and cyanoarens in catalytic cross-coupling reactions [2] or different variants of Wurtz-Fitting reaction [3]. However, applicable halogenated cyano arenes are of limited availability, and the experimental techniques are rather complicated. We have shown that the interaction of alkaline salts of phtalodinitrile anion-radical (**1**) with ω-alkenyl- and allylbromides in liquid ammonia opens an unrivalled for shortness approach to 2-alkenylbenzonitriles (**2**), 4-alkenyl-1,2-dicyanbenzenes (**3**) and 2,5-dialkenylbenzonitriles (**4**):



In all cases alkenylbenzonitriles **2** are the main products. The other products formation is governed by the corresponding alkylating agent structure. Phthalonitriles **3** are formed in reactions between substance **1** and ω-alkenylbromides, while benzonitriles **4** result from the reactions with allyl- or benzylbromides. Therefore, the interaction between **1** and alkenyl- and/or benzylbromides provide an universal one-step rout to fundamental original substances to be used in the synthesis of promising bioactive derivatives belonging to cyclopropane and phthalocyanine series.

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P-44

SUPRAMOLECULAR COMPLEXES OF CAROTENOIDS. INVESTIGATION BY PHYSICAL METHODS

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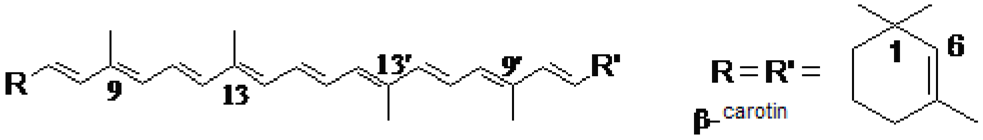
Recently in organic and medical chemistry there was considerable growth of interest in the research on supramolecular complexes of «guest-host» type. There is particular interest in complexs formed by natural macrocycle compounds, particularly, by oligo- and polysaccharides. Multiple examples show that complexation of biologically active substances may result not only in growth of those compounds solubility and prolongation of their action, but also increases their therapeutic activity.

We report the results of research using physical methods (optical spectroscopy, fluorescence, electrochemistry, NMR and ESR) of supramolecular complexes of carotenoids with oligosaccharides having macrocycle (cyclodextrine) and open-chained structures (glycyrrhizin), and with arabinogalactan polysaccharide produced from Siberian larch.



It was found that complexation with cyclodextrine results in the growth of carotenoid stability, however, not in that of its water solubility, and in fact it inhibits completely reactions between carotenoids and free peroxide radicals [1]. With carotenoids glycirrhizin gives more stable complexes (their stability constant is $K = 10^4\ M^{-1}$ as to compare with $10^3\ M^{-1}$ for cyclodextrine) not only in aqueous solutions, but also in some polar organic solvents: alcohols, acetonitrile, DMSO [2]. Complexation with glycirrhizin decelerates considerably carotenoid oxidation-reduction reactions, and decreases lifetime of carotenoid cation-radicals due to the influence of complexation on their oxidation potentials. At the same time those complexes' capacity for trapping peroxide radicals (antioxidant activity) is much higher [3]. Complexation with arabinogalactan made it possible to produce water soluble carotenoid for the first time.

The study was carried out within framework of SB RAS Project № 146, RAS Presidium Programme №18.2 and supported by DE-FG02-86ER13465 grant (USA).

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SYNTHESIS, MOLECULAR AND CRYSTAL STRUCTURES OF 3-(1-AMINO-2,2,2-TRIFLUOROETHYLIDENE)-1,1,4,5,6,7-HEXAFLUOROINDANE-2-ONE, 2-AMINO-1,1,4,5,6,7-HEXAFLUORO-3-TRIFLUOROACETYLIDENE AND IT'S DIOXANE AND PYRIDINE COMPLEXES

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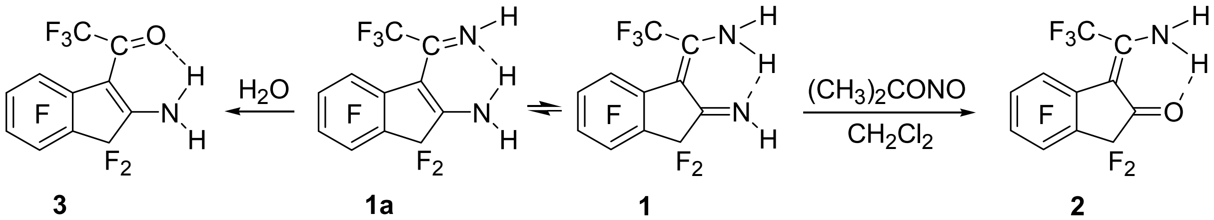
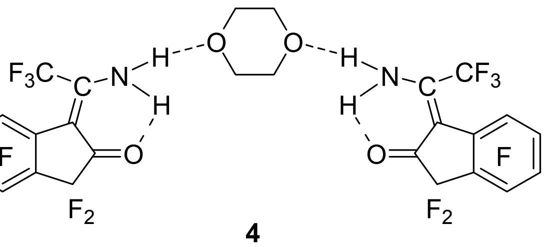
The interaction between 3-(1-amino-2,2,2-trifluoroethylidene)-2-imino-1,1,4,5,6,7-hexafluoreindane (**1**) and isopropylnitrite was used to synthesize 3-(1-amino-2,2,2-trifluoroethylidene)-1,1,4,5,6,7-hexafluoreindane-2-on (**2**), and hydrolysis of (**1**) resulted in 2-amino-1,1,4,5,6,7-hexafluoro-3-trifluoroacetylindene (**3**).



We also report growth of monocrystals and studies of molecular and crystal structure of thus produced enaminoketones, complex of **2** with 1,4-dioxane and complex of **3** with pyridine.



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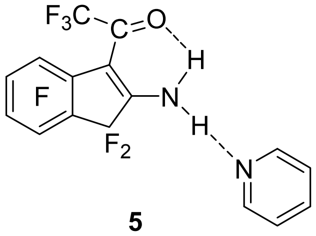

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The method of density functional was used in *ab initio* calculations of reaction heat values for gas-phase reactions of **2** and **3** with dioxane.

This study was supported by Russian Fund of Fundamental Research (project 06-03-32229).

P-46

SYNTHESIS OF NEW POLYFLUORINATED DERIVATIVES OF 2-AMINO-1,4-NAPHTOQUINONE

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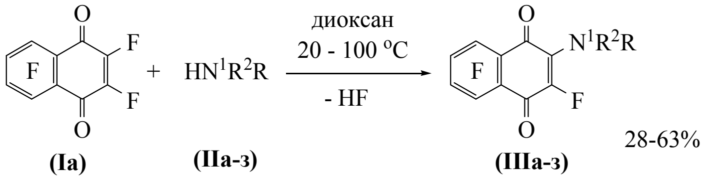
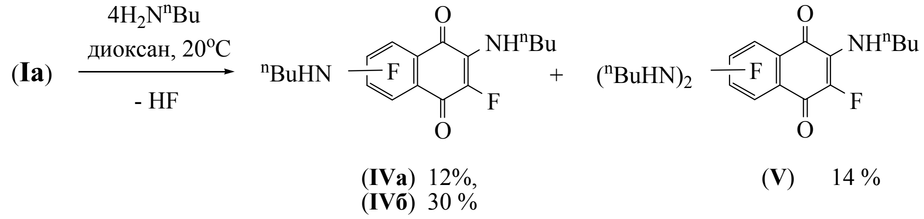
Polyfluorinated derivatives of 1,4-naphtoquinone are promising preparations to be used in anticancer therapy [1]. Reactions between hexafluoro-1,4-naphtoquinone (**Ia**) and primary or secondary amines (**IIa-з**) resulted in corresponding novel derivatives of 2-aminopentafluoro-1,4-naphtoquinone (**IIIa-з**):

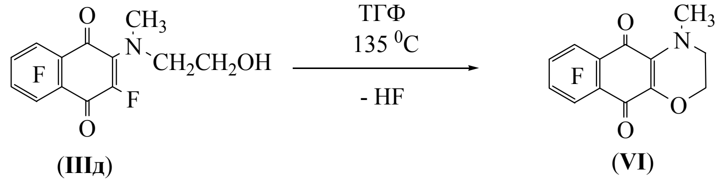


HN^1R^2R = H_2N^nBu (**IIa**), H_2N^tBu (IIб), H_2NPh (**IIв**), $HNEt_2$ (**IIг**), $HNCH_3(CH_2CH_2OH)$ (**IIд**), $HN(CH_2CH_2OH)_2$ (**IIe**), $H_2NCH_2CH_2SCH_3$ (**IIж**), морфолин (**IIз**)

The reaction mixture from the reaction of quinone (**Ia**) with excess of *n*-butylamine contained isomers of di- and three-substituted quinones of types (**IV**) and (**V**):



Intermolecular cyclization of 2-(2'-hydroxyethyl-methylamino)pentafluoro-1,4-naphtoquinone (**IIIд**) used for a model to show possible synthesis of heterocyclic derivatives that is 3,4-dihydro-4-methyl-6,7,8,9-tetrafluoro-2*H*-naphto[2,3-*b*][1,4]oxazin-5,10-dione (**VI**):



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P-47

HYDRODEHALOGENATION OF POLYHALOAREN ES BY HYDROGENE AND Pd/C

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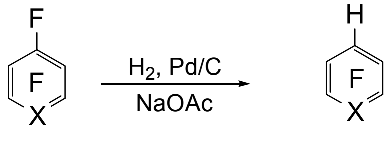
Catalytic hydrogenolyse of C-Hal bonds in polyfluoropolychloroarenes is a promising technological pathway to otherwise difficultly accessible compounds with three or four fluorines in their aromatic rings, the said compounds being precursors in the synthesis of biologically active substances used in medical formulations.

It is established that fluorines to hydrogens exchange occurs under conditions using carbon supported palladium for catalyst (0.4% Pd). Thus interaction of hexafluorobenzene with hydrogen (70 atm) at 130°C in the presence of Pd/C and K_2CO_3 (or AcONa) after 8 hours results in reaction mixture comprising ~70% of pentafluorobenzene besides of initial compound (less than 15%) and traces of isomeric tetrafluorobenzenes, and after 24 hours over 2/3 of the product mixture are tetrafluorobenzenes (1,2,4,5-isomer more than 80%) the conversion of original compound being complete.

Selective hydrogenolyse of C-F bond is realizable in monoderivatives of hexafluorinebenzene and pentafluoropyridine. Thus, hydrodefluorination of octafluorotoluene and pentafluoropyridine in the presence of sodium acetate results in α,α,α,2,3,4,5-heptafluorinetoluene and 2,3,5,6-tetrafluoropyridine, the yields of corresponding purified products being >80%.



X = CCF_3, N

At similar conditions pentafluorophenol converts to 2,3,5,6-tetrafluorophenol with high yield, while pentafluoroaniline conversion results mainly in 2,3,5,6-tetrafluoroaniline.

It is shown that using of the said catalytic system facilitates hydrodechloration of polyhalogenated arenes more than defluorination. Thus we produced pentafluorobenzene from pentafluorochlorobenzene, and 2,4,6-trifluoropyridine from 3,5-dichlorotrifluoropyridine with the related yields exceeding 80%.

Hydrohenolysis of mixtures of dichlorotetrafluorbenzenes and/or trichlorotrifluorobenzenes (both being wastes in the manufacture of polyfluoroarenes using «Russian method») resulted in mixtures of tetrafluorobenzenes or trifluorobenzenes isomers. Individual substances were then isolated through rectification.

Variation of the process temperature and duration allow us to achieve either complete or partial dechlorination of substances comprising more than one chlorine.

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2,3-EPOXYPERFLUOROBUTANE IN THE REACTION WITH 2-AMINOTHIOPHENOL

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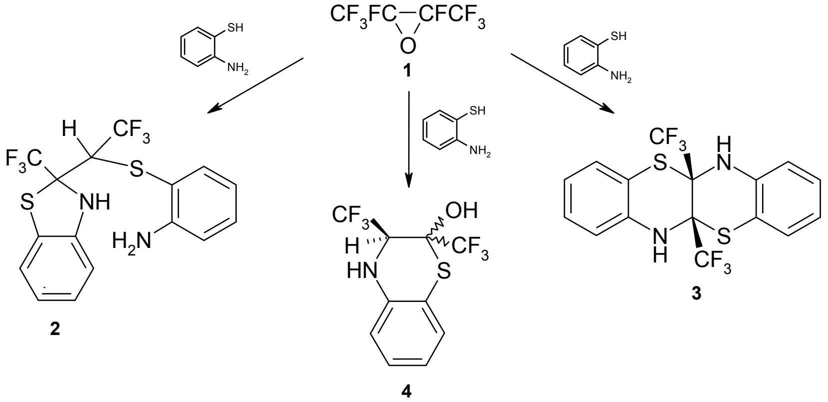
Earlier it was shown that 2-aminothiophenol (ATPH) easily reacts with 1,2-epoxyperfluoropropane in *N,N*-dimethylacetamide (DMAA) to give 2-fluoro-2-trifluoromethyl-3,4-dihydro-2*H*-1,4-benzothiazine-3-on as a result of primary attack of *SH*-dinucleophilic group on the central epoxy-group carbon [1].

We found that in the reaction of 2,3-epoxyperfluorobutane (**1**) with ATPH the product composition depends on the solvent polarity. Thus interaction of oxide (**1**) with ATPH in polar solvents DMSO and DMAA results mainly in a mixture of 2-trifluoromethyl-2-[1-(2-aminophenylthio)-2,2,2-trifluoroethyl]-1,3-benzothiazoliden (**2**) that is a blend of *RSSR* and *RRSS* diastereoisomers and small amount of 5a,11a-bis(trifluoromethyl)-5a,6,11a,12-tetrahydro-5,11-dithia-6,12-diazanaphtacene (**3**).

If one use aprotic solvents with low polarity, such as dioxane or tetrahydrofuran, the process unexpectedly results in 2,3-bis(trifluoromethyl)-3,4-dihydro-2*H*-1,4-benzothiazine-2-ol (**4**) that is a blend of *RSSR* and *RRSS* diastereoisomers. In contrast to the results of [1] here compound (**4**) resulted probably from the primary attack of dinucleophil aminogroup by one of epoxy-group carbons.

The assumed reaction schedules are discussed where ATPH performs not only as a nucleophilic reagent, but also as a reducer of C=N and C=O in intermediates.

The structures of resulting substances were confirmed by NMR ^1H, ^{19}F, ^{13}C, IR-spectroscopy, mass-spectrrometry and X-ray structural analysis.



The study was financially supported by State Program for support of leading scientific schools of the Russian Federation (project № НШ-9178.2006.3).

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[1] N. Ishikawa, S. Sasaki, Bull. Chem. Soc. Jpn. 50 (1977) 2164-2167.

P-49

CERTAIN SYNTHETIC MODIFICATIONS OF 2,3',4'-TRICYANODIPHENYL

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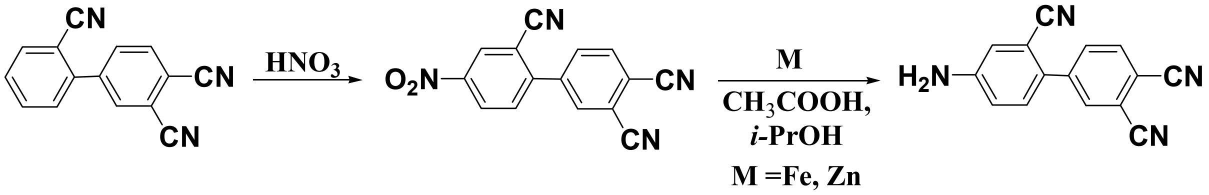
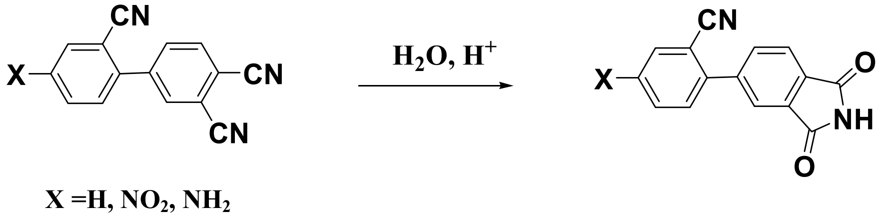
Reduction condensation of phtalodinitrile offered a short pathway to 2,3',4'-tricyandiphenyl [1] earlier difficultly accessible and practically non-studied substance, that, however is of considerable interest being a main half-product in thin organic synthesis. It was particulaly interesting to investigate its possible modification through the reaction of electrophilic substitution that expectedly should result in 4-substituted 2,3',4'-tricyandiphenyls, those being precursors of functionalized arylphtalocyans. It is found that treating 2,3',4'-tricyandiphenyl with nitric acid at room temperature results in smooth formation of 4-nitro-2,3',4'-tricyandiphenyl, its yield being 72%. Reduction of iron or zinc 4-nitro-2,3',4'-tricyandiphenyl in the presence of acetic acid in boiling isopropyl alcohol easily results in 4-amino-2,3',4'-tricyandiphenyl formation.



Hydrolysis of 2,3',4'-tricyandiphenyl, 4-nitro-2,3',4'-tricyandiphenyl, and 4-amino-2,3',4'-tricyandiphenyl in the presence of chlorosulfonic acid results, correspondingly, in the formation of the main products as follows: 4-(2-cyanophenyl)-phtalimide, 4-(4-nitro-2-cyanophenyl)-phtalimide and 4-(4-amino-2-cyanophenyl)-phtalimide, correspondingly. The presence of phtalimide groups was confirmed by their IR spectra containing bands at 1778-1764 and 1714-1712 cm^{-1}.



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[1] Е.В. Пантелеева, Т.А. Ваганова, Е.А. Лукьянец, В.Д. Штейнгарц, ЖОрХ, *42*, 1301-1309 (2006)

P-50

INTERACTION OF PERFLUORO-1-PHENYLBENZOCYCLOBUTENE WITH PENTAFLUOROBENZENE IN SbF_5 MEDIUM

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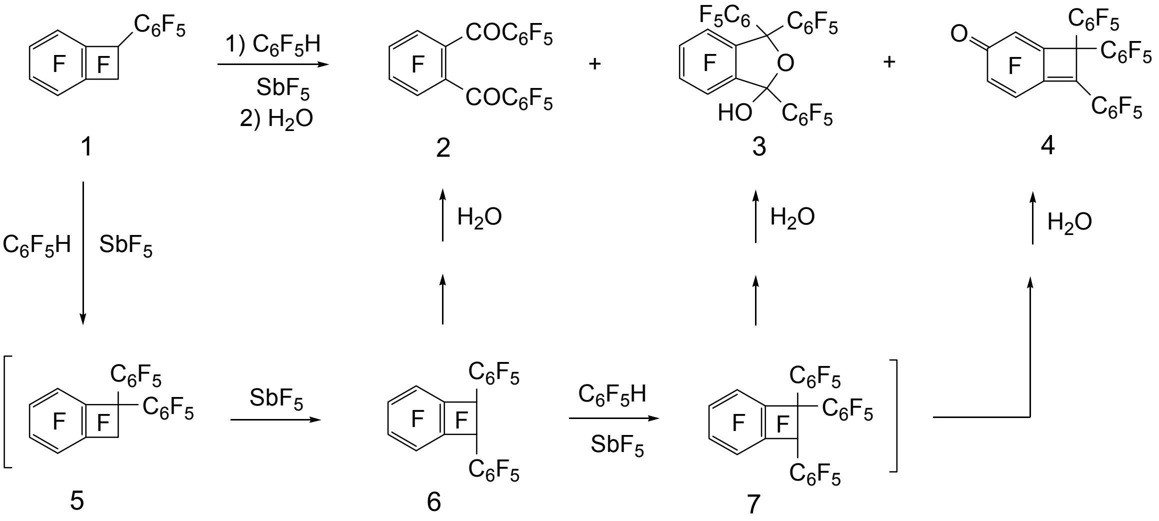
Interaction of perfluoro-1-phenylbenzocyclobutene (**1**) with excess of pentafluorobenzene in SbF_5 (at 50 °C) followed by hydrolysis of the reaction mixture results in the formation of perfluoro-1,2-dibenzoylbenzene (**2**), 1-hydroxyperfluoro-1,3,3-triphenylphtalan (**3**), and perfluoro-7,8,8-triphenylbiscyclo[4.2.0]octa-1,4,6-triene-3-on (**4**).



There are strong grounds for believing that the reaction between **1** and C_6F_5H in SbF_5 results at first not in 1,2-, but in 1,1-diphenylbenzocyclobutene **5**, the latter is then converted to 1,2-isomer **6** under the action of SbF_5. Isomer 6 then reacts with pentafluorobenzene to form triphenyl derivative **7**. At the reaction conditions both **6** and **7** undergo their 4-member rings opening and fluorination followed by hydrolysis that results in products **2** and **3** correspondingly. Hydrolysis of benzocyclobutene **7** results in ketone **4**.

P-51

BORON- AND PHOSPHORUS CONTAINING DERIVATIVES OF CYCLOPROPYLMETHANOLS

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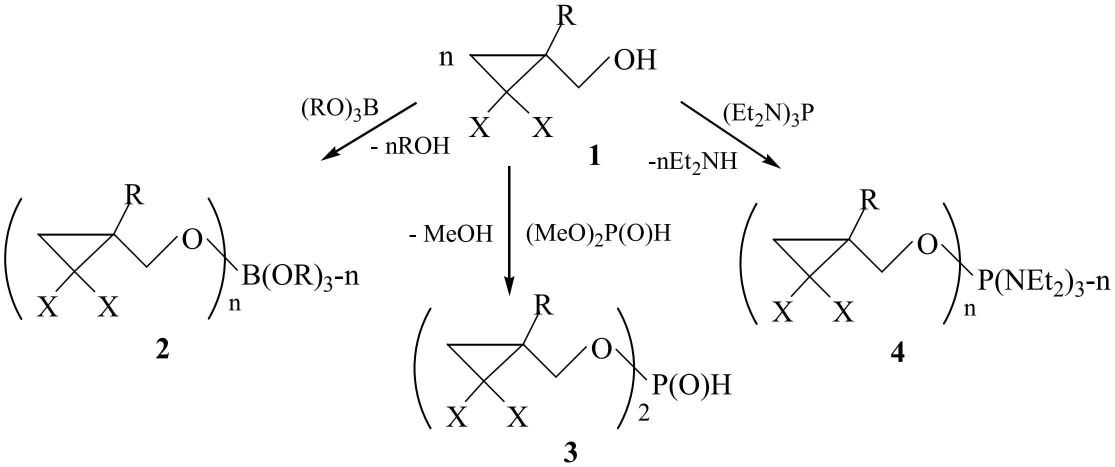
Functional derivatives of cyclopropane possess a wide range of biologically active properties. One would expect that inserting of boric and phosphoric groups would increase the said activity and emergence of new earlier unknown useful properties. In this connection and having in mind developing of new methods for the synthesis of boron and/or phosphorus containing cyclopropanes we investigated interaction of cyclopropylmethanols [**1** (X = H, Cl; R = H, CH_3)] with hexaethyltriamideophosphite and esters of boric and phosphorous acids. Such choice of initial compounds was due to high selectivity of cyclopropylmethanol to acid and basic reagents producing alteration of three-member cycles.

Re-esterification was conducted at mole ratio from 1:1 to 3:1 at 40-60°C for amideophosphites, and at 100-110°C for dimethylphosphites and trialkylborates. The reaction was controlled by the quantity of released diethylamines and aliphatic alcohols. Our study of thus produced compounds using the methods of IR, NMR ^1H and ^{31}P spectroscopy has shown that the reaction results in cyclopropylmethyl esters of boric and phosphorous acids (**2-4**).



The esters (**2-4**) are transparent colorless liquids, soluble in organic solvents and hydrolysable by water. Phosphites (**4**) easily cut in sulfur to give related thiophosphates, the latter are known to improve germinating energy and stimulate germination of seeds, and therefore are applicable in agriculture. Phosphite (**3**) interacts with aldehydes, esters, ethers and α,β-non-saturated к carboxylic and phosphonic acids without opening of its three-member cycle.

P-52

INTERACTION OF NITROPHENOLS AND NITRONAPHTHOLS WITH ALUMINIUM BROMIDE

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Interaction between phenols and halogenated aluminium, particularly, with aluminium bromide in non-aqueous solutions may be followed by the formation either of oxycomplexes, or of ketocomplexes when donor substituents such as alkyl or hydroxy groups are present in their aromatic rings [1,2]. By now complexation of phenols with acceptor groups was studied non-sufficiently [3,4].

The methods of thermochemistry were used to investigate the reaction of 2-nitrophenol with aluminium bromide in bromobenzene. It was established that two complexes are formed in solution. The formation enthalpy for complex 1:1 is 31,5 kJ/mole; that for complex 1:2 is 51,6 kJ/mole. The analysis of NMR ^{1}H and ^{13}C spectra for those complexes and quantum-chemical calculations lead to the conclusion about chelatic structure of the said complexes. NMR was also applied to investigate the reactions of 2-nitro-4,6-dichloro-, 2,4-dinitro-, 2,4,6-trinitrophenols, and also of 1-nitro-2-naphtol, 2-nitro-1-naphtol in nitromethane solutions. The particularity of nitrophenol and naphtol complexes' spectra is that the signals of aromatic protons and that of hydroxyl hydrogen shift to the weak, but to the strong field (see table) that agree well with chelatic position of the relevant acceptor.

Table

Chemical shifts for nitrophenols and complexes in nitromethane

Nitrophenol	$AlBr_3$	H-2	H-3	H-4	H-5	H-6	OH
2-Nitrophenol	1:0		8,12	7,08	7,69	7,17	10,4
	1:1		7,89	6,92	7,75	6,92	8,37
	1:2		7,89	6,92	7,75	6,92	8,13
2-Nitro-4,6-дichlorinephenol	1:0		8,14		7,84		10,7
	1:1		7,84		7,81 7,80		8,54
	1:2		7,84		7,81 7,80		8,28
2,4-Dinitrophenol	1:0		9,05		8,49	7,45	10,7
	1:1		8,79		8,55-8,62	7,29 7,24	8,98
	1:2		8,79		8,55-8,62	7,29 7,24	8,65
2,4,6-Trinitrophenol	1:0		9,10		9,10		11,0
	1:1		8,91		8,91		8,64
	1:2		8,91		8,91		8,40
Nitrobenzene	1:0	8,11	7,50	7.66	7,50	8,11	
	1:1	8,09	7,48	7,72	7,48	8,09	

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[1] Голоунин А.В., Коптюг В.А. // ЖОрХ. 1972. Т.6. Вып.12. С. 2555-2558.
[2] Голоунин А.В., Коптюг В.А. // ЖОрХ. 1972. Т.8. Вып. 2. С. 607-610.
[3] Суворов Б.А. // Ж. прикл. спектр. 1990. Т. 53. Вып.6. С. 4023-4026.
[4] Голоунин А.В., Рубайло А.И., Павленко Н.И. // ЖОХ. 1998.Т.68. Вып.4. С. 562-565.

P-53

REACTIONS OF ACETYLENIC COMPOUNDS CATALYZED BY ALUMINIUM HALOGENIDES

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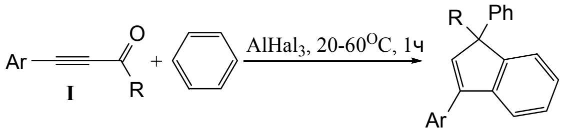
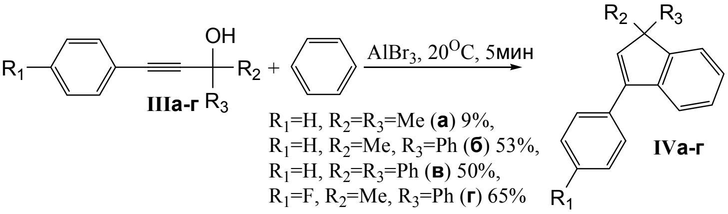
At the conditions of Friedel-Crafts reaction in the presence of aluminium halogenide catalysts ($AlBr_3$ or $AlCl_3$) acetylenic carbonyl derivatives (**I**) react with benzene to give substituted indenes (**II**)[1]. When so doing two benzene molecules interact with cation intermediates generated from substrate (**I**). Electrophilic centres in those intermediates are carbons of carbonyl groups activated by aluminium halogenide and vinyl cation centre formed due to protonation of acetylene bond.



R = H, Me, Ph
Hal = Cl, Br

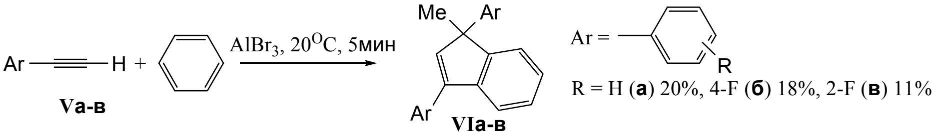
II (15-95%)

In a similar reaction propargyl alcohols (**IIIа-г**) give indene sructures (**IVа-г**) formed through the condensation of one benzene molecule with one molecule of acetylene alcohol.



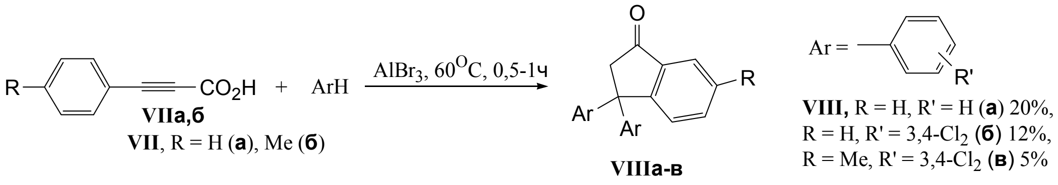
R_1=H, R_2=R_3=Me (**а**) 9%,
R_1=H, R_2=Me, R_3=Ph (**б**) 53%,
R_1=H, R_2=R_3=Ph (**в**) 50%,
R_1=F, R_2=Me, R_3=Ph (**г**) 65%

When catalyzed by $AlBr_3$ interaction of two arylacetylene molecules (**Vа-в**) with one benzene molecule results in indenes (**VIа-в**).



R = H (**а**) 20%, 4-F (**б**) 18%, 2-F (**в**) 11%

Arylacetylene acids (**VIIа, б**) react with benzene and 1,2-dichlorobenzene in the presence of $AlBr_3$ generating 3,3-diarylindanones (**VIIIа-в**).



VII, R = H (**а**), Me (**б**)

VIII, R = H, R' = H (**а**) 20%,
R = H, R' = 3,4-Cl_2 (**б**) 12%,
R = Me, R' = 3,4-Cl_2 (**в**) 5%

Here we report new methods for the synthesis of indane-type derivatives on the basis of electrophilic transformation of acetylenic compounds catalyzed by aluminium halogenides.

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[1] Васильев А. В., Щукин А. О. *ЖОрХ*. **2006**, *42*, 1256.

P-54

PENTAFLUOROPHENYLSUBSTITUTED PYRILIUM SALTS: REACTIONS WITH PHENYL HYDRAZINE

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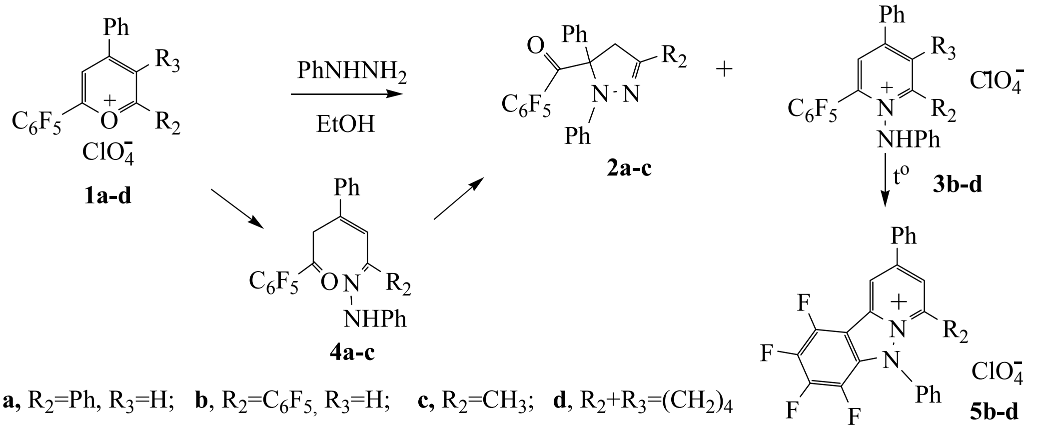
Pyrylium salts due to their extremely high reactivity provide unique feedstock for the synthesis of difficultly available heterocycle derivatives. Using of fluorinated pyrylium salts in reactions with nitrous nucleophilic and amphiphilic reagents makes it possible to synthesize new fluorinate heterocycles those being promising bioactive compounds. Earlier we have studied the reactions of pentafluorophenyl-substituted pyrylium salts with methylamine and hydrazine [1,2]. Here we report the results of our investigation of interaction between pyrylium salts, comprising pentafluorophenyl groups either in one or in both α-positions of pyrylium cycle, with phenylhydrazine.

It is shown that reactions between pyrylium perchlorates **1a-d** and phenylhydrazine result in pentafluorophenacyl-substituted pyrazolines **2a-c** and/or in perchlorates of *N*-phenylaminopyridine **3b,d**. The formation of pyrazolines occurs via intermediate monophenylhydrazones **4a-c,** being stable those substances were isolated. The formation of pyridine salts in some cases was followed by their intermolecular cyclisation giving perpchlorates of pyrido[1,2-*b*]indazolyl resulting from the reaction of nucleophilic substitution of *orto*-fluorine in pentafluorophenyl ring by an amino groups.



a, R_2=Ph, R_3=H; **b**, R_2=C_6F_5, R_3=H; **c,** R_2=CH_3; **d**, R_2+R_3=$(CH_2)_4$

The study was financially supported by SD RAS Integration Projects № 15, 33, 65.

1. Каргаполова И.Ю., Орлова Н.А., Герасимова Т.Н., *ХГС*, **1991**, *8*, 1100.
2. Kargapolova I.Yu., Kardash T.Yu., Orlova N.A. *Theses of 3th EuroAsian Heterocyclic Meeting "EAHM 2004"*, **2004**, Novosibirsk, Russia. P.158.

P-55

NEW POLYIMIDES BASED ON DIAMINES OF POLYFLUORO NAPHTHALENE, PYRIDINE AND TOLUENE

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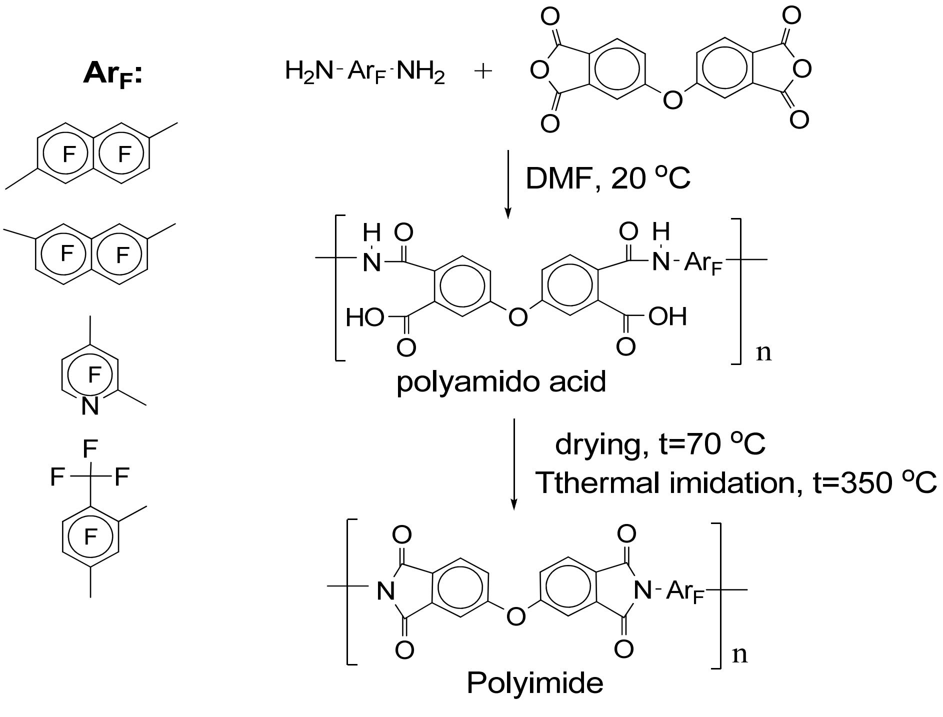
It is well known that introduction of fluorine atoms into the structure of aromatic polyimides allows producing polymers soluble in organic solvents. The polymers are characterized by high thermal and chemical stability, low optical and dielectric losses.

We have synthesized polyfluoroaromatic diamines in high purity, such as 2,3-diaminohexafluorotoluene, 2,4-diaminotrifluoropyridine, 2,6- and 2,7-diaminohexafluoronaphthalene and new polyimides based on them. Polycondensation of diamines with dianhydride of diphenyloxide-3,3',4,4'-tetracarbonic acid was carried out according to the following two-stage scheme:

a)producing polyamido acid in *DMF* at 20 °C;

b) thermal imidation of the polyamido acid at 350 °C under vacuum;



By the method of synchronous DSC/TG analysis it has been determined that the polyimides synthesized have high glass-transition temperatures (Tg > 400 °C) and high thermal stability ($T_{5\%}$ > 450 °C). At that they are well soluble in DMF, DMSO, N-methyl pyrrolidone, ethyl acetate, chloroform, that allows producing thin polymer films.

The characteristics of the polyimides synthesized demonstrate availability of using polyfluorinated diamines as monomers for polycondensation polymers.

P-56

PHOTOLYSIS OF 4,5- SUBSTITUTED 3,6-DI-*TERT*-BUTYL-*ORTO*-BENZOQUINONES

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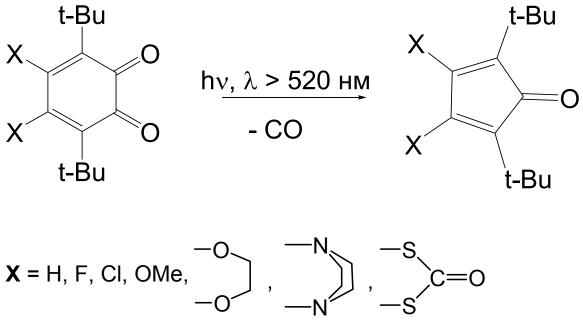
Almost all the works devoted to photolysis of quinones are limited by investigation of kinetics and/or reaction products only under action of UV-irradiation. The only example for ortho-benzoquinones is 3,6-di-*tert*-butyl-*ortho*-benzoquinone that dissociates under the action of UV-irradiation to 2,5-di-*tert*-butyl cyclopentadienone with a CO molecule release. We have revealed that this reaction runs under the action of irradiation λ > 520 nm as well. During the course of the work there was studied the kinetics and reaction products of quinones decarbonilation by the example of a series of seven 4,5-disubstituted 3,6-di-*tert*-butyl-*ortho*-benzoquinones. It has been determined that in all cases photolysis of quinones results in formation of the sole end product, corresponding 3,4-disubstituted 2,5-di-*tert*-butyl-cyclopentadienone.



All 3,4-disubstituted 2,5-di-*tert*-butyl-cyclopentadienones are formed in the yield close to quantitative. The products of *ortho*-benzoquinones photolysis were isolated individually and characterized by NMR-, IR-spectroscopy, elementary analysis.

The investigation of photolysis of *ortho*-benzoquinones by means of NMR-spectroscopy allowed to detect the presence of an intermediate compound, that decomposed spontaneously to form cyclopentadienones.

Kinetics of the reaction of decarbonylation of *ortho*-benzoquinones under exposure to radiation λ > 520 nm was studied by spectrophotometry as a decrease of the absorption band of quinones within the range of wave length of 380-410 nm. It has been shown that the reaction rate is determined by the structure of *ortho*-benzoquinone. All 4,5-substituted 3,6-di-*tert*-butyl-*ortho*-benzoquinones decompose more fast than 3,6-di-*tert*-butyl-*ortho*-benzoquinone.

The work has been fulfilled by financial support of Russian fund for fundamental investigations and RF President Grant № НШ – 4947.2006.3.

P-57

2,6- AND 2,7-DIAMINOHEXAFLUORONAPHTHALENES SYNTHESIS: ORIENTATION CONTROL BY THE REVERSIBLE MODIFICATION OF THE SUBSTITUENT

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E.V. Malykhin (Novosibirsk, Russia)

N.N.Vorozhtsov Novosibirsk institute of organic chemistry SB RAS
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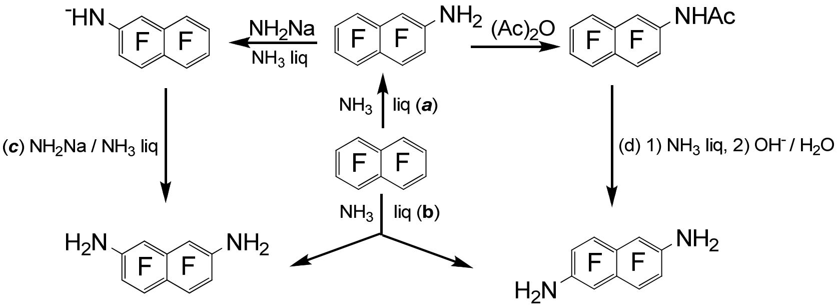
Mono- and diamination of octafluoronaphthalene (OFN) with liquid ammonia leads accordingly to 2-aminoheptafluoronaphthalene (way *a* in the scheme) and to a mixture of diaminohexafluoronaphthalenes (way *b*) in high yields. The processes may be separated effectively due to different temperatures of their running. For the first time for nucleophilic substitution in OFN was revealed preferred 2,7 orientation and its enthalpy preference that was interpreted as a result of more strong deactivating electron-donating influence of the pseudo-para-*arranged* amino group in comparison with the fluorine atom.



	conditions	*products*	*yield, %*
a	20 °C	2-NH_2	85
b	90 °C	2,7 + 2,6 (6:1)	60
c	-40 °C	2,7	80
d	50 °C	2,6	60

Taking that into consideration, methods to control orientation of amino defluorination of 2-aminoheptafluoronaphthalene were developed. Its transformation to naphthylamide anion by the action of $NaNH_2$ provides entering the second amino group exclusively in position 7 of the naphthalene skeleton (way *c*). On the contrary, in the course of amination of 2-acetylaminoheptafluorohapthalene electron-donating influence of the amino group, weakened by acetylation, and increased steric hindrance for appearance of the substituent resonance effect are favourable to enetering the amino group in position 6 (way *d*). Hydrolysis and subsequent separation of minor components by selective complexation with crown ether leads to 2,6-diaminohexafluorohaphthalene.

Thus, 2,6- and 2,7-diaminoheptafluoronaphthalenes, interesting substances as monomers for producing polycondensation polymers, have been obtained selectively in high yields by means of reversible modification of the substituent.

P-58

SYNTHESIS OF PERFLUORODIARYLS FROM PERFLUOROAROMATIC ORGANOZINC COMPOUNDS AND PERFLUOROARENES

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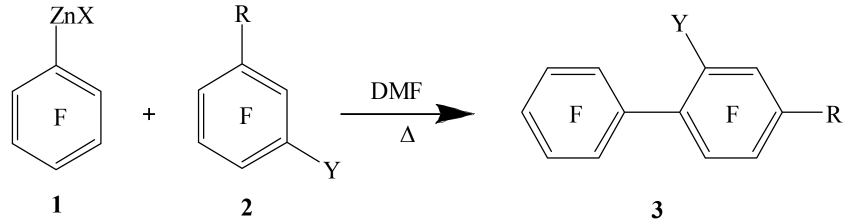
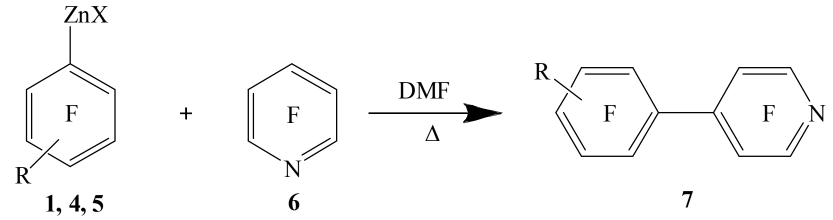
Synthesis of symmetrical perfluorodiaryls from perfluoroaromatic organozinc compounds and $CuCl_2$ has been described [1]. We have shown that perfluoroaromatic organozinc compounds may be used also to obtain asymmetrical perfluorodiaryls. Synthesis of these diaryls is realized by interaction of perfluoroaryl organozinc compounds (**1**) with perfluoroarenes (**2**).



X = Cl, C_6F_5

R = CF_3, Y = F;
R = CF_3, Y = CF_3;
R = CN, Y = F;
R = NO_2, Y = F;

Zinc organic compounds (**1**), (**4**) and (**5**) were used in the reaction with pentafluoropyridine (**6**) resulted in corresponding heteroanalogues of perfluorodiaryls (**7**).



R = 3-CF_3, X = Cl, 3-$CF_3C_6F_4$ (**4**);
R = 4-CF_3, X = Cl, 4-$CF_3C_6F_4$ (**5**).

The observed orientation of the perfluoroaryl group in the perfluoroarene is in agreement with orientation in reactions of nucleophilic substitution of given perfluoroarenes [1]..

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[1] Brooke G.M. The Preparation and Properties of Polyfluoro Aromatic and Heteroaromatic Compounds. // J.Fluorine Chem. 1997. Vol. 86. № 3. P. 1–76.

P-59

HIGH PRESSURE SYNTHESIS OF FOTOCHROMIC HYBRIDES, BEARING FULGIMIDE AND DIHETARYLETHENE MOIETIES.

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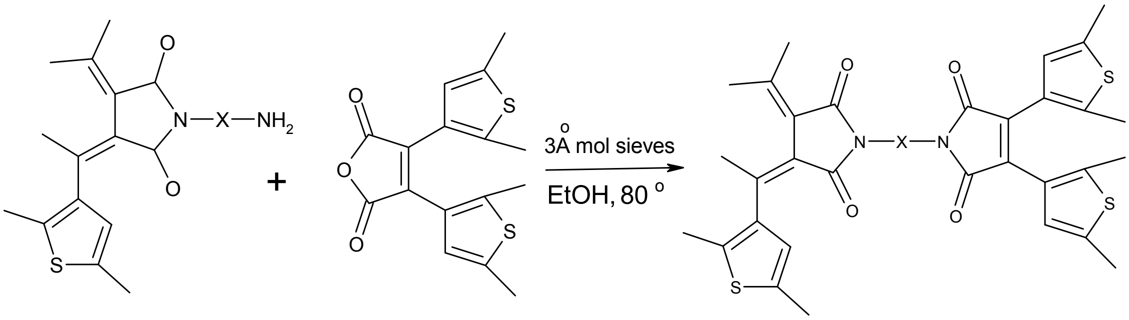
(Russia, Japan)

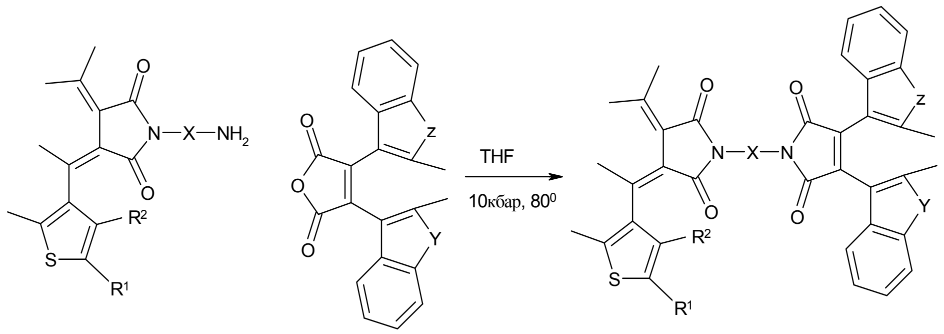
By the interaction of aminofulgimides with 3,4-dihetarylmaleic anhydrides for the first time there were synthesized hybrid compounds bearing concurrently two different photochromic moieties. In the case of 3,4-dihetarylmaleic anhydrides with indol or benzothiophene moieties the reaction runs under high pressure conditions following by *E*-/ *Z* -isomerization of the fulgimide moiety [1].



1 x=m-C_6H_4
2 x=p-C_6H_4

3

4 x=m-C_6H_4; 61%
5 x=p-C_6H_4 ; 75%



6 R^1=CH_3, R^2=H, X= -
7 R^1=CH_3, R^2=H, X=m-C_6H_4
8 R^1 R^2=-(CH=CH)$_2$-, X=p-C_6H_4

9 Y=Z=S
10 Y=S, Z=NH

11 R^1=CH_3, R^2=H, X=m-C_6H_4, Y=Z=S; 57%
12 R^1R^2=-(CH=CH)$_2$-, X=p-C_6H_4, Y=Z=S; 11%
13 R^1=CH_3, R^2=H, X=m-C_6H_4, Y=NH, Z=S; 34%
14 R^1=CH_3, R^2=H, X= -, Y=Z=S; 19%

The structure of photochromic compounds **4,5,11-14** has been confirmed by NMR ^{1}H, NMR ^{13}C mass spectra and elementary analysis data. Photochromic properties of the compounds obtained were studied.

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[1] Шорунов С.В. Диссертация канд. наук. М., ИОХ РАН, 2005.

P-60

PUBLICATIONS OF ACADEMICIAN N.N. VOROZHTSOV: A BIBLIOMETRIC ANALYSIS DONE WITH CHEMICAL ABSTRACTS AND SCIENCE CITATION INDEX DATABASES OF STN INTERNATIONAL

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A bibliometric analysis of scientific publications by academician N.N.Vorozhtsov (1907-1979), director and founder of Novosibirsk institute of organic chemistry SB RAS, has been fulfilled with use of *Chemical Abstracts* and *Science Citation Index* databases of *STN International*, an online provider of scientific and technical information. Comparison with the official list of works has shown that *Chemical Abstracts* database includes 90% of publications by N.N.Vorozhtsov for 1929-1977y. Citing N.N.Vorozhtsov publications was studied and works, most cited in 1974-2006, were identified according to *Science Citation Index* database and for the period of 1996-2006y according to *Chemical Abstracts* database. Most part of them is connected with chemistry of polyfluorinated aromatic compounds. It was revealed that for the studied period the citing of publications by N.N.Vorozhtsov was monotone increasing (Fig.) in spite of that the used databases allowed to study the citing only since 1974, i.e. in fact since the time of completion of his almost 50-years scientific career. Such a tendency is the best evidence of scientific importance of the scientist. The data about N.N.Vorozhtsov's co-authors and authors of publications citing his works show that N.N.Vorozhtsov life-work is going on with his disciples and followers working at the institute bearing his name.

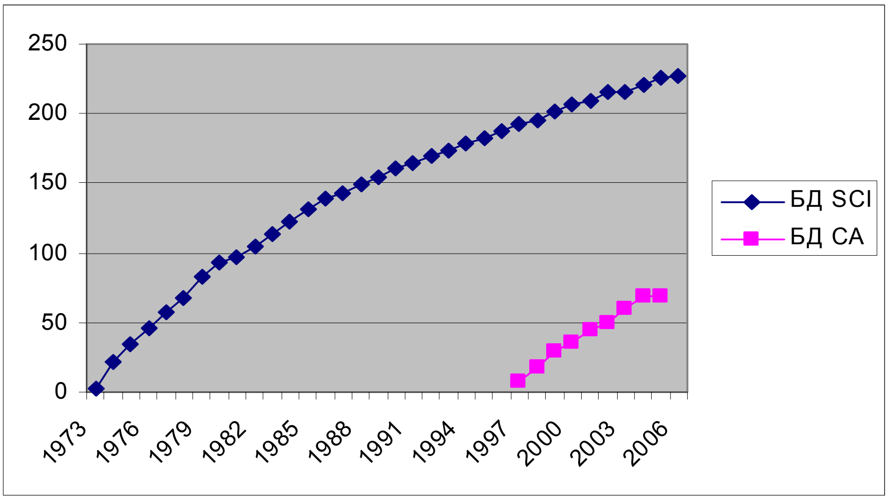

Fig. Citing N.N.Vorozhtsov publications in 1974-2006y.

P-61

TRANSFORMATION OF PERFLUOROAROMATIC COMPOUNDS TO CARBONYL DERIVATIVES UNDER THE ACTION OF CF_3COOH/SbF_5

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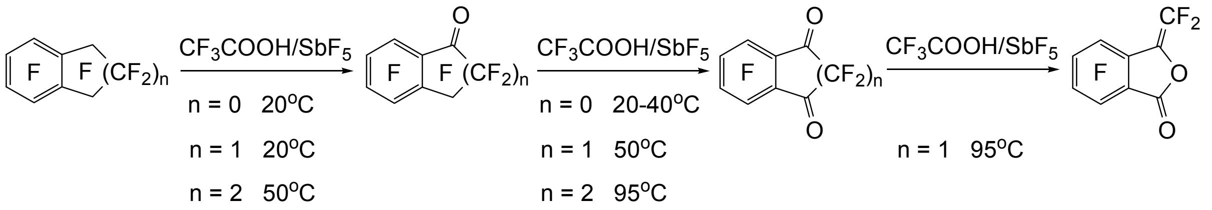
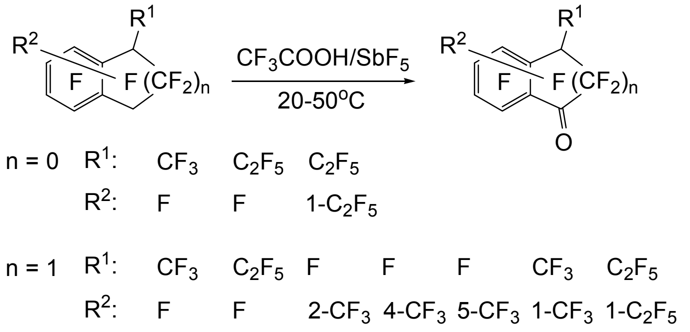
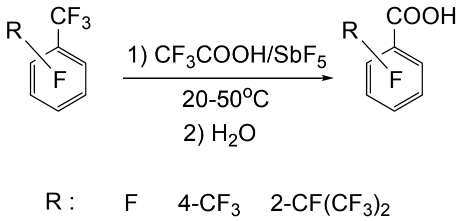
The interaction of perfluorinated benzocyclobutene(**1**), indan (**2**) and tetralin (**3**) with CF_3COOH in the presence of Sb F_5 proceeds smoothly to afford monocarbonyl derivatives, from which under more sever conditions diketones are obtained. Indan **2** under the action of CF_3COOH/SbF_5 at 95°C is converted to perfluoro-3-methylphthalide.

By the method of competitive reactions it has been determined that the reactivity of perfluorinated benzocycloalkenes in their interaction with CF_3COOH/SbF_5 at 20°C depends on the size of the substrate alicyclic moiety and is reducing at transfer from benzocyclobutene 1 to indan **2** and tetralin **3**. This consecution is in an agreement with the sequence of decreasing relative stability of appropriate perfluorobenzocycloalken-1-yl cations.







Perfluorinated alkyl benzocyclobutenes and alkylindans react with CF_3COOH/SbF_5 under mild conditions to form appropriate ketones and in case of 4- and 5-methylindans the carbonyl function is introduced in metha-position with respect to CF_3 group. Perfluoroalkylbenzenes, containing a trifluoromethyl group on the aromatic ring, interact with CF_3COOH/SbF_5 to form corresponding benzoic acids after hydrolysis of the reaction mass.

P-62

BASICITY OF DIALKYLAMINO NAPHTHALENE DERIVATIVES

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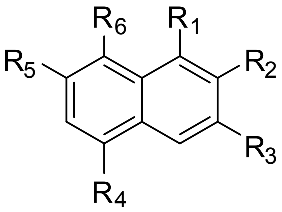
In spite of that 1,8-bis(dialkylamino) naphthalenes is a well studied class of organic bases and 1,8-bis(dimethylamino) naphthalene (“proton sponge”) [1] synthesized already in 1968 is the most known from them, there is no integrated data in literature for values p*Ka* of the compounds with a different arrangement of amino groups that makes impossible the complex analysis of factors influencing the basicity of this series amines.

We have synthesized and studied for the first time acid-base properties of bis(dimethylamino) naphthalenes **3-7** series according to the unified acidity scale.



1 $R_1 = N(CH_3)_2$, $R_2 = R_3 = R_4 = R_5 = R_6 = H$
2 $R_2 = N(CH_3)_2$, $R_1 = R_3 = R_4 = R_5 = R_6 = H$
3 $R_1 = R_2 = N(CH_3)_2$, $R_3 = R_4 = R_5 = R_6 = H$
4 $R_2 = R_3 = N(CH_3)_2$, $R_1 = R_4 = R_5 = R_6 = H$
5 $R_1 = R_4 = N(CH_3)_2$, $R_2 = R_3 = R_5 = R_6 = H$
6 $R_1 = R_6 = N(CH_3)_2$, $R_2 = R_3 = R_4 = R_5 = H$
7 $R_2 = R_5 = N(CH_3)_2$, $R_1 = R_3 = R_4 = R_6 = H$

The values of compounds **3-7** as well as 1 (**1**) and 2-dimethylaminonaphthalene (**2**) were determined by potentiometric titration in 80% dioxane hydrate according to Van Uitert method [2]. Besides, the basicity of the mentioned amines was evaluated by means of quantum-mechanical calculation of their proton affinity in gas phase.

Table 1. Basicity in 80% dioxane hydrate (25 °C) and proton affinity of 1-, 2-dimethylaminonaphthalenes and bis(dimethylamino)naphthalenes series.

Compound [a]	$N(CH_3)_2$-group position	pKa_1	PA (kcal·mole^{-1}) [b]
6	1,8	10.22±0.04	252.3
3	1,2	7.64±0.02	247.4
4	2,3	5.89±0.02	249.9
7	2,7	5.82±0.01	239.0
5	1,5	5.77±0.03	236.9
1	1 (α)	5.54±0.03	233.2
2	2 (β)	5.44±0.03	232.6

[a] For the convenience the amines are listed according to decreasing p*Ka* values

[b] Proton affinity in gas phase is given according to the data of quantum-mechanical calculations, B3LYP/6-31G+(d) method

P-63

SYNTHESIS OF SOME AMINOAROMATIC ACIDS AND PHENOLS IN ELECTROCATALYTIC SYSTEM

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Electrocatalysis is one of the methods successfully used for synthesis of various organic compounds.

We have studied electrocatalytic hydrogenation of a series of nitroaromatic compounds, such as nitrophenols, nitrobenzoic and nitrosalicylic acids, with the purpose to obtain appropriate amino derivatives widely used in pharmaceutical and paint industries as well as for manufacture of explosives.

The reduction was carried out in an electrocatalytic cell. The optimal conditions for producing *para*-aminobenzoic acid and *ortho*-aminophenol were developed by an experimental run followed by mathematical treatment of the data with use of a probabilistic and deterministic planning approach for the experiment: current density was 4 кA/m^2 (at visible surface of the copper cathode of $5 \cdot 10^{-4}$ m^2), the catalyst was Rheney nickel of 0.5g weight retained on the cathodes by an external magnet, the temperature was 303K, the concentration of hydrogenated substance was 0.074 кmole/m^3, the catholyte 60 ml of 2% solution of sodium hydroxide and 50 ml of 20% solution of sodium hydroxide as the anolyte. Under the present optimal conditions with 100% hydrogen absorption there were also obtained *para*-aminophenol, *ortho*-aminobenzoic and 5-aminosalicylic acids. The experimental results are given in the table.

Table. Comparison characteristics of the process of electrocatalytic synthesis of aminoaromatic acids and phenols.

Compound	Product	$W_{av.}$, ml H_2/min
5-nitrosalicylic acid	5-aminosalicylic acid	8,1
n-nitrophenol	*n*-aminophenol	9,4
o-nitrophenol	*o*-aminophenol	9,6
n-nitrobenzoic acid	*n*-aminobenzoic acid	10,6
o-nitrobenzoic acid	*o*-aminobenzoic acid	12,7

W_{av} is the average rate of the electrocatalytic reduction calculated for the period of 50% hydrogen absorption.

According to the Table data , the reduction of nitrobenzoic acid proceeds more rapidly and the rate of this process for *ortho* isomer is slightly higher than for *para* isomer. The hydrogenation rates for two nitrophenol isomers differ in a similar way that may be explained by a decrease of π-coupling of the nitro group with the benzene ring in the case of *ortho* isomers caused by the interaction effect of two neighboring groups. At the same time it may be expected that reduction of 5-nitrosalicylic acid would run more actively in comparison with nitrobenzoic acid owing to occurrence of one more electron-seeking substituent (of the hydroxyl group) on the ring. The observed lower hydrogenation rate of 5-nitrosalicylic acid is obviously determined by its lower solubility in water-alkaline medium of the catholyte.

P-64

TRIS(4-R-TETRAFLUOROPHENYL)PHOSPHINES: PREPARATION AND COMPLEXATION

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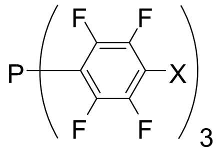
Electron-deficient phosphines, for example tris(pentafluorophenyl)phosphine, is a class of ligands important for complexation with transient metals. Similar complexes, exhibiting catalytic properties analogous to the properties of the complexes based on electron-excess phosphines, possess solubility, uncharacteristic for the latter, in non-classical reaction media such as supercritical carbon dioxide or organofluoric two-phase systems. Another peculiarity of these complexes arises as a result of electron density transfer from a metal atom to the phosphine and a subsequent increase in its Lewis acidity, that brings to catalysis of reactions of polymerization of unsaturated compounds, Baeyer-Viliger oxidation and similar transformations not characteristic (unusual) to the complexes with participation of electron-deficient phosphines.

The object of the investigation is synthesis of series of *para*-substituted derivatives of tris(pentafluorophenyl)phosphine **1-5** and producing complexes with palladium and rhodium on their basis.



1 X = CN
2 X = CF_3
3 X = H
4 X = OCH_3
5 X = $N(C_2H_5)_2$

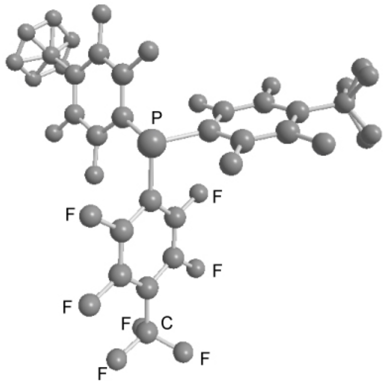


Fig.1 . Crystal structure of tris(4-trifluoromethyltetrafluorophenyl)phosphine according to X-ray crystallographic analysis data.

The mentioned phosphines were obtained by means of organometallic synthesis, compounds **1-3** and **5** by means of Grignard reagents, prepared from appropriate organic bromine compounds by interaction with phosphorus trichloride. Compound **4** was synthesized starting from 2,3,5,6-tetrafluoroanisole by means of metalation with *n*-butyl lithium followed by phosphorus trichloride action. The structure of phosphines **1-3** has been confirmed by the data of X-ray crystal structure analysis further to the conventional analysis methods (Fig.1)

The synthesized phosphines, except **1**, give square-planar complexes with palladium (II) and rhodium (I). In both cases organofluoric ligands are in *trans* configuration with respect to the metal atom.

P-65

HIGH PRESSURE SYNTHESIS OF PYRIDINES FROM 1,2,4-TRIAZINES

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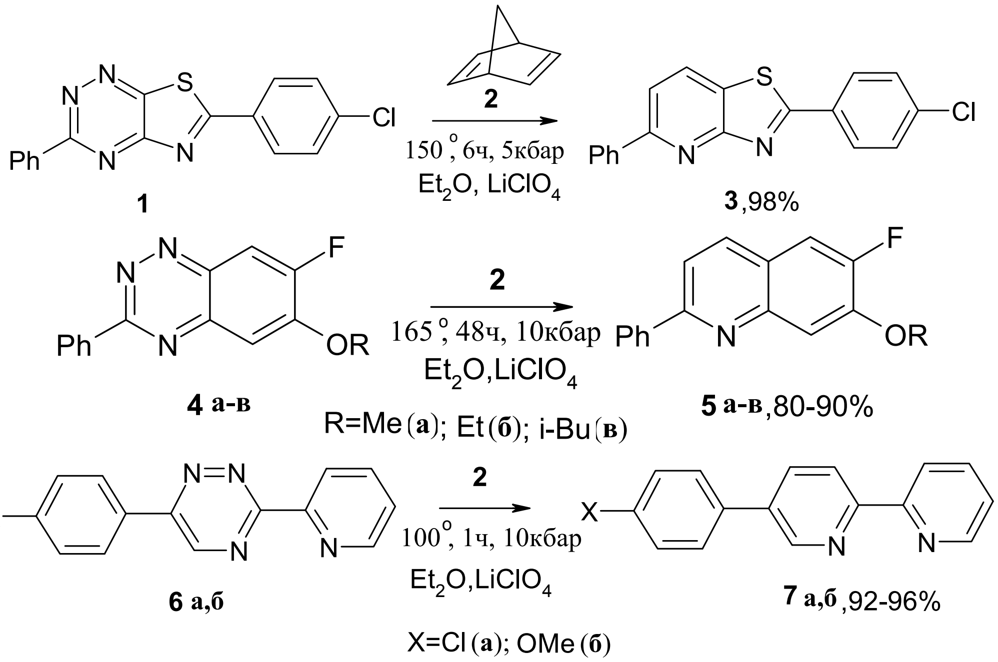
Pyridine derivatives, including condensed compounds containing the pyridine cycle are part of many natural substances and found a wide application in synthesis of various biologically active compounds.

We have studied the influence of different factors (pressure, catalysts, solvents, process time) on the reactions of cycloaddition of bicyclo[2.2.1]heptadiene to 1,2,4-triazines that are impossible at atmospheric pressure [1]. As a result of the work there was proposed a general method to produce pyridines by interaction of asymmetric triazines with bicycle[2.2.1]heptadiene under high pressure in the presence of lithium perchlorate. We have successfully applied the new approach for the reaction both with condensed and non condensed triazines.



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[1] Krayushkin M.M., Yarovenko V.N., Sedishev I.P., Andreyko A.A., Mochulskaya N.N., Charushin V.N. *Mendeleev Commun.* **2005**, 151.

P-66

SYNTHESIS OF NOVEL SPIROCYCLIC DERIVATIVES OF 1,3-DIAZAADAMANTANE

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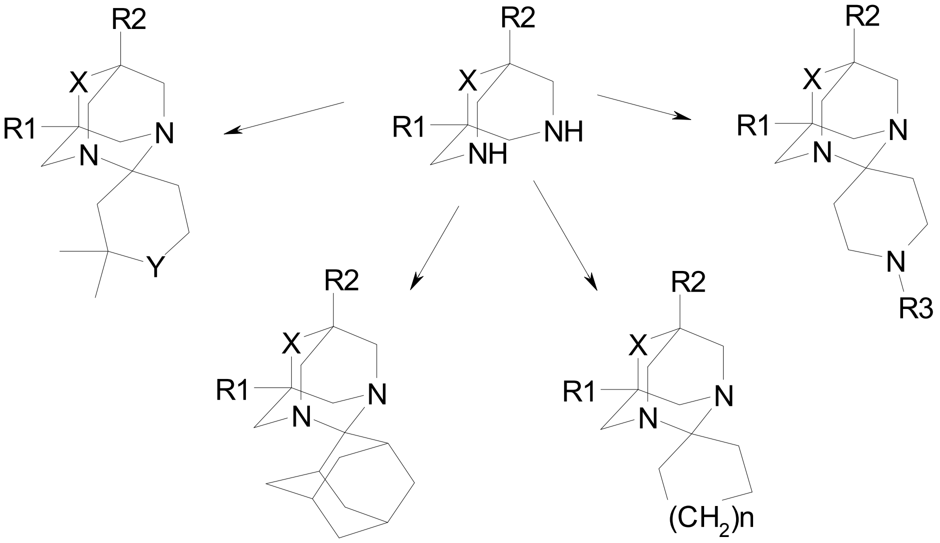
In contrast to adamantine derivatives, which biological activity, in particularly antivirus activity, was described widely in literature, 1-3 diazaadamantanes close to them in structure have not been almost studied. Meanwhile, in the frame of the study of biological activity, 1,3-diazaadamantanes and particularly their spiro-derivatives are of great interest. The study of some spirocyclic derivatives of diazaadamantane has revealed that they show anticancer, coronary vasodilating , antibacterial, adrenerging blocking activity [1,2]. With the purpose of further investigation of this class we suggest a simple and convenient method to synthesize these compounds by means of condensation of 3,7-diaza-bicyclo/3.3.1/nonane with various cyclic ketones.

The methods to synthesize novel spirocyclic derivatives of 1,3 diazaadamantane developed by our team make these compounds accessible for synthesis and versatile investigation of their biological activity.



Y= O, S; X= CO, CHOH, CH_2;
R_1= R_2= CH_3, C_2H_5, n-C_3H_7; R_1= CH_3, R_2= n-C_3H_7, n-C_4H_9; R_3= CH_3, $CH_2C_6H_5$; n= 1, 2.

[1] Агаджанян Ц.Е.,Арутюнян А.Д., Арутюнян Г.Л. и др. - Взаимосвязь, химическая структура – биологическая активность". Ереван 1998, с.92 Ts.E. Agadazhanyan, A.D.Arutyunyan, G.L.Arutyunyan etc.,-Interconnection, chemical structure, biological activity, Yerevan 1998, 92p
[2] Арутюнян Г.Л., Чачоян А.А., Агаджанян Ц.Е.,Гарибджанян Б.Т. - Хим.-фарм.журн., 1996, №12, с.20 G.L.Arutyunyan, A.A.Chachoyan , Ts.E. Agadazhanyan, B.T.Garibdzhanyan- Chem.-farm.Journal, 1996, , №12, p.20

P-67

THE SYNTHESIS AND THE PROPERTIES OF ACETYLATES AND MESYLATES 1-AMINO-2-ARYLOXY-4-HYDROXY-9,10-ANTHRAQUINONES

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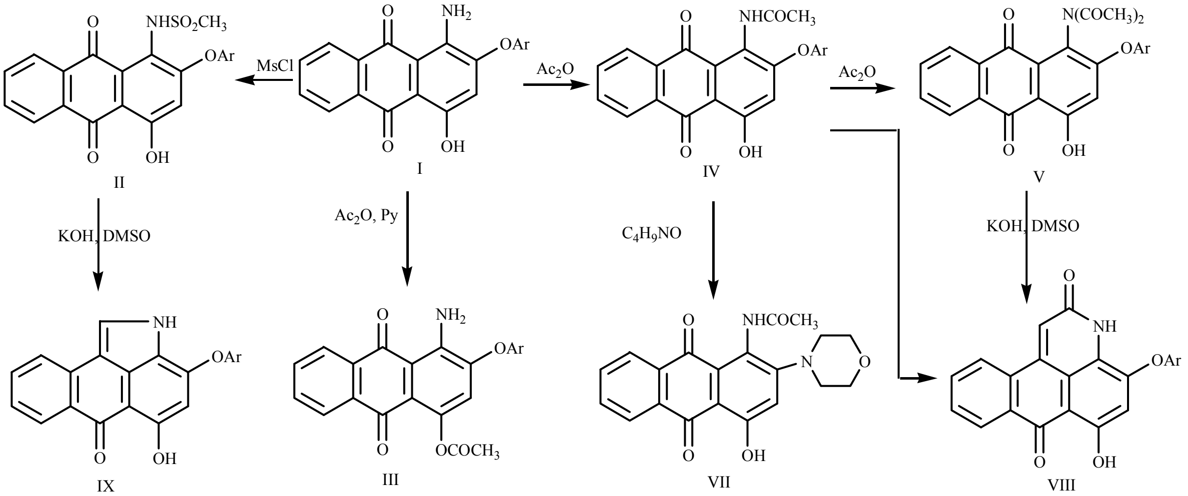
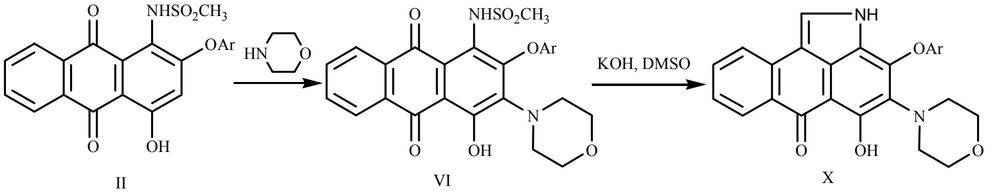
1-Amino-2-aryloxy-4-hydroxy-9,10-anthraquinones (I) are used as disperse dyes and as dyes for liquid crystal compositions [1].The structure modification of substances I is usually carried out by means of introduction of corresponding radicals into the aryl fragment. Reactions running with participation of amino or hydroxyl group are scantily known.

We have found that aminoanthraquinones I are mesylated at heating in the excess of methane sulfochloride involving the aminogroup only, whereas acetylation of substrates I may run selectively with participation of one or both active groups:





Amination of sulfamides II proceeds involving free position 3 and does not affect the aryloxy group, while amination of acetamides IV includes nucleophilic substitution of the aryl group. Amides (II,IV-VI) may be used for obtaining 4-aryloxy-6hydroxy-7H,3H[f,j,i] isoquinolinodiones-2,7(VIII) and 2,6-dihydronaptho[1,2,3-cd]indol-6-ones (IX,X).

The report considers possible routes of the found reactions, structural features of the substances obtained.

[1] Файн В.Я. 9,10-Антрахиноны и их применение. М.: Центр фотохимии РАН, 1999 г.
[1]V.Ya.Fine 9,10-Anthraquinones and their application. M. Photochemistry center of RAS, 1999y.

P-68

THE PECULIARITY OF AMINATION SOME 3-HALOGEN-4-NITROSOANILINES AND 3-HALOGEN-4-NITROSOPHENOLES

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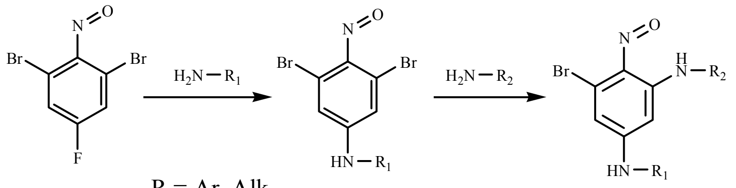
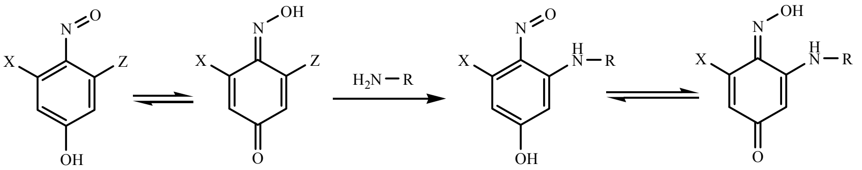
It is known that nitrosoarenes react with amines with direct participation of the nitroso group [1].The exception is 4-fluoro-2,6-dibromonitrosobenzene (I), which amination under mild conditions [2] brings to nitrosoaniline derivatives (II):



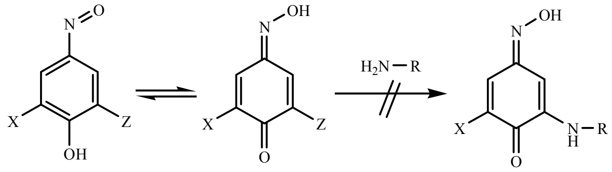
I R = Ar, Alk II III

Conversion II → III generates a particular interest because in this case the nitroso group is not affected. We have found that not only nitrosoamines (II) but also nitrosophenols (quinonoximes) (IV) unlike isomeric to them quinonoximes (VI) react with aliphatic, heterocyclic and aromatic amines at 25 ^{0}C by replacement of halogen without direct participation of nitroso- or hydroxyl group:



IV V

X,Z = Br; X = H, Z = Br; X = H, Z = Cl



VI

Such route of reaction IV → V seems not trivial as it is known that 4-nitrosophenols (1,4 benzoquinonoximes) react with primary amines with participation of hydroxyl (carbonyl) group [3].

In the report the examined reactions will be analyzed on the basis of the results of quantum-chemical calculations of electronic structure of nitroso compounds under consideration and thermodynamics of their reactions. Also there will be given a theoretical interpretation of electronic absorption spectra of potential tautomers III and V.

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[3] Беляев Е. Ю. Ароматические нитрозосоединения / Е. Ю. Беляев, Б. В. Гидаспов. – Л., Химия, 1988.E.Yu.Belyaev.Aromatic nitrosocompounds/ E.Yu.Belyaev, B.V.Gidaspov.-L., Khimiya, 1988

P-69

TRIHALOGENPROPANE-2-OL-2-THIOLS – A NEW SYNTHONES IN ORGANIC SYNTHESIS

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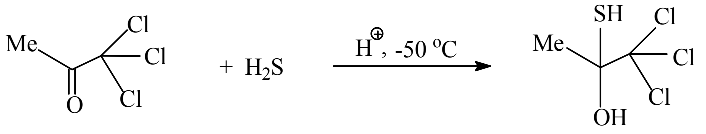
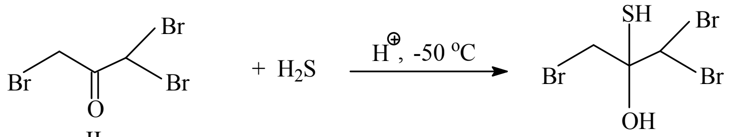
With the purpose to develop novel types of organic sulfur compounds for a design of acyclic and heterocyclic systems there has been studied a cryochemical acid-catalytic reaction of hydrogen sulfide with α,α,α- and α,α,α′-trihalogen substituted acetones. On the basis of the reaction of 1,1,1-trichloropropan-2-one and 1,1,3-tribromopropan-2-one with hydrogen sulfide at 50 °C both in the absence and in the presence of solvent (ether as an aprotic solvent and methanol as a proton solvent) there were obtained first representatives of heminal olthiols containing three halogen atoms in the molecule, namely 1,1,1-trichloropropan-2-ol-2-thiol and 1,1,3-tribromopropan-2-ol-2-thiol in 81-85% yield.



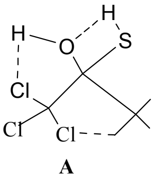
I III



II IV

The structure of hem-olthiols (III,IV) has been established by IR and ^{1}H, ^{13}C NMR spectroscopy methods. The presence of characteristic absorption bands of mercapto [2578 (III), 2562 (IV) cm^{-1}] and hydroxy [3447 (III), 3446 (IV) cm^{-1}] groups in the IR spectra(thin layer) and protons signals of these groups in the NMR spectra within a range of 3.11(SH) (III), 1.56 (SH) (IV), 3.68 (OH) (III), 3.68 (OH) (IV) m.p. and those of carbon atoms of the heminal ***olthiol*** group within a range of 91.72 (III) и 84.75 (IV) is a strong evidence confirming their structure.

Quantum-chemical analysis of the mechanism of reaction of trihalosubstituted acetones with hydrogen sulfide and investigation of rotational mobility of ***ol-thiols*** within the frames of GAUSSIAN 98 program complex allowed to determine a probable cause of stabilization of ***ol-thiol*** intermediates in the hydrothiolysis reaction. It has been established that the most favourable for elimination of water or hydrogen sulfide are ***rotamers*** of A and B type, while those of C type are unfavourable and are stabilized by strong intermolecular interaction of protons of mercapto- and hydroxy- groups with halogens atoms.



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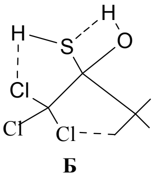

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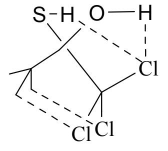

С

The work has been fulfilled by financial support of Russian fund for fundamental investigations (grants № 05-03-32041, 05-05-64191)and RF President's Grant Counsil (НШ-4575,2006.3)

P-70

UNUSUAL METHOD OF SYNTHESIS AND STRUCTURE OF ORGANOSILICON COMPLEX OF MALTOLE, CONTAINING COORDINATED CENTER O_4SiF_2

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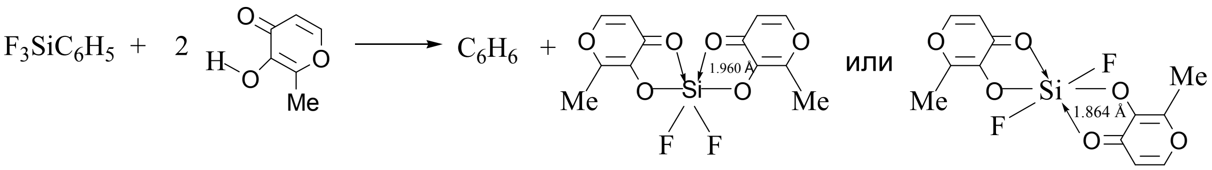
Earlier we found that the reaction of protodesilylation of phenyltrifluorosilane with 8-hydroxy-, 8-mercaptoquinoline, 2-hydroxyethylamine, its mono- and di-N-methyl and O-trimethylsilyl derivatives leads to new chelate heterocyclic compounds containing pentacoordinated silicon atom and coordination bond N→Si [1-3].

The reaction of $PhSiF_3$ (I) with 3-hydroxy-2-methyl-4-pyrone (maltol) (II) proceeds with Ph-Si bond cleavage, benzene elimination and generation of chelate O→Si←O′-bis(3-hydroxy-2-methyl-4-pyrone)silicate (III),containing hexacoordinated silicone atom and coordination node O_4SiF_2.



I II IIIa (цис) IIIб (транс)

The composition and structure of complex III have been proved by methods of elementary micro analysis, multinuclear NMR, IR spectroscopy and quantum chemistry.

According to the data of the calculations by DFT method (B3LYP/6-311G*) two molecule configuration with cis- (IIIa) and trans- (IIIb) arrangement of fluorine atoms are energy stable. Form IIIa is more stable than IIIb by 3.7 ccal/mole, though the length of O→Si bond in structure IIIa is 0.1E more than in IIIb. In IIIa form the coordination bonds of two axial O→Si-F fragments are located at angle of 90° to each other, while in IIIb they form axial O→Si←O fragment.

The IR spectrum of complex III in comparison with the calculated values of frequencies of normal molecules vibrations in the both configuration witnesses that in crystal state and in solution the compound is present in cis form (IIIa). That has been also confirmed by the data of ^{19}F, ^{29}Si NMR .

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[1] Voronkov M. G., Trofimova O. M., Chernov N. F., Albanov A. I., Chipanina N. N., Grebneva E. A. Appl. Organometal. Chem. 2005, 19(4) 538.

[2] Воронков М. Г., Гребнева Е. А., Трофимова О. М., Чернов Н. Ф., Албанов А. И., Чипанина Н. Н. Докл. АН. 2006. Т. 409. № 6. С. 1.

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P-71

SOLVENT-FREE OXIDATION OF ALIPHATIC ALCOHOLS BY Pb(IV) AND Ce(IV) COMPOUNDS

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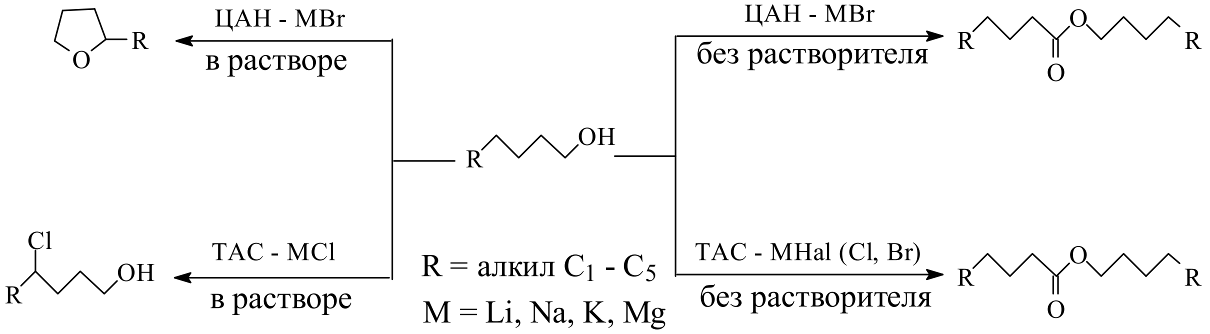
In recent years solid phase reactions and reactions in the absence of solvent are widely used in organic synthesis. These reactions often proceed more region- and stereoselectively, in high yields and to the greater degree meet the environmental requirements in comparison with analogous processes in liquid phase.

We have realized solid phase reactions of lead tetraacetate (LTA) and cerium ammonium nitrate (CAN) , actively used oxidizers in organic chemistry. Aliphatic alcohols were chosen as substrates to be oxidized.

The oxidation of primary alkanols of $C_5 – C_9$ composition was realized with $Pb(OAc)_4$ – MHal и $Ce(NH_4)_2(NO_3)_6$ – MBr systems. The reactions were carried out in the absence of solvent keeping the thoroughly mixed mixture at room temperature for 20-24 h. Under these conditions alkanols are converted into esters in ~ 80-90% yield. The process selectivity is about 90-95%.



For comparative appraisal of the oxidation reaction in the absence of solvent there was carried out the oxidation of the mentioned alcohols in liquid phase with the use of solvent. The obtained result was surprising. It lies in the fact that liquid phase oxidation of alkanols with CAN– MBr system brings to formation of 2-alkyltetrahydrofuran, while the main product at oxidation with LTA – MCl system is δ-chloroalkanol. Thus, different reaction products are formed in the course of the reactions in the solvent and in its absence. This fact may be explained by a change of the reaction mechanism at the change of the reaction conditions. Oxidation of alcohols in the absence of solvent proceeds according to a two-electron mechanism resulted in intermediate both aldehydes and acetals that under the reaction conditions are oxidized to esters. In case of the liquid phase reaction the one-electron mechanism is realized, the alkoxyl radicals forming from the alcohols are rearranged with 1,5-migration of the hydrogen atom. Then C- centralized radicals are oxidized to δ-chloroalkanols or are cyclized to 2-alkyltetrahydrofurans.

P-72

ADDITION OF SULFENATE ESTERS ACTIVATED BY HALO(TRIMETHYL)-SYLANES TO DOUBLE BOND WITH THE PARTICIPATION OF EXTERNAL NUCLEOPHILES

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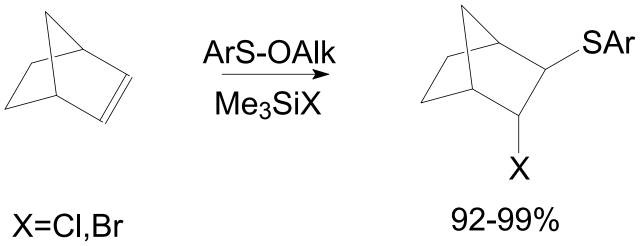
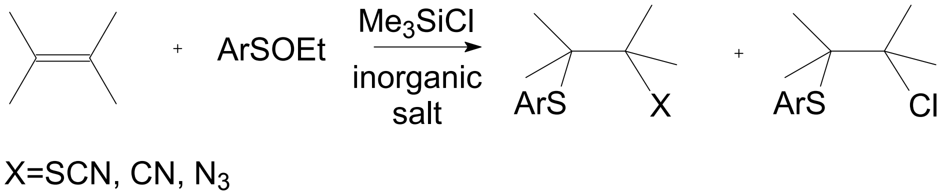
Earlier [1] we showed the possibility to activate sulfenic acids ethers by trimethylsilylhalides in processes of addition to the multiple bond, the reactions proceed smoothly at room temperature for 15-20 minutes and are characterized by easy implementation, high yields and high purity of the products.

For example



The absence of the products of Wagner-Meerwein rearrangement proves low effective electrophilicity [2] of the forming halosulfenilating systems.

Now we have shown the possibility to introduce thiocyanate-, cyanate- and azid-anions into the molecule of external nucleophile by means of corresponding inorganic salts.



β-Sulfenchloride is formed as a by product. The product ratios depend on the reaction conditions and external nucleophile used. In case of salts poorly soluble in organic solvents, the yields may be increased by using an interphase catalyst, for example 18-crown-6. The reactions occur at 0-20°C for 12-24 hours with the use of methylene chloride as the solvent.

The work has been fulfilled by financial support of Russian fund for fundamental investigations (grant№ 05-03-32737)and RAS Program "Theoretical and experimental investigation of the nature of chemical bonds and chemical processes"

P-73

REARRANGEMENTS OF *O*-PROPARGYL-β-AMINOPROPIOAMIDOXIMES

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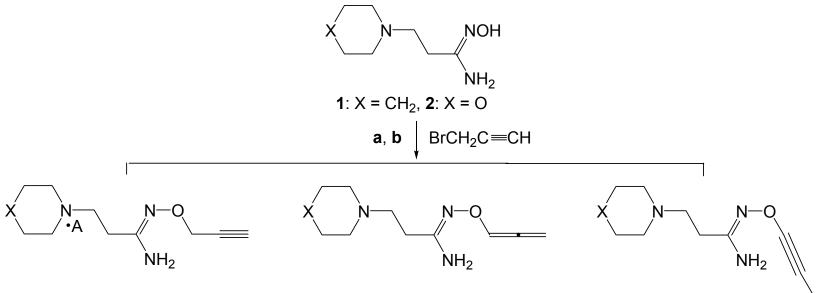
As a result of the interaction of β-aminopropioamidoximes (**1** and **2**) with propargyl bromide equivalent in acetone in the presence of K_2CO_3 (**a**) and in DMSO in the presence of KOH (**b**) were obtained hydrobromides and bases of O-propagyl-β-aminopropioamidoximes in the following yields: 65 % (**3·HBr**) and 70 % (**4·HBr**) (conditions **a**), and 75 % (**3**) and 80 % (**4**) (conditions **b**).



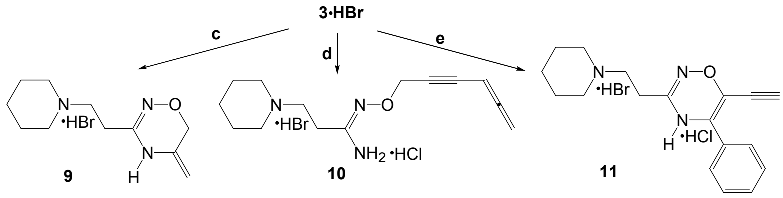
3: X = CH$_2$, A = ноль; **4**: X = O, A = ноль **5**: X = CH$_2$, **6**: X = O **7**: X = CH$_2$, **8**: X = O

3·HBr: X = CH$_2$, A = HBr; **4·HBr**: X = O, A = HBr **a**: ацетон, 60 °C, 4 ч; **b**: DMSO, KOH, комн. темп.

An increase in the reaction duration under conditions **b** leads to isomerization of the *O*-propagyl substitutent in **3** and **4** to *O*-allenic one to form **5** and **6** and to isomerization of *O*-1-propynyl substituent to form **7,8** existing in approximately equal ratio.

Hydrobromide **3·HBr** was taken as the raw product in a number of transformations:

c: Heating a mixture of **3·HBr** and $PdCl_2$ at a ratio of 10:1 at 70 °C for 1 hour affords hydrobromide of 5-methylen-3-(2-piperidin-1-yl-ethyl)-5,6-dihydro-4H-[1,2,4[-oxadiazine (**9**), being a structural isomer of **3·HBr,** in 70% yield**.**



9 **10** **11**

c: PdCl$_2$, MeCN; **d**: BrCH$_2$C≡CH, NH$_2$OH·HCl, CuBr; **e**: AcOEt, C$_6$H$_5$COCl

d. propagylation of hydrobromide of O-propagyl-β-piperidinopropioamidoxime **3·HBr** with propagyl bromide under the conditions of Cadiot-Chodkiewicz reaction (10% molar CuBr, hydroxylamine muriate in water-ethanol medium) affords hydrobromide, hydrochloride of *N*-hexa-4,5-dien-2-ynyloxy-3-piperidin-1-yl-propionamidine (**10**) in 50% yield.

e: The reaction of **3·HBr** with benzoyl chloride in ethyl acetate brings to the product of internal heterocyclization,that is forming at H_2O elimination, namely to hydrobromide, hydrochloride of 3-(2-piperidin-1-yl-ethyl)-5-phenyl-6-ethynyl-4*H*[1,2,4]-oxadiazine (**11**) in 40% yield.

Thus, *O*-propagyl-β-aminopropioamidoximes are perspective synthons bearing several functional groups that allows carrying out their synthetic modification to form linear and heterocyclic systems.

P-74

THE REACTION OF DIVINYL SULFIDE WITH SELENOUREA

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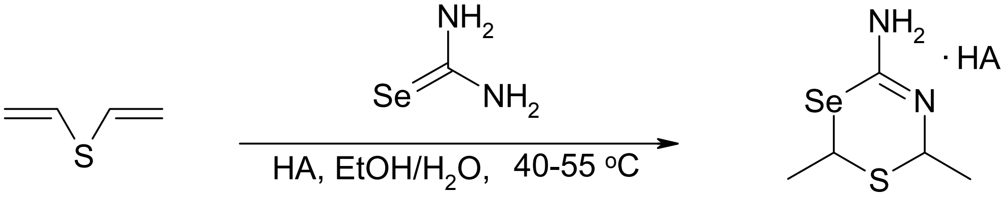
There is no data on interaction of divinyl sulfide with selenourea in literature.

For the first time we have realized the reaction of divinyl sulfide with selenourea. The reaction proceeds in a water-ethanol medium in the presence of acids at a temperature of 40-55 °C and brings to unknown before salts of 2*H*,6*H*-2,6-dimethyl-4-amino-1,3,5-thiaselenazine in a yield up to 90%.



A = Cl, p-TolSO$_2$, ClO$_4$, Br

The reaction products are a mixture of *cis* – and *trans*-isomers approximately in equimolar ratio. The structure of the compounds was proved by ^{1}H, ^{13}C, ^{77}Se NMR methods and confirmed by the data of IR spectroscopy and elementary analysis. Two-dimensional spectra (HMBC, HSQC, COSY) were used to attribute signals in the *cis* – and *trans*-isomers.

The reaction opens an easy way to a new class of heterocyclic systems, 1,3,5-thiaselenazines, potential biologically active substances, intermediate products for synthesis of more complex substances.

P-75

SYNTHESIS OF MONOTHIOXAMIDES OF AMINONITRO ARENE'S SEQUENCE

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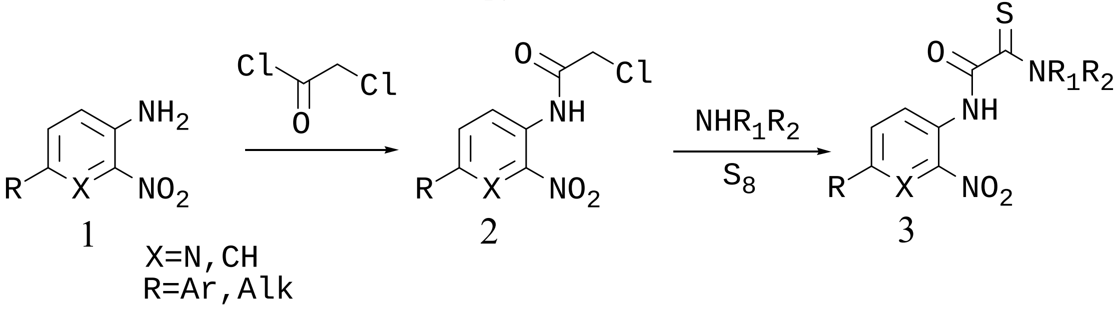
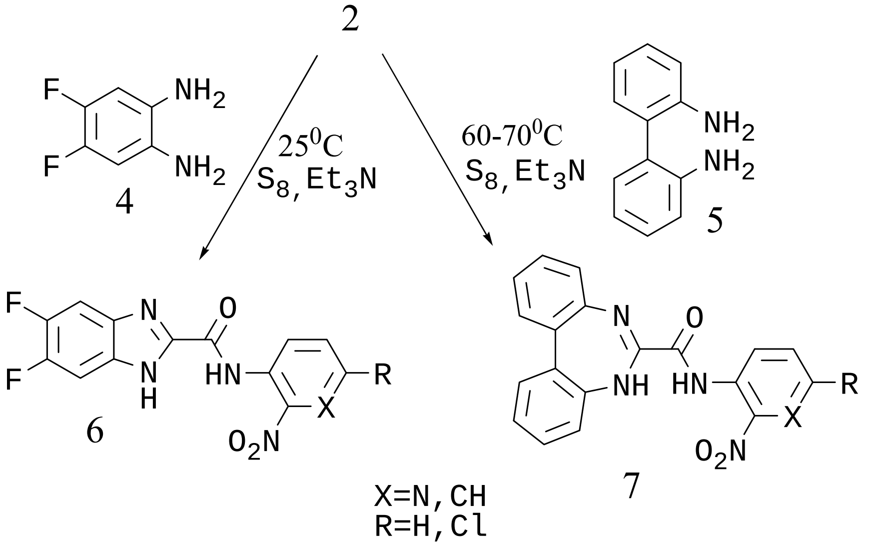
Derivatives of monothioxamides possess considerable synthetic abilities and are of an original interest as biologically active compounds.

With the help of computer program PASS we have selected the most perspective monothioxamides of aminonitroarene series (3) with a wide spectrum of biological activity and developed the method of their synthesis that lies in the interaction of chloroacetamides obtained from aminonitrobenzenes and aminonitropyridines with elemental sulfur and amines.



The reaction of chloroacetamides **2** with diamines **4** and **5** results in formation of heterocyclic compounds **6** and **7**.



P-76

PUMMERER'S REACTION IN THE SYNTHESIS OF SUBSTITUTED CYCLOCOMPONENTS

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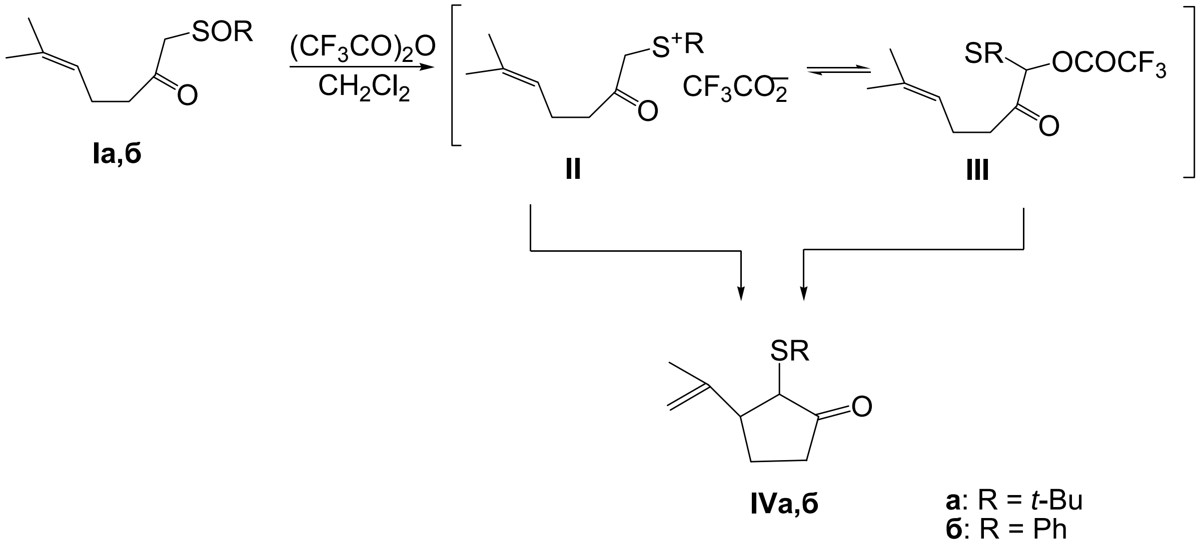
The synthesis of many natural objects of *iridone* and guaiane series is based on using properly functionalized cyclopentanes as start compounds.

We have shown that ketosulfonides **Ia,b** under the action of trifluoroacetic anhydride may be smoothly converted to corresponding *trans*-disubstituted cyclopentanones **IVa,b** with a 15% admixture of *cis*-epimer in both cases. This transformation is interpreted within the frames of internal reaction of enene type of Pummerer intermediate **II** obviously existing in equilibrium with hem-acyloxysulfide **III**.



At that in case **Ia** (when the reaction runs in the sensor of an NMR-spectrometer) the proton signal HCS **III** (R = *t*-Bu) is revealed at -40°C already, within the range of $\delta \sim 6$ ppm, its relative integral intensity reaches its maximum at -20°C and further at heating up to 25°C is decreasing along with simultaneous increasing relative integral intensity of the end product signals .

In case **Ib** the corresponding signal **III** (R = Ph) was found quite stable and was isolated by means of chromatography. Boiling the latter in toluene affords cyclopentanone **IVb** in 60% yield.

P-77

REVERDIN TYPE REARRANGEMENT AT REACTION OF ADAMANTYLATION OF 4-IODOPHENOL

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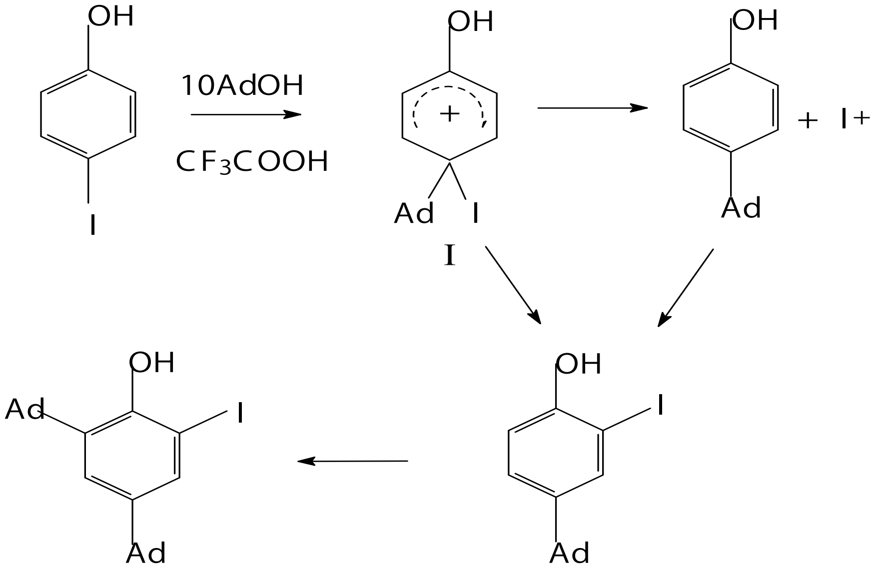
We have found that in the reaction of adamatylation of 4-iodophenol with 1-oxyadamantane in a trifluoroacetic acid medium 2-iodo-4,6-di(adamantly-1)phenol is formed, which structure has been determined by ^{1}H and C^{13}NMR methods. In the PMR spectrum of this compound in strong field (2.0-1.7 ppm) was found complex multiplet (30H) of protons of two adamantyl groups, while two signals of equal intensity (1H,7.51 ppm и 1H, 7.24 ppm) with the splitting constant 1.8Hz were revealed in weak field in the region of aromatic protons. That denotes that aromatic protons are in *meta*-position each other. Thus, the iodine atom is transferring from *par*a-position to *ortho*-position along with adamantylation. Similar reaction occurring at nitration of 4-iodphenol is known as Reverden rearrangement [1,2].

This rearrangements mechanism apparently includes ***ipso***-attack of the adamantly cation towards C-4 carbon to form σ-complex (**I**).Further the iodine atom transfer proceeds according to the intra- and intermolecular mechanism.

There is no Reverden rearrangement in 4-bromophenol adamantylation and 2-(adamantly-1)-4- bromophenol is formed.



[1] Вацуро К.В., Мищенко Г.Л. Именные реакции в органической химии. М. Химия. 1976.С.346.
[2] Махоньков Д.И., Чепраков А.В., Белецкая И.П. ЖОрХ . 1988. Т. 24.Вып.11.С.2251-2258.

P-78

A NEW WAY TO THE SYNTHESIS OF STRONG ORGANIC BASES: 1,8-BIS(DIALLYLAMINO)NAPHTHALEN AND ITS DEALKYLATION

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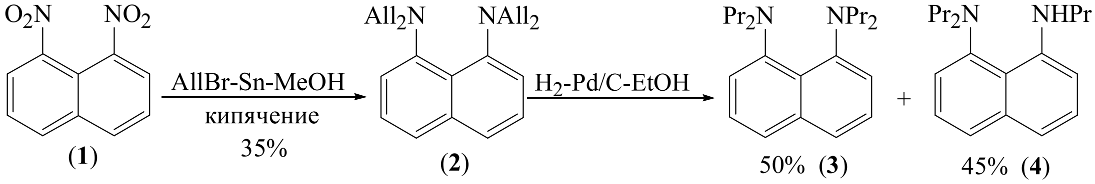
1,8-Bis(dialkylamino) napthalenes (naphthalene “proton sponges”) are remarkable for their extraordinary high thermodynamic and low kinetic basicity [1]. In connection with wide application of these diamines in organic synthesis and with the necessity to obtain even more complex derivatives of 1,8-diaminonaphthalene, studies of new rational approaches to this class of compounds have been continued. In particular, we have realized the following variant of the synthesis of 1,8-bis(diallylamino) naphthalene (**2**) based on nucleophilic substitution of the nitro groups at the nitrogen atoms in easily available 1,8-dinitronaphthalene (**1**):



In contrast to the methods developed before and based on the scheme $-NO_2 \rightarrow -NH_2 \rightarrow -NAlk_2$, our approach does not include the stage of nitro-groups reduction, that allows carrying out the reaction in one synthetic step. The yield of tetraalkylated product **2** was studied in dependence of the effect of solvent acidity, temperature and ration of the reagents.

Also we have found that in the course of the catalytic hydrogenation of base **2** there is formed by-product *N,N,N'*-tripropyl-1,8-diaminonaphthalene (**4**) along with product 3.Additional experiments with 1,5- and 1,8-bis(diallylamino)naphthalenes as well as with diallylaminobenzene have shown that this reaction is common for compounds containing $NAll_2$ group and namely the allyl group is lost up to its reduction; dipropylamino derivatives are stable under similar conditions. It was found that acid medium (for example, transition from EtOH to MeOH or addition of mineral acid) makes the dealkylation easier. On the contrary, introduction of a base to the mixture to be hydrogenated (KOH, Et_3N) brings to accumulation of compounds of type **3**. The analysis of published data showed that analogues examples of reductive bifurcation of N–All bond were not found. Thus, the found transformation is a new method of dealkylation of dialkylamino arenas [3].

The transfer from 2 to dipropylamino derivative 3 is followed by a step-wise increase in basicity. Thus, values pK_a (deprotonation of cations, ^1H NMR transprotonation, DMSO- d_6) for 2 and 3 are equal to 5.4 and 7.5 accordingly. The basicity, for example, of pyridine and *N,N*-dimethylaniline is considerably lower (pK_a 3.4 and 2.5, DMSO).

P-79

SYNTHESIS THIOUREA DERIVATIVES OF CYTOSINE, *L*-EPHEDRINE AND *D*-PSEUDOEPHEDRINE

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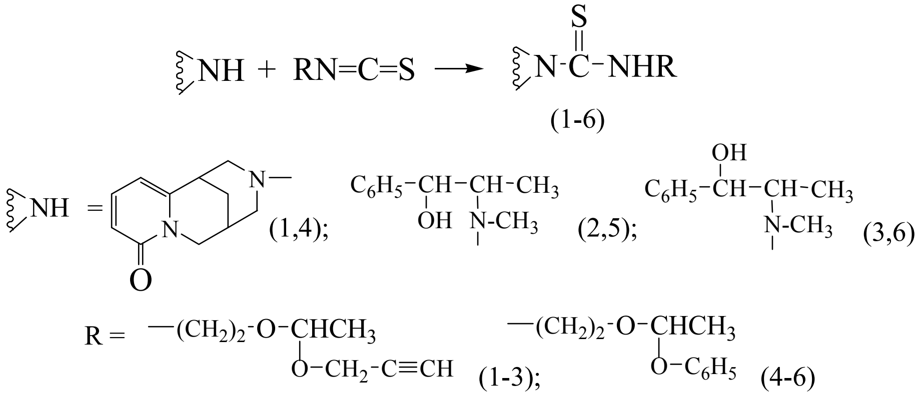
Thioureas are an important class of chemicals that have found wide application both in organic synthesis and in practice- in industry, agriculture, medicine. Most of thiourea derivatives possess valuable pharmacological properties and are applied as antitubercular, anticancer, anti-inflammatory, antiinfective, antiulcer and other therapeutically active substances [2], [3].

Because of that the synthesis of thiourea derivatives derived from physiologically active cytosine, *L*-ephedrine and *D*- pseudoephedrine was of interest for us. The synthesis was realized in alcohol medium by isothiocyanate method, i.e. by direct addition of alkaloids to 1-propagyloxyethyl isothiocyanate and to 1-phenyloxyethoxyethyl isothiocyanate.



The synthesized compounds (1-6) are white crystal substances moderately soluble in organic solvents. The composition, structure and individuality of the compounds synthesized (1-6) have been confirmed by the data of elementary analysis, IR-, PMR-spectroscopy and thin-layer chromatography.

In the IR spectra of compounds (1-6) within a range of 1170-1200см$^{-1}$ thiocarbonyl group (C=S) is displayed. An intense signal of amide group (N-C=O) of cytosine alkaloid is present in the IR spectrum of compound (1) at 1651 cm^{-1}, compounds (**2,3,5,6**) exhibit valence vibrations of the hydroxyl and N-H group in the range 3300-3400 cm^{-1}.

The ^{1}H NMR spectra of compounds (**1-6**) along with the protons of the alkaloid moiety also protons of the thioamide constituent are shown The ^{1}H NMR spectrum (DMSO-d6, δ, ppm, J, Hz) of compound (**5**): 0,97 d (3H, CH_3-CH, 5.1), 1,4 d (3H, CH_3-CHO, 4.0), 2,50 m (1H, CHN), 2,85 s (3H, N-CH_3), 3,50-3,75 m (4H, CH_2-CH_2), 4,75 d (1H, CHO, 3.5), 5,43 к (1H, CH_3-CHO, 4.0), 7,30-7,40 m (10H, 2 C_6H_5).

P-80

FURFURYL ALCOHOL IN LEVULINIC ACID ESTER SYNTHESIS UPON THE ACTION OF Fe AND Rh COMPLEXES

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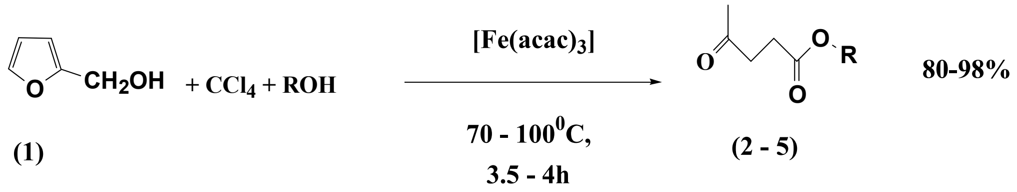
Levulinic acid esters are used as aromatizing agents in perfumery, tobacco and food industry.

We have found that the interaction of furfuryl alcohol (1) with aliphatic alcohols in the presence of Fe and Rh complexes results in formation of ethers of levulinic acid (γ-oxopentanic acid) (2-5) in high yields.



R = CH_3, (2)
C_2H_5, (3)
i-C_3H_7, (4)
n-C_3H_7, (5)

Reaction (**1**) with alcohols is preferably to carry out at the boiling temperature of the aliphatic alcohol in CCl_4 medium at permanent stirring. Under such conditions reaction (**1**) with CH_3OH comes to completion for 4 hours to form (**2**) in a quantitative yield.

Interaction (**1**) with ethyl, propyl and isopropyl alcohols runs in a similar way.

It should be noted that the increase in the reaction duration up to 5 hours with the purpose to increase the yield of ethers (4,5) is undesirable, because in this case occurs formation of a solid oligomeric product insoluble in water and organic solvents.

The carrying out of the reaction under the said conditions with the use of Rh-containing catalyst does not change the direction of transformation (**1**), but the process is accomplished in a shorter time, 2-3 hours.

The following optimal concentrations of the catalyst and reagents have been found experimentally: $[Fe(acac)_3]$: [furfuryl alcohol]: [ROH] : $[CCl_4]$ = 1 : 100 : 400 : 200

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P-81

CHEMICAL COMPOUND AND PROPERTIES OF FLAVONOID-CONTAINING EXTRACTS FROM WASTES OF FRUIT PROCESSING

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Flavonoid-containing extracts were obtained by extraction of wastes of fruit and berry treatment with 60% aqueous solution of alcohol with subsequent concentration by evaporation of the extract to 70% concentration of the dry substance. [4].

The chemical composition have been determined for the following extracts obtained from: grist of sea buckthorn *Hippophae rhamnoides* (1),grist of guilder rose *Viburnum opulus* (2), press of black rowan *Aronia melanocarpa* (3),press of mountain cranberry *Vaccinium vitis-idaea* L(4)(see the table) The mass fractions of flavonols and anthocyans were determined according to the author's procedure [5].Furthemore,there was determined the macro- and microement composition of the extracts containing all vitally important elements and not exceeding standards for toxic elements according to Sanitary standards for biologically active additives(BAA)

Indices	Mass fraction, wt.%			
	ЭГШО (1)	ЭГШК (2)	ЭГЖЧ (3)	ЭГЖБ
Fructose	(3,1…6,8)±0,3	22,6±0,3	14,4±0,3	(18,3…21,8)±0,3
Glucose	(7,2…15,1)±0,3	18,2±0,3	15,5±0,3	(1,2…5,1)±0,3
Saccharose	–	–	8,2±0,2	–
Polyols, total	0,8	–	–	–
Acidity,titration (malic acid)	(8,0…18,1)±0,1	(5,0…8,5)±0,1	(3,5…3,8)±0,1	(9,8…14,8)±0,1
incl.valeric acid	0,8±0,1	–	–	–
Tanning substances	(2,3…4,8) ±0,1	(12,1…18,3) ±0,1	(4,0…6,5) ±0,1	(3,3…5,3) ±0,1
Ash soluble in HCl	4,8±0,2	2,2±0,2	(10,0…15,0)±0,2	(3,0…5,0)±0,2
Flavonols(rutin)	(0,6…3,0)±0,07	(0,5…1,5)±0,07	(0,7…1,39)±0,07	(1,1…1,5) ±0,07
Anthocyans(cyanidin)	–	–	(5,0…9,0)±0,4	(4,2…8,4)±0,4
Ascorbic acid, mg/100g	185…343	140	185	210…260

The extracts are moderately soluble in water and alcohol, well mixed with sugar syrup and emulsified food protein in formulas of yoghurt, ice-cream, confectionery cream, adding color, smell and taste to the product.

The experiments with animals have determined that the extracts are not toxic and manifest specific activity characteristic for flavonoids.

P-82

CATALYTIC INTERACTION OF 1,3-DIOXOLANES BASED ON *L*-TARTARIC ACID WITH DIAZOCOMPOUNDS

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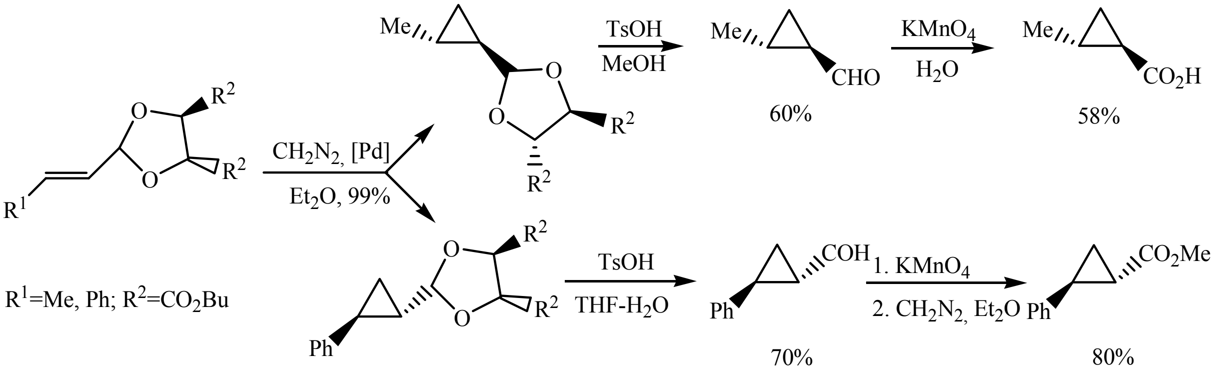
The interaction of methyldiazoacetate with cyclic acetals, 1,3-dioxolanes, in the presence of copper and rhodium compounds is known to bring to introduction of methoxycarbonyl carbene to the C-O bond to form ethers of 3-substituted 1,4-dioxan-2-carbonic acids.

With the purpose to synthesize optically active aldehydes of cyclopropane series being of interest as synthons for the synthesis of biologically active polyfunctional compounds (for example, 5.6-methanoleucotriene A_4 ,a stable and selective inhibitor of leucotriene biosynthesis) there was studied the influence of the dioxolane fragment on the direction of catalytic interaction of 1,3-dioxolanes derived from L-tartaric acid with diazo-compounds under the action of Cu-, Pd- and Rh-catalysts.

The acetal substituents at β- or γ-positions towards C=C bond were determined to activate the yield of the cyclopropanation products in comparison with the starting unsaturated carbonyl compounds forming side adducts of 1,3-dipolar cycloaddition with CH_2N_2. Olefins containing trans-4,5-di(butoxycarbonyl)-1,3-dioxalane substituent react with diazomethane in the presence of $Pd(acac)_2$ to form selectively the cyclopropanation products. Catalyst $Pd(acac)_2$ was found the most effective for cyclopropanation of double bonds.



Preparative methods for the synthesis of optically active cyclopropanes and cyclopropane carbonic acids were developed on the basis of dibutyl ethers of 2-[(*E*)-1-propenyl]- and 2-[(*E*)-phenylethenyl]-1,3-dioxolan-4,5-dicarbonic acids derived from dibutyl (*L*) tartrate and α,β-unsaturated aldehydes.

It should be noted that the presence of butoxycarbonyl groups at 4 and 5 positions of the dioxolane ring affects negatively and formation of the products of introduction of methoxycarbonylcarbene to the C-O bond does not occur neither for saturated nor for unsaturated acetals.

P-83

SYNTHESIS OF NEW CHIRAL TERPENE BASED α-THIOOXIMES AND CORRESPONDING MACROCYCLES

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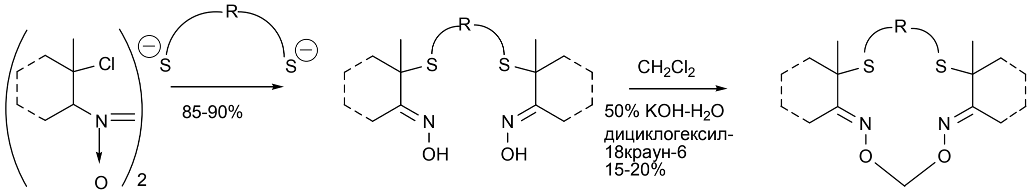
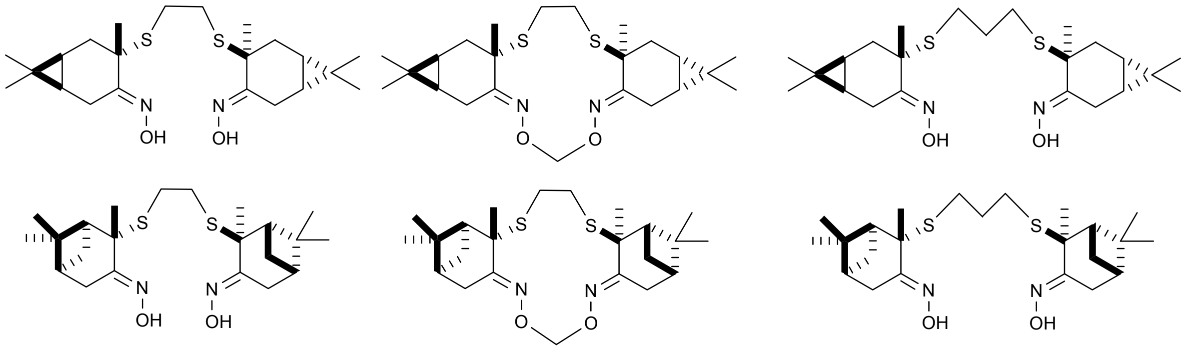
Nitrosochlorides of natural monoterpenes have been convenient starting compounds for the synthesis of optically active reagents of various application. At present the interaction of nitrosochlorides with amines to form α-aminoximes being the basis for a great number of complex compounds [1] has been studied in detail. With the purpose to expand the range of chiral α-substituted oximes we have studied the reaction of nitrosochlorides with mercaptanes and developed the methods to obtain bis- α- thiooximes and corresponding macrocyclic compounds according to the scheme:



According to this scheme we have synthesized novel derivatives of 3-carene and α-pinene series:



All the substances were obtained in optically active form. The structure of the substances was determined by means of ^{1}H, ^{13}C NMR methods, detailed analysis of the spin-spin splitting constants, IR-spectrometry, high resolution mass-spectrometry, elementary analysis data, vapor phase osmometry.

[1] С.В. Ларионов, А.В. Ткачёв // Российский химический журнал. 2004. № 4. С. 154-165.

P-84

SYNTHESIS OF NEW POLYFUNCTIONAL COMPOUNDS FROM (-)-*cis*-VERBENOL EPOXIDE

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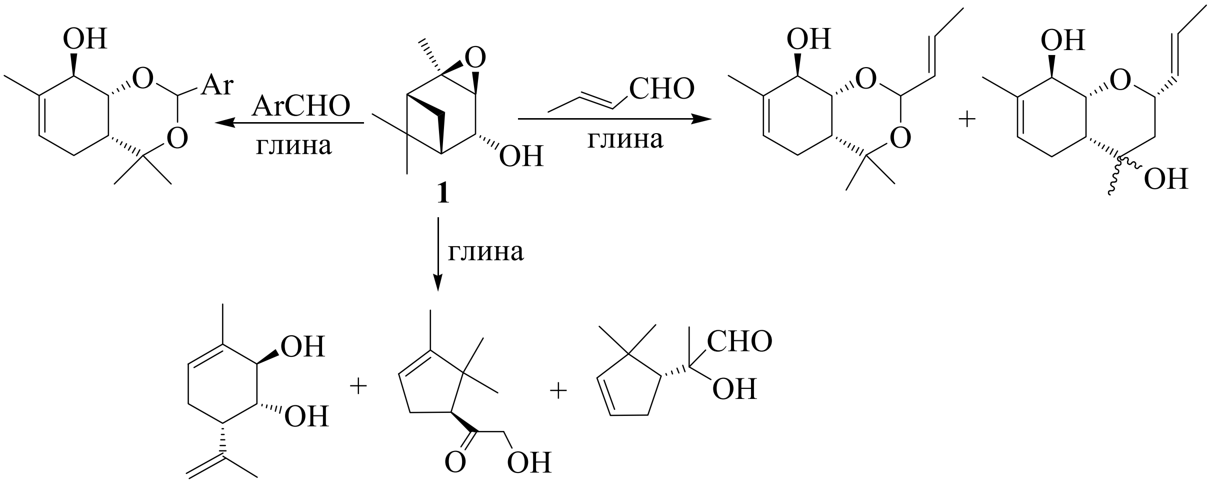
Oxygen-containing derivatives of monoterpenes of pinane series are easily available compounds being the source of biologically active substances and intermediates in asymmetric synthesis. In acid media they easily undergo multiple transformations to give complex mixtures of products. Earlier we showed that the use of montmorillonite clay askanit-bentonite as a catalyst for transformations of terpenoids of pinane series makes possible to obtain selectively complex and interesting products in a number of cases [1].

In the present work we for the first time have studied the reactions of (-)-cis-verbenol epoxide **1** in the reactions catalyzed by natural montmorillonite clay askanit-bentonite. As a result we have obtained a whole number of polyfunctional compounds, most of them have not been described in literature earlier. All the compounds obtained during the course of the present work possess optical activity, part of them may be considered as starting materials for asymmetric synthesis of complex compounds.



P-85

SYNTHESIS OF ALKENYLFURFURYLAMIDES OF LABDANOIDS AND THEIR INTRAMOLECULAR CYCLOADDITION

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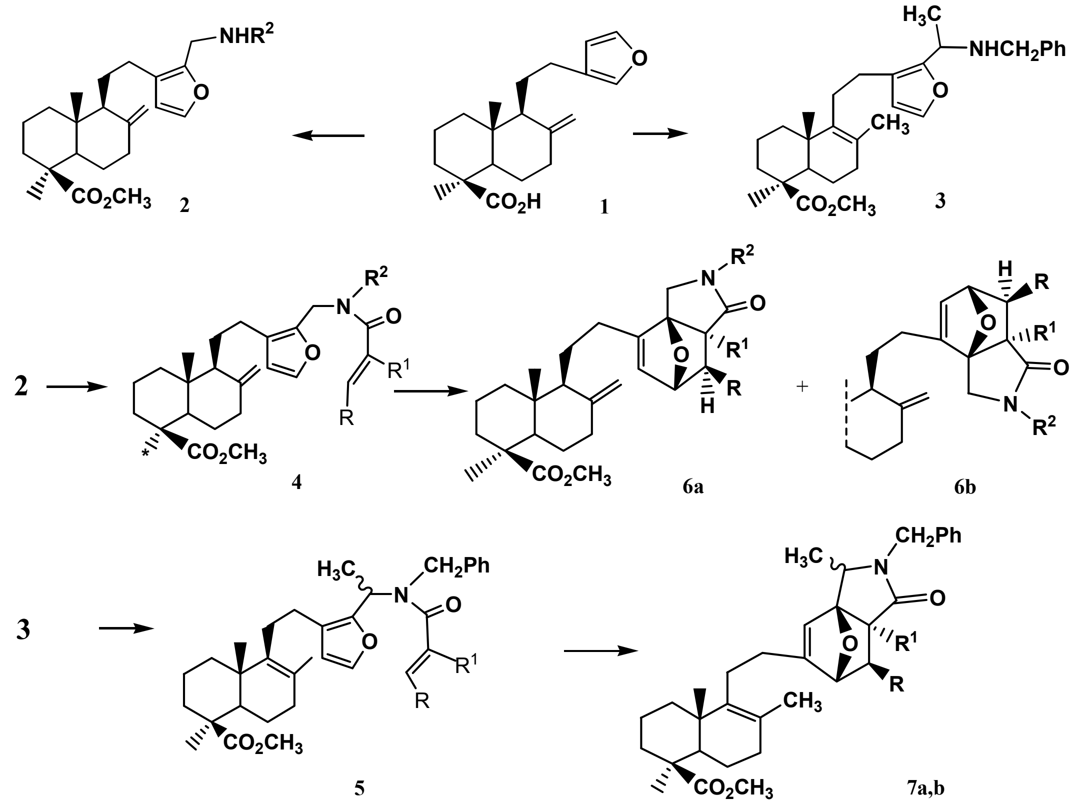
Diels-Alder intramolecular reaction for N-alkenfurfurylamines and alken-substituted furfurylamides is a convenient method to produce diverse derivatives of epoxyisoindole and epoxyisoquinoline.

We have proposed a synthesis of terpenoid derivatives of labdane type containing a fragment of 10-oxa-3-azatricyclo[5.2.1.0^{1,5}]decenones derived from lambertianic acid **1**. The acylation of 16-[(*N*-benzyl)aminomethyl]-methyllambertianate **2** with methylacryloyl chloride or maleic anhydride resulted in alkenylfurfurylamides **4**. The intramolecular cyclization of the mentioned compounds brings to (1*R*,5*S*,7*R*)- and (1*S*,5*R*,7*S*)-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]decenones **6a,b**. The effect of the substituent at the nitrogen atom on cyclization stereoselectivity has been studied. Alkenfurfurylamides **5** obtained by acylation of furfurylamines **3** by 2-methylacryloyl chloride or maleic anhydride are cyclized to form a mixture of diastereoisomer adducts 7a,b differing in configuration of the methyl group at C^{2} atom of the oxatricyclic fragment.



R=H, CO_2H; R^1= H, CH_3; R^2=CH_2Ph, $(CH_2)_2C_6H_4OH$-(4), $CH(CO_2Me)(CH_2)_2SCH_3$, $CH(CO_2Me)CH(CH_3)_2$

P-86

SYNTHESIS AND EVALUATION OF INHIBITING ACTIVITY OF SULFUR-CONTAINING ANTIOXIDANTS ON THE BASIS OF 2,6-DIMETHYLPHENOL

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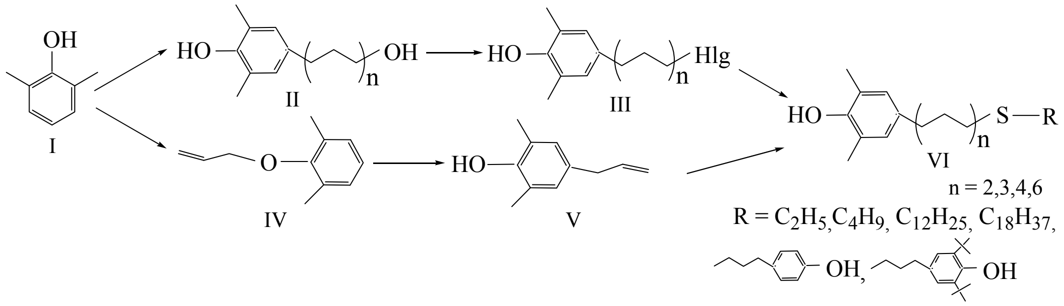
Thio-derivatives derived from 2,6-di-tert-butylphenol with a sulfur-containing functional group separated from the phenol fragment by two and more carbon atoms are among the most effective polyfunctional antioxidant (AO) investigated at present. That is determined by bifunctional mechanism of their antioxidizing effect. Meanwhile ,it is known that antiradical activity of 2,6-di-tert-butylphenols is lower than that of their 2,6-dimethyl-substituted analogs. Besides, derivatives of 2,6-dimethylphenols are structural analogs of α-tocopherol, a basic natural phenol antioxidant. Thus, these compounds are similar in the structure to natural compounds and are of doubtless interest as biologically active synthetic antioxidants.

With the purpose to find new polyfunctional AO exceeding the existing analogs in effectiveness in the present work the synthesis of sulfur-containing derivatives of *para*-substituted 2,6-dimethylphenol was realized and their gross-inhibiting effect on liquid paraffin oxidation was studied.

Thio-derivatives **VI** derived from 2,6-dimethylphenol **I** were obtained by two different methods. The first route was the synthesis of alkanols **II** , from them under the action of halogen anhydrides and haloid acids the corresponding haloalkanes **III** were obtained. The second synthesis route was realized in a following way: according to the reaction of phenol **I** with allyl chloride we synthesized ether **IV**, its rearrangement resulted in para-allylphenol **V**. By the addition of alkanthiols of different structure to the latter we obtained corresponding asymmetric sulfides **VI**:



The structure of all synthesized compounds has been confirmed by the data of PMR-, IR-spectroscopy, chromato-mass-spectrometry. According to STN International data compounds VI are new and have not been described in publications.

The evaluation of antioxidant activity of sulfides **VI** was carried out by the model

P-87

SYNTHESIS AND ASYMMETRIC OXIDATION OF BENZOTRITHIANES – ANALOGS OF *VARACIN C*

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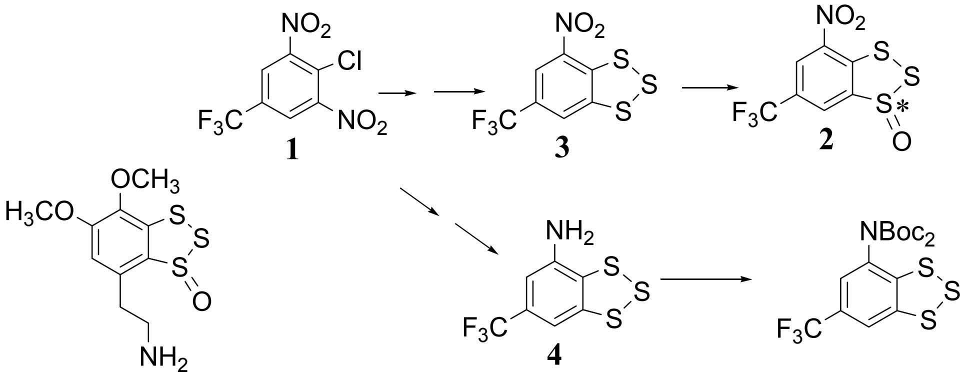
Organic cyclic polysulfides are interesting molecules due to their structure, chemical transformations, metabolism as well as biological activity. Varacines A,B,C, isolated from sea organisms in small quantities, possess fungicidal, antiinfection and anticancer activity, The most promising anticancer substance is varacine C which effectiveness repeatedly exceeds many commonly used medicines. Such unique properties of the compound are explained by the presence of the sulfoxide group along with the trisulfide cycle in the molecule.

In the present work we have synthesized novel derivatives of benzotrithiane starting from commercially available dinitrotrifluoromethylbenzochloride **1**. Chiral sulfoxide **2** was obtained by asymmetric oxidation of trisulfide **3** with cumene hydroperoxide in the presence of the complex of titane(IV) isopropylate and (+)-diethyl-(*L*)-tartrate.



Варацин C

For the first time we have studied the influence of benzotrithiane derivatives on the central nervous system. Aminosubstituted benzotrithiane **4** has shown maximal antianxious activity comparative with the effect of seduxen, tranquilizer of the benzodiazepine series, as well as high anticonvulsant activity.

P-88

SYNTHESIS OF NEW CHIRAL SHIFF BASES FROM (+) - AND (-) - α-PINENES SUITABLE FOR USE IN ASYMMETRIC OXIDATION OF SULFIDES

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N.F. Salakhutdinov, A.G. Tolstikov (Novosibirsk, Russia)

Starting from common monoterpenes (+)- and (-)-α-pinenes, novel chiral Schiff bases have been synthesized. They are suitable for application as ligands in sulfides oxidation catalyzed by vanadium ions to chiral sulfoxides. Asymmetric oxidation of thioanisole was optimized, the optical purity of the obtained phenylmethylsulfoxide made up to 32%.The influence of various substituents in the aromatic ring of the ligands on the oxidation enantioselectivity was studied. Variation of the substituents in the ligand influences much not only enantioselectivity of the reaction but also absolute configuration of the forming sulfoxide.