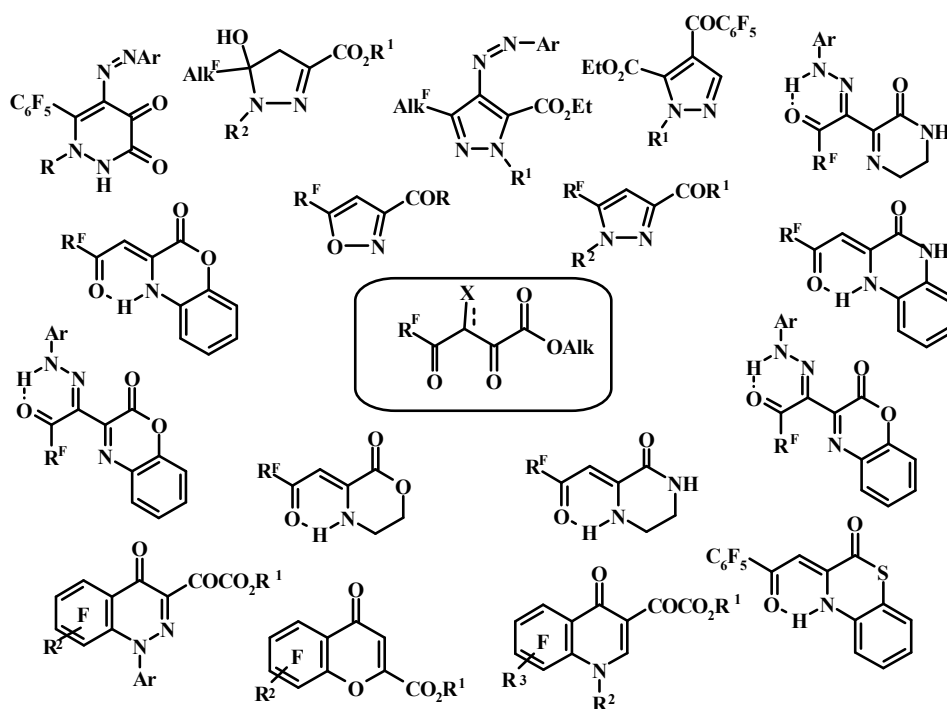


FLUOROCONTAINING 2,4-DIOXO ACIDS IN AZAHETEROCYCLES SYNTHESIS

V.I. Saloutin, Ya.V. Burgart, O.N. Chupakhin (Ekaterinburg, Russia)

One of the ways to evolve methods of building heterocyclic systems is development of new block-synthons and for that fluorinated tricarbonyl compounds containing both α - and β -dicarbonyl fragments concurrently may be used. We have developed methods to produce unknown before 4-polyfluoroalkyl- and 4-pentafluorophenyl-2,4-dioxobutane acids and their esters. Functionalization of these compounds allows obtaining new block-synthones suitable for construction of different heterocyclic molecules. 4-Fluoroalkyl(pentafluorophenyl)-2,4-dioxobutanoates and their derivatives have ability for cyclocondensation with dinucleophilic reagents at α -, β - or γ -dicarbonyl fragments in dependence on the fluorinated substituent construction, dinucleophile type and reaction conditions, as the result a wide range of heterocycles may be obtained. A distinctive feature of 4-pentafluorophenyl-2,4-dioxobutanoates is their ability to generate heterocycles at the expense of intermolecular substitution of the fluorine ortho-atom.



The work was supported by the State Program for Supporting Leading scientific Schools (grant № 9178.2006.3)

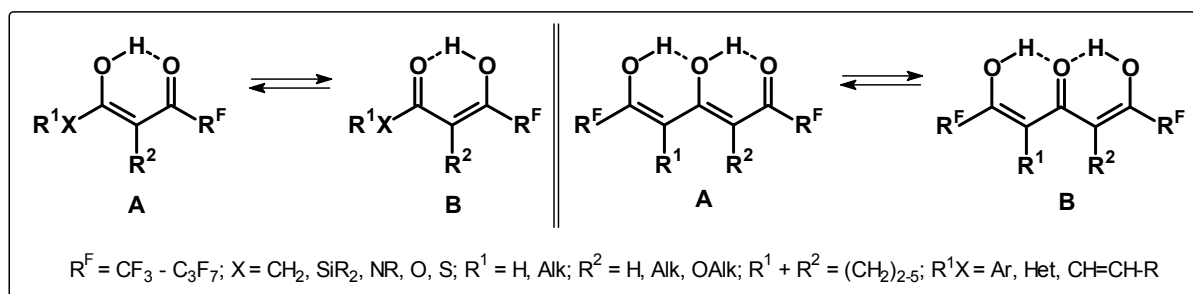
FAST "ENOL-ENOL" TAUTOMERISM OF FLUORINATED 1,3-DICARBONYL AND 1,3,5-TRICARBONYL COMPOUNDS

M.I. Kodess, D.L. Chizhov, I.I. Bilkis, K.I. Pashkevich, G.-V. Rösenthaller, **D.V. Sevenard** (Germany, Israel, Russia)

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A new methodology for quantitative description of rapid tautomerism "enolA-enol B" is presented in solutions of fluorinated 1,3-dicarbonyl and 1,3,5-tricarbonyl compounds. KCCB $^1J_{C-F}$ values proved to be characteristic for C=C-CF₂R and O=C-CF₂R fragments, that allowed to distinguish coexisting tautomers A and B and to evaluate their concentration in the mixture. The parameters of NMR of *o*- (trifluoroacetyl)phenols, which 6-membered chelate ring with O-H...O=C-CF₃ fragment was fixed by the aromatic nucleus, were used to determine model values $^1J_{C-F}$ of boundary structures of A and B.



The equilibrium "enol-enol" was analyzed within a wide temperature range for solutions of more than 100 compounds in various solvents. The tautomerism type under discussion was discovered for the first time for straight and cycle-containing 1,3-ketoesters, 1,3-ketoamides, 1,3-keto thioesters and sila-1,3-diketones. In general, our results are in contradiction with a routine opinion about preferable enolization of non-symmetrical 1,3-carbonyl compounds through the fluorinated acyl group. The equilibrium state for cyclic compounds [$R^1 + R^2 = (CH_2)_{2-5}$] is mainly controlled by the cycle size, whereas for compounds with $R^1X = Ar, Het,$ and $CH=CH-R$ the conjugate chain length plays the decisive role. The solvent nature, in contrast to temperature, does not affect much the "enol-enol" equilibrium state. The experimental data are in good agreement with the results *ab initio* for HF и DFT quantum-mechanical calculation.

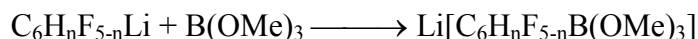
FLUORINATED AROMATIC OXYGEN BORON COMPOUNDS: SYNTHESIS AND PROPERTIES

N.Yu. Adonin, V.V. Bardin, H.-J. Frohn
(Russia, Germany)

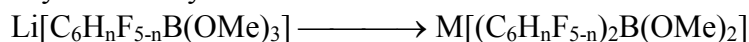
The report summarizes the last data on fluorinated oxygen-containing boron compounds, the following questions will be under consideration:

1. Fluorinated phenylalcoxyborates, $M[(C_6H_nF_{5-n})_mB(OMe)_{4-m}]$:

By the reaction of fluorinated lithium-organic compounds with trimethoxyborane a representative series of corresponding lithium phenylmethoxyborates were synthesized which were isolated in individual form and characterized completely.



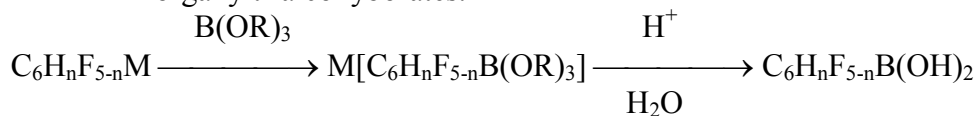
Coordination of the lithium cation by action of ester, TGF, DMF etc. or at substitution of Li^+ by another cation (K или Bu_4N) leads to conversion of pentafluoro-, 2,3,4,6- and 2,3,4,5-tetrafluorophenyltrimethoxyborates to corresponding polyfluorinated diphenyldimethoxyborates



Whereas 2,3,4,5-tetrafluorophenyltrimethoxyborate of lithium does not undergo this type of conversion.

2. Fluorinated phenylboric acids:

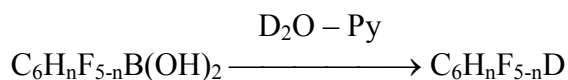
- a) Fluorinated phenylboric acids were obtained by acid hydrolysis of organyltrialcoxyborates.



$M = Li, MgBr$

At heating or under the action of dehydrating means fluorinated phenylboric acids are converted to corresponding anhydrides.

- b) In the presence of bases, fluorinated phenylboric acids $C_6H_nF_{5-n}B(OH)_2$ are subjected to hydrodeboration, the rate of this process depends both on the number of fluorine atoms in the ring and on their arrangement with regard to the boron atom.



The report considers the matter of spectral (multinuclear NMR, mass-spectrometry) identification of the products and their reactivity.

PERSPECTIVE DIRECTIONS OF DEVELOPMENT OF PHENOLIC ANTIOXIDANTS CHEMISTRY

A.E. Prosenko (Novosibirsk, Russia)

At present a great potential in the development of phenol antioxidants chemistry is linked with producing polyfunctional inhibitors which molecules contain several reaction centers inhibiting oxidizing processes via different mechanisms and possessing an intermolecular synergetic effect.

Over the past 5 years the research institute of antioxidants chemistry at NSPU has synthesized hundreds new sulfur-, nitrogen-, phosphorus-containing phenol compounds forming *structure related* series with variations in the degree of space screening phenol OH-group; in the length of the hydrocarbon chain separating sulfur- (nitrogen-, phosphorus-) containing and aryl fragments; in the structure of the sulfur- (nitrogen-, phosphorus-) containing groups.

The synthesis of a wide scope of compounds was followed by an extended study of their antioxidative activity interrelated to the structure and opened up new promising lines of development of the chemistry of polyfunctional phenol antioxidants.

The report exhibits different realized approaches to the synthesis of polyfunctional antioxidants on the basis of commonly used raw materials such as phenol, cresol, 2,3-di-tert-butylphenol, 2,6-dimethylphenol, hydroquinone and a number of others.

The data on system (integrated?) study of the antioxidative activity of the compounds synthesized are given in connection with the structure related to various substrates such as methyloleate, lard, cumene, styrene, liquid paraffin, polyethylene, hexadecane as well as with antioxidative and biological activity *in vitro* and *in vivo*

The data on the revealed regularities of the changes of inhibitory properties of the compounds synthesized are presented in dependence on their structure, substrate properties and oxidation conditions.

On the basis of the discovered regularities, novel polyfunctional phenol inhibitors, considerably exceeding the efficiency of commonly used industrial oxidants, were modeled and synthesized

The technologies for production were developed for the most effective antioxidants, these inhibitors may be recommended for application as inhibitors for polymeric materials, lubricating oils, fat-containing products, makeup preparations as well as pharmaceutical substances for further studies.

The results of the studies held allow to conclude about the development of the novel generation of antioxidants with the polyfunctional mechanism of antioxidative activity and pronounced effect of intermolecular synergism.

REDUCED DERIVATIVES OF TETRAAZAPORPHINES AS NOVEL CLASS OF TETRAPYRROLIC MACROCYCLES

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Tetraazachlorines(TAC), tetrazabacteriochlorines(TABC) and tetraazaisobacteriochlorines (TAiBC), being tetraazaporphine (TAP) derivatives halogenated through one or two double bonds, are of great theoretical and practical interest due to intensive absorption in red and near IR spectral region. As a result of the investigations being hold by our team in recent years there were developed two new methods of synthesis of these compounds. One of the methods is based on a mixed condensation of phthalogenes with different absorption level. Thus, by interaction of derivatives of phthalic 1,2- and 2,3-naphthalenedicarboxylic acid (dinitriles, anhydrides and imides), as well as of diphenylmaleonitrile with tetramethylsuccinonitrile in the presence of salts of metals or lithium alcoholates there were synthesized for the first time benzo-, 1,2- and 2,3-naphthocondensed as well as phenylsubstituted TAC, TABC and TaiBC [¹⁻⁴]. When derivatives of heteroaromatic 1,2-dicarboxylic acids were used in analogues condensation, their 1,4-pyrazine-, 2,3- and 3,4 pyridine-condensed analogues were obtained, being of interest as potential photosensitizers due to possibility to obtain their cationic forms in quaternization of pyridine and pyrazine nitrogen atoms. As a saturated component there were investigated also other derivatives of succinic acid with substitutes at carbon sp³-atoms, 2,2-pentamethylene пентаметилен- and 2,2-diphenylsuccinonitrile и 2,2-dimethylsuccinimide

The second method to synthesize hydrogenated TAP derivatives is based on cycloaddition reactions to quaziisolated double bonds of the TAP macrocycle. A reaction of [4+2]-cycloaddition of unsubstituted TAP as a dienophile with dienes of anthracene [³] and cyclopentadiene series was studied. Also there was studied a reaction of 1,3-cycloaddition of tetraazaporphines with azomethenylides and nitrones with the purpose to synthesize TAP hydro derivatives containing five-member heterocycles. Electronic absorption spectra of the synthesized compounds were investigated in organic solvents. It was shown that hydrogenation of β -positions of pyrrole rings of tetraazaporphine, as well as annelation of benzene and heterocyclic rings, leads to a considerable bathochromic shift of a long-wave absorption band up to 930 nm.

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[2] *Fukuda T., Makarova E. A., Lukyanets E. A., Kobayashi N.* // Chem. Eur.J. 2004. V. 10. N. 1. P. 117 - 133.

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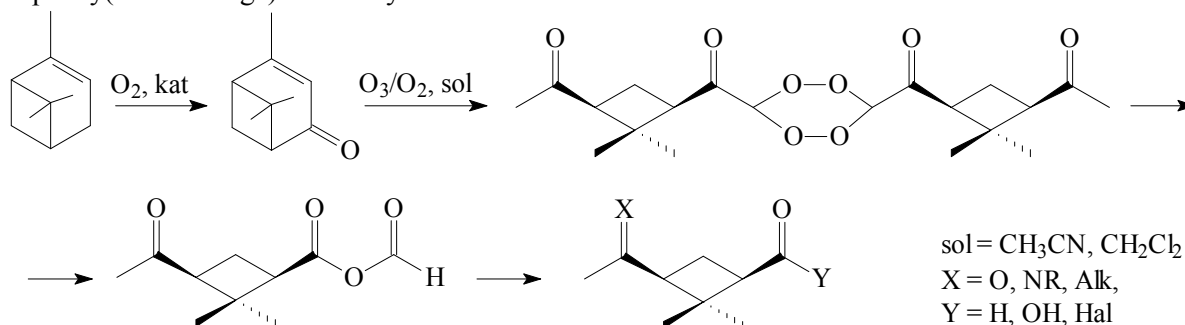
[5] *Makarova E. A., Korolyova G. V., Tok O. L., Lukyanets E. A.* // J. Porphyrins Phthalocyanines. 2000. V. 4. N. 5. P. 525 - 531.

OXIDATIVE TRANSFORMATIONS IN THE SYNTHESIS OF BIOLOGICALLY ACTIVE COMPOUNDS

O.S. Kukovinets, N.N. Kabal'nova, V.G. Kasradze, T.I. Zvereva,
E.V. Salimova, M.I. Abdullin, F.Z. Galin (Ufa, Russia)

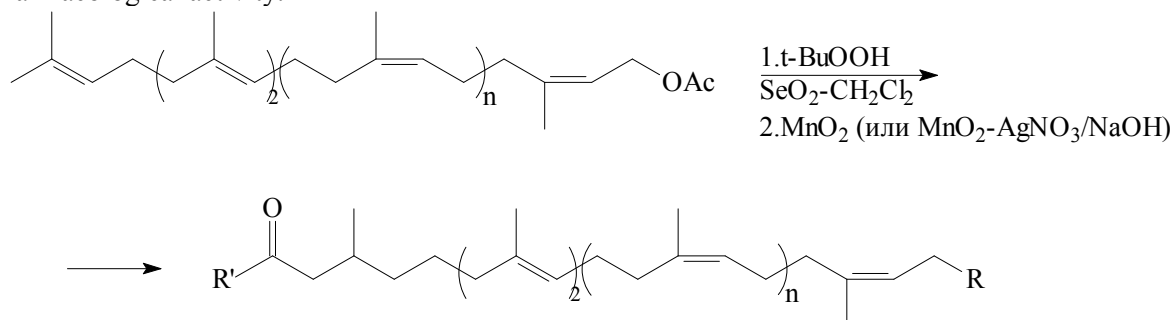
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A choice of rational route for region- and stereoselective synthesis of a desired compound is one of the important problems in producing low-molecular bioregulators as well as other biologically active substances. We have developed universal approaches allowing production of multifunctional synthons for a wide range of biologically active substances by oxidative transformations. The main advantage of the method, besides its variability, is spontaneous rearrangement of peroxide compounds into desired products, that simplifies the process significantly and makes it attractive for low-capacity (low-tonnage) chemistry.



Another cyclic and acyclic enones react similarly. The process *rules* were revealed on the basis of the ¹H and ¹³C NMR spectroscopy data, kinetic study and analysis of the reaction products.

Oxidative transformations of mono- and polyene compounds at allyl position were taken as the basis for chemical modification of natural objects, such as polyprenoles, terpenes, lipids, to compounds possessing wound healing, anti-inflammatory, antiulcer and other types of pharmacological activity.



R = OH или OAc, COOH, CHO, остаток полипrenoла
R' = OH, H или OCH₃

DESIGN AND SYNTHESIS OF NANOMOLECULAR MACHINES FOR SELECTIVE DELIVERY OF DRUGS

V.N. Silnikov (Novosibirsk, Russia)

SELEX (System Evolution of Ligands by EXponential enrichment) technology proposed about 10 years ago and the progress achieved in practical application of this technology in recent years open up fundamentally new (novel) opportunities in the development of high selective and low-toxic medical products.

In the present work we attempt to develop a "molecular designer" allowing on the basis of SELEX technology and well known selective and high efficient organic reactions to produce self-collecting molecular ensembles, nanomolecular devices, able to recognize malignant cells in the body, to contact selectively with them and to deliver a necessary acting agent inside. A possibility of this approach was demonstrated by a pattern of development of a model self-collecting nanomolecular device able to deliver a fluorescent dye into prostate tumor cells.

SELEX technology allows to obtain the key element of the nano device, an aptamer, which is a target product of selection of oligonucleotide nature, possessing high affinity and specificity to the given target, in our case to PSMA (prostate specific membrane antigen), a well known membrane receptor of malignant cells of prostate. In order to increase the aptamer stability with regards to extracellular ferments all the hydroxyl groups of the oligonucleotide at the 2' -position were replaced by fluorine (pyrimidine nucleosides) or by methoxy group (purine nucleotides). The end (negligible) of the aptamer carries a number of precursor groups providing self-collection on its basis of the whole nanomolecular device. Other important elements of the molecular ensemble are the following

Linker group of oligonucleotide nature, stable with regard to the hydrolytic ferments of the extracellular environment, but it is easily cleaved during the endocytosis process

Polyethylenepolyamine residue, carrying the residues of the fluorescent dye (molecules of medical product are in sight)

All the nano-device elements of oligonucleotide nature were synthesized by solid phase amidophosphite method of synthesis using amidophosphites, standard ones or those carrying necessary precursor groups. The following pairs were used as complementary precursor groups:

Monoamide of cyanoethyl ether of oxalic acid- aliphatic amino group (introduction of hydrophobic fragments)

Terminal triple bond- aliphatic azido group (formation of the bond aptamer-linker group)

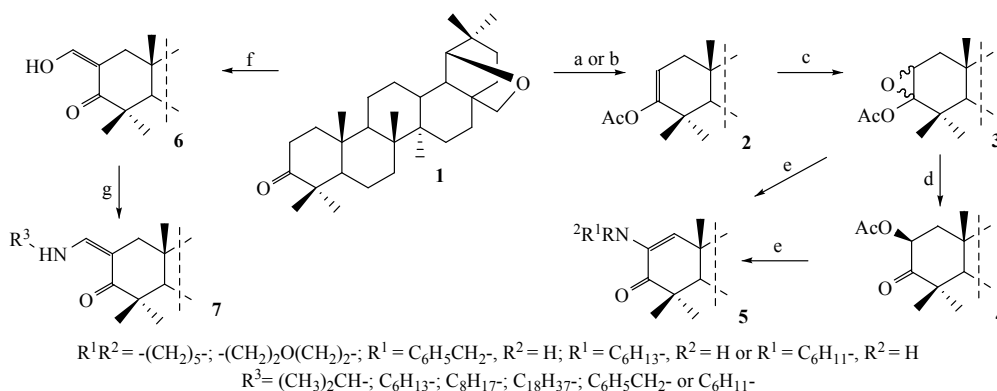
Anthracene residue- maleimide group (formation of the linker group-polyethylenepolyimine bond)

The work was financially supported by RFFI grant 07-04-00990-a

SYNTHESIS OF β -ENAMINOCARBONYL OLEANANIC DERIVATIVES

I.A. Tolmacheva, L.N. Shelepen'kina, V.V. Grishko, V.A. Glushkov, A.G. Tolstikov (Perm, Russia)

The methods to synthesize two novel types of oleanane β -enamineketones on the basis of allobetulin **1** were developed as a result of the investigations carried out.



Reagents and conditions: (a) $(CH_3CO)_2O$, H_2SO_4 ; (b) $CH_2=CH(CH_3)OCOCH_3$, H_2SO_4 ; (c) *m*- $ClC_6H_4CO_3H$, CH_2Cl_2 ; (d) R^1R^2NH , C_6H_6 ; (e) boiling in R^1R^2NH ; (f) $HCOOC_2H_5$, CH_3ONa , C_6H_6 ; (g) R^3NH_2 , DCC, C_6H_6 .

The interaction of 3-acetoxy-19 β ,28-epoxyolean-2-ene with *m*-chloroperbenzoic acid resulted in a mixture of diastereomeric 3-acetoxy--(2,3),(19 β , 28)-diepoxyoleananes **3**, its heating in aliphatic amines resulted in formation of nitrogen-containing derivatives **5**, containing the enamine fragment in the ring A. 2 β -Acetoxy-19 β ,28-epoxyolean-3-one was isolated as an intermediate reaction product, its directed synthesis runs at addition of a mixture of organic solvents to the reaction mixture.

The possible mechanisms of stereoselective rearrangement of diepoxides **3** into acetoxyketon **4** followed by transformation of compound **4** into desired β -enaminoketones **5** were proposed.

2-Alkylaminomethylene-19 β ,28-epoxyolean-3-ones **7** were synthesized by the reaction of 2-hydroxymethylene-19 β ,28-epoxyolean-3-one **6** [2] with linear and cyclic amines in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC).

The work was fulfilled under support of the RF President's grant on State support of leading scientific schools of RF (№ IIII-5812.2006.3) and Program of Presidium of RAS "Directed synthesis of substances with targeted properties and development of functional materials on their basis"

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EFFECT OF STERIC STRUCTURE OF CHIRAL DERIVATIVES OF NATURAL TERPENES ON COMPLEXATION CHARACTER WITH TRANSITION METALS

S.V. Larionov, A.V. Tkachev (Novosibirsk, Russia)

An interesting line of organic and coordination chemistry is synthesis of "hybrid" ligands by chemical modification of natural organic substances as well as producing complexes of novel ligands with metals. Methods to synthesize several types of chiral polydentate ligands of open-chain and closed topology, built with the use of natural monoterpene compounds (3-carene, α -pinene and limonene) as building blocks and as initial sources of chirality, such as primary α -aminooximes, diaminomono oximes, symmetric and asymmetric macrocyclic compounds [1].

Investigation of the structure and properties of the complexes of novel chiral organic ligands series with transition metals has revealed a number of curious examples of the influence of the spatial constitution of the ligands on the complexing character [2].

The interaction of CuCl_2 with 3-carene dimethylamino oxime and limonene morpholine oxime gives paramagnetic binuclear complexes of $\text{Cu}_2(\text{HL})_2\text{Cl}_4$ composition with the dimethylamine and oxime groups at the cis-position with regards to metallocycle Cu_2Cl_2 and the morpholine and oxime groups at the trans-position. The reaction of $\text{Ni}(\text{NO}_3)_2$ with diaminodioximes from 3-carene and limonene in a EtOH environment results in paramagnetic ionic complexes of $[\text{Ni}(\text{H}_2\text{L})\text{NO}_3]\text{NO}_3 \cdot n\text{H}_2\text{O}$ ($n = 0.2$) composition. In the reaction of bis-pinane and asymmetric diaminodioximes, containing one pinane fragment, the diaminodioxime anion is coordinated to form diamagnetic ionic complexes $[\text{Ni}(\text{HL})]\text{NO}_3$.

In the interaction of CoCl_2 in air with bis-caran ethylenediaminodioxime, Co(II) maintain the oxidation degree to form paramagnetic complex $\text{Co}(\text{H}_2\text{L})\text{Cl}_2$. A reaction of Co^{2+} oxidation to Co^{3+} , affording molecular complexes of Co(III) of $\text{Co}(\text{HL})_2\text{Cl}$ composition, is characteristic for the reaction of CoCl_2 with propylenediaminodioximes. As a result of the reaction of PdCl_2 with ethylenediaminodioxime from 3-carene, the molecular binuclear complex $\text{Pd}_2(\text{H}_2\text{L})\text{Cl}_4$ with PdCl_2 fragments at the trans-position is obtained. The interaction of with 3-carene meta- α, α' -diaminoxyloldioxime results also in a binuclear complex containing PdCl_2 at the cis-position. The reaction of Co(II) with macrocyclic dioxatetraaza- derivative of 3-carene and dioxapentaaza derivative of α -pinene led to the formation of ionic complexes that contained ions Co^{2+} with the coordination number 5 and 7.

This cycle of investigations was financially supported by RFFI (grants 01-03-32374-a, 03-03-32096-a, 04-03-32147-a).

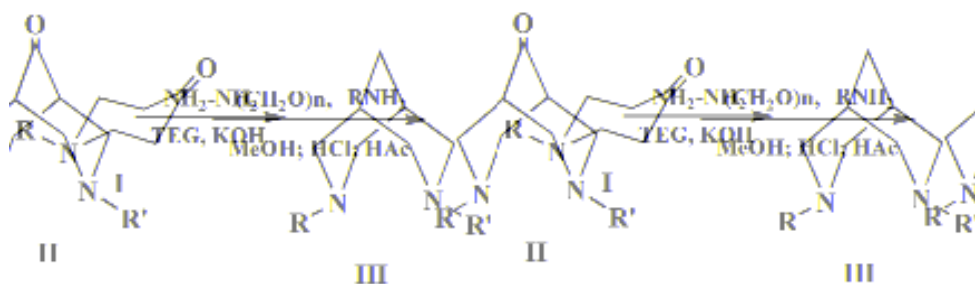
MOLECULE DESIGN OF BICYCLIC PIPERIDINES

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The investigations carried out at the laboratory of pharmaceutical substances of the Institute of chemical sciences after A.B.Bektourov have demonstrated exclusive opportunities for the synthesis of piperidine derivatives, mono- and polycyclic analogues of piperidine possessing a wide spectra of pharmacological activity. 3,7-Diazabicyclo[3.3.1]nonanes take a special place among piperidine bicyclic analogues. The fact that some derivatives of 3,7-di(alkoxyalkyl)-3,7-diazabicyclo[3.3.1]nonane possess a wide range of pharmacological activity (in particular, relatively simple molecules of N,N-dialkoxyalkyl-3,7-diazabicyclo[3.3.1]nonanes exhibited a high analgesic activity) contributed to further investigations on the synthesis of this class of organic compounds.

In order to reveal the influence of the change of alkoxyalkyl substituent on the one of the nitrogen atoms for morpholine-ethyl, cyclopropylemethyl, hydroxyethyl and hydroxiethoxyethyl substituent on the properties of compounds, including pharmacological ones, there were synthesized 3,7-diazasubstituted 3,7-diazabicyclo[3.3.1]nonan-9-ones (**II**) (**I**) by simultaneous condensation of N-substituted piperidin-4-ones (**I**) with paraform and various primary amines in acetic-methanol environment. The obtained values of the vicinal constants, below 7.0Hz, prove that the molecules of 3,7-diazabicyclo[3.3.1]nonan-9-ones under investigation are in a "double chair" conformation.



In the IR spectra of 3,7-diazabicyclo[3.3.1]nonan-9-ones synthesized there were identified the characteristic bands of valence vibrations of the carbonyl group in the region 1720 cm⁻¹ and those of the ether bond in 1112-1118cm⁻¹. The ¹³C NMR spectra of bispidinones (II) at 215 ppm exhibit singlet signals of the carbonyl group. The formation of bicyclic ketones is confirmed by doublets C1,5 in the 47ppm region, triplets of the carbon atoms C2,4 and C6,8 in the region 58.3-59.3ppm as well as the signals of the carbon atoms of the substituents on the nitrogen atoms.

The reduction of 3,7-diazabicyclo[3.3.1]nonan-9-ones (II) under conditions of the Huang-Milon reaction results in formation of corresponding 3,7-diazabicyclo[3.3.1]nonanes (III). On the basis of the ¹H NMR spectra data it has been shown that double chair conformation of hydrogenated derivatives is maintained.

Primary pharmacological screening has revealed among the compounds synthesized the substances possessing immunopotentiating, antibacterial and antispasmodic activity.

THE APPLICATION OF C- AND N-NITROCOMPOUNDS FOR SYNTHESIS AROMATIC AND QUINOID SUBSTANCES

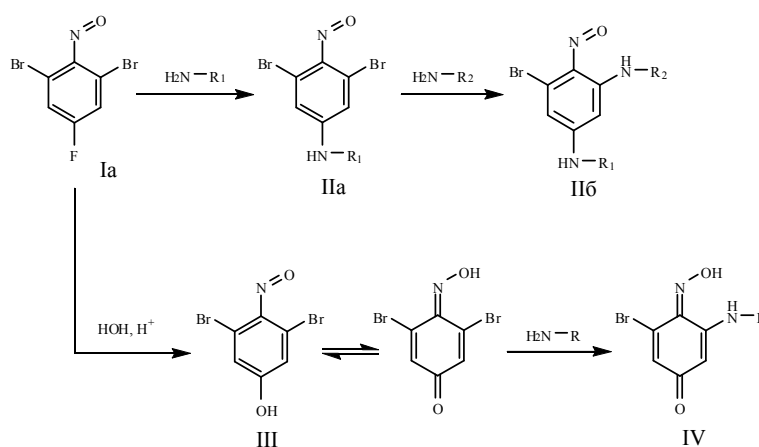
L.M. Gornostaev, E.A. Bocharova, N.V. Geets, L.V. Dolgushina, T.I. Lavrikova, M.S. Sokolova (Krasnoyarsk, Russia)

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Nitroso compounds have found a rather wide application as intermediate products in chemical industry, some of them are of separate practical importance [1].

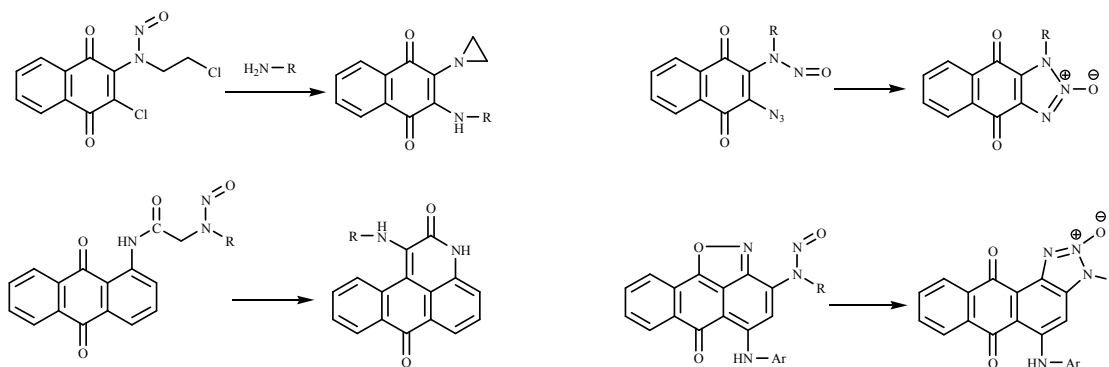
This work cites data obtained recently by the authors about new opportunities of using nitroso compounds in organic synthesis.

It was found that 2,6-dibromo-4-fluoronitrosobenzene (Ia) is a convenient substrate for the synthesis of nitrosoanilines (II-III) containing one, two substituted amino-groups or the hydroxy-group and substituted amino-group at the ortho-positions (IV):



Polyhalogen nitrosoarenes (I) react quite selectively with morpholinocyclohexene, phenylacetylene with participation of the nitroso-group in particular.

N-Nitrosoderivatives of naphthquinones, heteroanalogues of anthraquinones are suitable for producing various heterocyclic derivatives of quinones:



The report considers prospects of practical application of the studied reactions.

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OXIDATIVE ALKYLAMINATION OF AZINONES AS A DIRECT ROUTE TO AMINOAZINONES

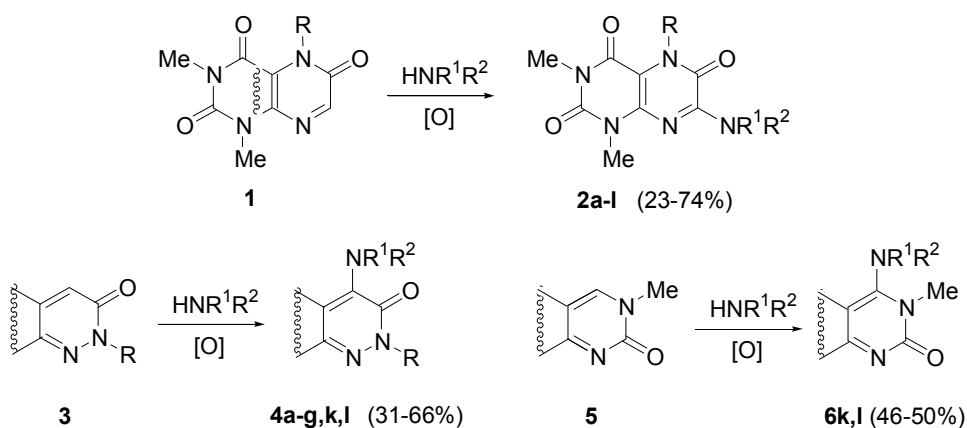
A.V. Gulevskaya, O.N. Burov, A.F. Pozharskii (Rostov-on-Don, Russia)

E-mail: Agulevskaya@rsu.ru

Azinones and aminoazinones are the most important class of biomolecules, which is pronouncedly presented by nitrogen bases of nucleic acids, folic acid, riboflavin etc. The unique properties of these natural substances are bound up with the presence of carbonyl amide, cyclic NH group and amino-group in their composition, because of that they are susceptible to formation of hydrogen bonds and to self-assembly. A whole number of medical products was found on the basis of azinones and amino derivatives.

The known methods to synthesize aminoazinones are mainly based on the reactions of cyclization and nucleophilic substitution of a halogen. This work for the first time reports about a possibility to obtain these substances by oxidative amination and alkylation of azinones. Lumazinone derivatives **1**, as well as their pyridazine **3** and pyrimidine **5** analogs, were used as the substrates. Mixing compounds **1,3,5** at the excess of the alkylamine in the presence of KMnO₄ or AgPy₂MnO₄ complex brings to formation of aminoazines **2, 4** and **6** in moderate and good yields. Both azinones **1,3,5** (R = H), unsubstituted at the nitrogen and corresponding N-methyl-derivatives come into the reaction.

Azinones are nonstandard substrates for the reaction of oxidative amination. The factors promoting its running in series of azinones and the field of application are under consideration.



[O] = KMnO₄, AgPy₂MnO₄

2, 4, 6:	a	b	c	d	e	f	g	h	i	j	k	l
NR ¹ R ² =	NHEt	NHPr	NHPr ⁱ	NHBu	NHBu ^t	NH-	NHCH ₂ Ph			NEt ₂	NHPr	NHBu
R =	H	H	H	H	H	H	H	H	H	H	Me	Me

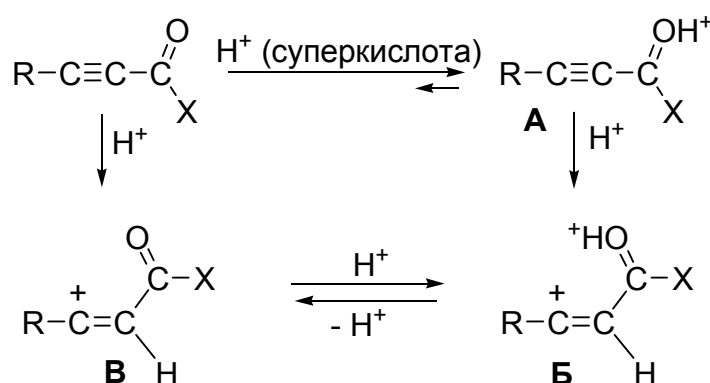
PROTONATION AND REACTIONS OF ACETYLENIC COMPOUNDS IN SUPERCACIDS

A.V. Vasilyev^a, J. Sommer^b, A.P. Rudenko^a (Russia, France)

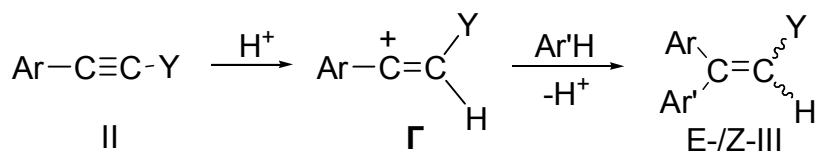
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Protonation of the triple bond of acetylene compounds in superacids HSO₃F, CF₃SO₃H, HF-SbF₅ brings to the formation of cations of vinyl type. Acetylene carbonyl derivatives (I) containing several base centers give in superacids inactive O-protonated forms (A) or reactive cations (B),(C) which are strong electrophilic moieties.



The cations of vinyl type (D) generated in HSO₃F and CF₃SO₃H from arylacetylene compounds (II) react effectively with various benzene derivatives according to the reaction of aromatic electrophilic substitution to form alkenylation products (E-/Z-III).¹



Y = CO₂H, CO₂Me, COAr', COMe,
COCF₃, COCO₂Et, CN, PO(OEt)₂, Ar'

¹ Vasilyev A.V., Walspurger S., Pale P., Sommer J. *Tetrahedron Lett.* **2004**, 45, 3379; Vasilyev A.V., Walspurger S., Haouas M., Sommer J., Pale P., Rudenko A.P. *Org. Biomol. Chem.* **2004**, 2, 3483; Васильев А.В., Walspurger S., Pale P., Sommer J., Haouas M., Руденко А.П. *ЖОрХ.* **2004**, 40, 1819; Walspurger S., Vasilyev A. V., Sommer J., Pale P. *Tetrahedron.* **2005**, 61, 3559; Савеченков П.Ю., Руденко А.П., Васильев А.В., Фукин Г.К. *ЖОрХ.* **2005**, 41, 1341.

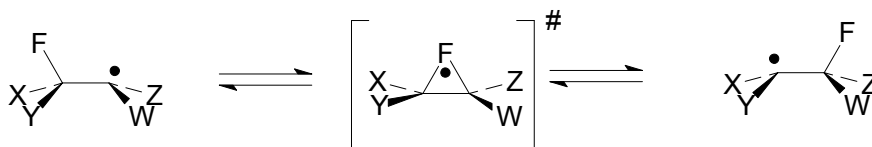
O-14

FLUORINE MIGRATION IN FREE RADICALS. THEORETICAL INVESTIGATION

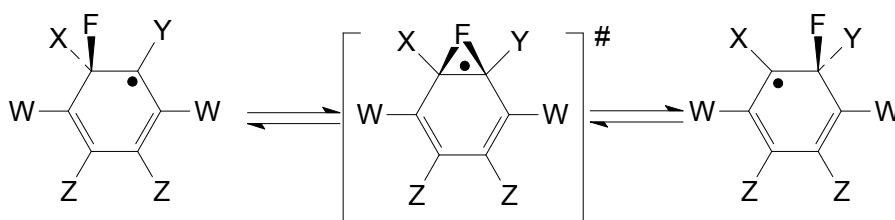
I. Bilkis

Institute of Biochemistry, Food Science and Nutrition, Faculty of Agriculture, Food and Environmental Quality Sciences, The Hebrew University of Jerusalem, POB 12, Rehovot, 76100, Israel. E-mail: Bilkis@agri.huji.ac.il

The 1,2-shift of the β -fluorine atom to the free radical terminus was primarily observed in polyfluorinated cyclohexadienyl free radicals (L.S.Kobrina and co-workers). Due to the absence of the kinetic data on the fluorine migration in free radicals, general features of the rearrangement are still not completely understood. The dependence of the rearrangement energy barriers (ΔE^\ddagger) on the structure (degree of fluorination) of the free radical, was investigated in the present work by theoretical means. Optimal geometries and electronic structures of the initial and final states, as well as of transition states were calculated at the UMP2/6-311+G**// UMP2/6-311+G* and B3LYP/6-311+G**// B3LYP/6-311+G* levels of theory. Following systems were studied:



- a) X=Y=W=Z=H; b) X=F, Y=W=Z=H; c) X=Y=F, W=Z=H; d) X=Z=F, Y=W=H;
e) X=W=F, Y=Z=H; f) X=Y=W=F, Z=H; g) X=Y=Z=F, W=H; h) X=Y=W=Z=F



The validity of the calculations was examined by comparison of the experimental and calculated energy barriers for chlorine migration in free radicals. The results of B3LYP/6-311+G**//B3LYP/6-311+G* calculations were found to fit the experimental data better than those obtained by UMP2/6-311+G**//UMP2/6-311+G* approach. The ΔE^\ddagger of the fluorine migration remarkably increases with the increase of fluorination degree of the free radical: $\Delta E^\ddagger=22.86$ Kcal/mol for 2-fluoroethyl radical and $\Delta E^\ddagger=40.61$ Kcal/mol for perfluoroethyl radical. This happens because initial free radical state is stabilized by this structural change in a greater extent than corresponding transition state. The ΔE^\ddagger of the fluorine migration in the cyclohexadienyl radicals are lower than ΔE^\ddagger in the alkyl radicals: $\Delta E^\ddagger=15.50$ Kcal/mol for monofluorinated cyclohexadienyl radical and $\Delta E^\ddagger=24.80$ Kcal/mol for perfluorinated cyclohexadienyl radical. The ΔE^\ddagger of fluorine migration in cyclohexadienyl radicals with two geminal fluorines are significantly higher than in cyclohexadienyl radicals with only one geminal fluorine. It is due to a strong stabilization of the initial free radical states without sufficient change in the energy of the corresponding transition states. The effect of fluorine atoms from other positions of cyclohexadienyl radical on ΔE^\ddagger of fluorine migration is complicated. In most of cases it is governed by stabilization-destabilization of transition states.

SPIN CHEMISTRY OF ASSOCIATES OF GLYCYRRHIZINIC ACID

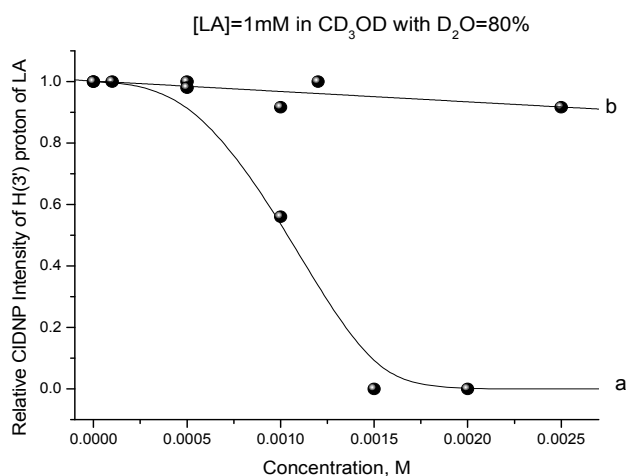
T.V. Leshina^a, V.S. Kornievskaya^a, A.I. Kruppa^a, N.E. Polyakov^a,
N.F. Salakhutdinov^b, G.A. Tolstikov^b (Novosibirsk, Russia)

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One of the main problems of supramolecular chemistry arising in research of processes in so called organized media (complexes, micelles, liquid crystals etc.) is establishment of mechanisms of the media impact on the reactivity of the 'included' compounds. The present work introduces a novel approach to investigation of the influence of the organized environment, including methods of the spin chemistry, by the example of associates of glycyrrhizic acid (GA), a biologically active natural compound, with organic molecules, lappaconitine(LC) and other esters of anthranilic acid (AA). Within the frame of this approach it is suggested to make a conclusion about formation of a complex or of solubilization in the GA micelle of an organic compound on the basis of comparison of effectiveness of nuclei chemical polarization, arising during the course of the radical chemical reaction with participation of the compounds under investigation, in the organized medium and in homogeneous solution. The work demonstrates correlation between the influence of the GA concentration in the solution on the micellization process and on effectiveness of separate stages of photodecomposition of LC and other AA esters.



The Figure presents the dependence of CIDNP intensity for the protons of the LC anthranyl fragment in the process of photo-induced deacylation of LC on the GA concentration, including the micellization area, and also the dependence of this process on the acetic acid concentration is given. It should be noted that the difference in sensitivity towards solubilization influence, recorded for separate stages of the photodecomposition process, allows to make conclusions about the nature of the organized medium influence.

NMR AND HYDROGENATION OF UNSATURATED COMPOUNDS WITH PARA-HYDROGEN

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The NMR method is a powerful tool, but it has a number of substantial disadvantages. In particular, many up-to-date applications of the method are limited by its relatively low sensitivity. Besides, any perturbation of the spin system damps for a rather short time (the spin relaxation time), that does not allow to study relatively slow chemical transformations and rearrangements, slow diffusion and flow processes etc. But recent investigations have shown that these disadvantages are quite surmountable and one of possible solutions lays at the turn of NMR and catalysis.

Molecular hydrogen (a system of A₂ type) is a mixture of two spin isomers, ortho-hydrogen (resultant spin of two nuclei I=1) and para-hydrogen (I=0). The latter itself does not give a NMR signal. But using nonequilibrium ortho-para mixtures in the reaction of homogeneous hydrogenation catalyzed by complexes of transient metals leads to multiplication of the NMR signal of the reaction product approximately 10⁴ times as much for a 300MHz spectrometer (and even more in weak fields). This fact (circumstance) is widely used for investigation of mechanisms of homogeneous hydrogenation and direct recording the reaction intermediates^[1]. Besides there is possible a polarization transfer in the product to the hetero-nuclei. Thus, polarization transfer from ¹H to ¹³C was used for recording two-dimensional NMR image of the blood vessels system of a laboratory animal, the images were obtained less than for one second at the natural content of ¹³C isotope in the substrate used^[2].

The use of a homogeneous catalyst is an obstacle for a number of practical applications. But the matter of principle for observation of polarization in the product is maintenance of correlation of the nuclear spins during the reaction course, that, due to the widespread notions, can not be provided using traditional heterogeneous catalysts (for example, Pd/Al₂O₃). That is why in the current work were synthesized and used catalysts on the basis of rhodium molecular complexes immobilized on a porous support. As a result it has been shown for the first time, by an example of styrene hydrogenation, that polarization in the reaction product is possible not only for homogeneous but also for heterogeneous hydrogenation. Besides, for the first time there was obtained gas polarization in hydrogenation with para-hydrogen (propylene hydrogenation to propane)^[3]. The work results open new opportunities to obtain pure polarized gases, for application of the polarized spins in a quantum computer realization, for application in NMR of long-living spin states with the life time $\gg T_1$ etc..

The work was supported by grants of RFFI (05-03-32472), CRDF (RU-C1-2581-NO-04) by support of leading scientific schools (NSh-4821.2006.3) and by the fund of domestic science support.

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[2] M. Goldman, H. Johannesson, O. Axelsson, M. Karlsson, *Magn. Reson. Imaging* **2005**, *23*, 153-157.

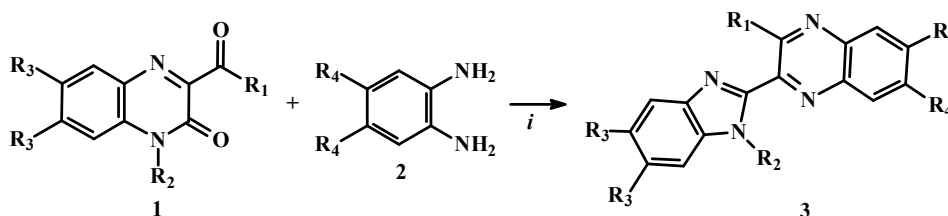
[3] I.V. Koptvug, K.V. Kovtunov, S.R. Burt, M.S. Anwar, C. Hilty, S. Han, A. Pines, R.Z. Sagdeev, *J. Amer. Chem. Soc.*, **2007** (принято к печати).

QUINOXALINONE-BENZIMIDAZOLE REARRANGEMENT IN THE REACTIONS OF 3-ACYLQUINOXALIN-2-ONES WITH *ortho*-PHENYLENDIAMINES

A.A. Kalinin, V.A. Mamedov (Kazan, Russia)

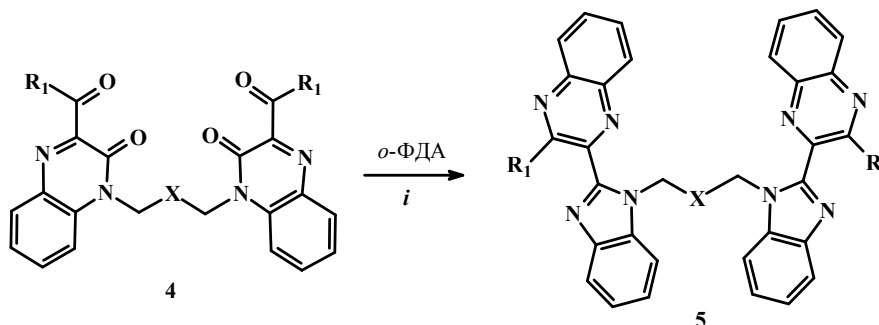
E-mail: mamedov@iopc.kcn.ru

We have found that 3-alkanoyl- and aroylquinoxalin-2-onyl ketones (**1**) under action of *o*-phenyldiamines at short-time heating in acetic acid undergo quinoxalino-benzimidazole rearrangement resulting in benzimidazoles, 2-benzimidazolylquinoxalines (**3**), in a high yield. Reaction of 3-acylquinoxalin-2-ones with monosubstituted 1,2-diaminobenzenes containing substituents, strongly differing in their character of electronic influence, on the benzene ring, nitro- and methyl groups, leads to formation of two isomeric products approximately in equal proportions. As a result of this reaction *o*-phenyldiamine (*o*-PDA) (**2**) condensation with alkyl-(or aryl)hetaryl ketones(**1**) takes place with participation of imine and ketone carbon atoms to form a new quinoxaline system and following contraction of the pyrazine ring to the imidazole one occurs.



$i = \text{AcOH, } 1\text{ч, } \Delta$; $R_1 = \text{Ph, Me, Pr}$; $R_2 = \text{H, Me, Et, Pr, Am, Bn}$; $R_3 = \text{H, Me}$; $R_4 = \text{H, Me}$

Bis-3-acylquinoxalin-2-ones(**4**) with spacers different in the length and nature also undergo quinoxalino-benzimidazole rearrangement to form corresponding bis-2-(quinoxalin-2-yl)benzimidazolyl alkanes (**5**).



$i = \text{AcOH, } 1\text{ч, } \Delta$; $R_1 = \text{Ph, Me}$; $X = \text{CH}_2, (\text{CH}_2)_4, (\text{CH}_2)_8, \text{CH}_2\text{OCH}_2, \text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$

The spectral features of the rearrangement products as well as the ways of their formation are under consideration in the work.

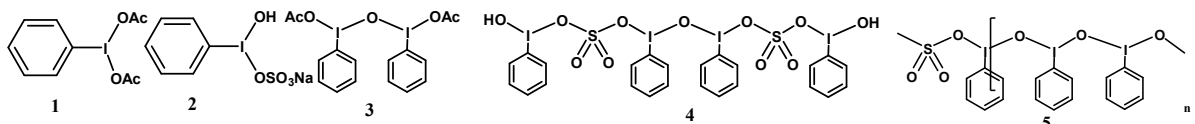
The work was implemented by financial support of Russian fund for fundamental investigations(grant# 07-03-00613) and grant by RF President "young candidates of science and their scientific advisers"(grant#MK-801.2006.3)

SYNTHESIS AND APPLICATION OF HYPERVALENT IODOARENES

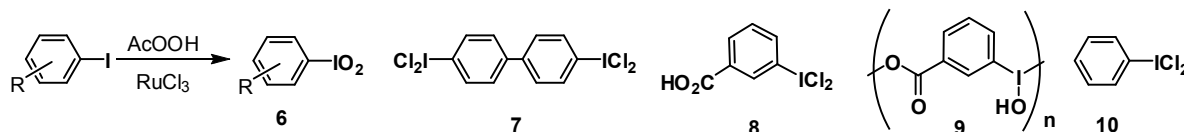
M.S. Yusubov, T.V. Funk, M.P. Gilmkhanova, G.A. Zholobova,
L.A. Drygunova, R.Ya. Yusubova (Tomsk; Russia)

Polyvalent iodine compounds (PIC) in III and V valent states take the key place among reagents of organic synthesis. Originality of these reagents is in their participation in oxidizing processes with formation of C-C- and C-X bonds, where X = O, N, S, Se, F, Cl, Br, I etc.

Since 2002y our research team has been engaged in development of synthesis methods and investigation of PIC chemical properties. We have found an easy method to synthesize from diacetoxyiodobenzene(1) new monomeric(2), dimeric, oligomeric(4) and polymeric(5) compounds of polyvalent iodine under solvent-free conditions and in aqueous medium [1]. We found a simple one-reactor method to synthesize iodylarenes (6) from iodoarenes using RuCl₃ [2].



For the first time we have proposed and studied chemical properties of monomeric PIC as an alternative to reagents on polymeric support with polyvalent iodine [3-5].



We have found new reactions for the most available PIC, diacetoxyiodobenzene(1) and dichloroiodobenzene(10) [6-10].

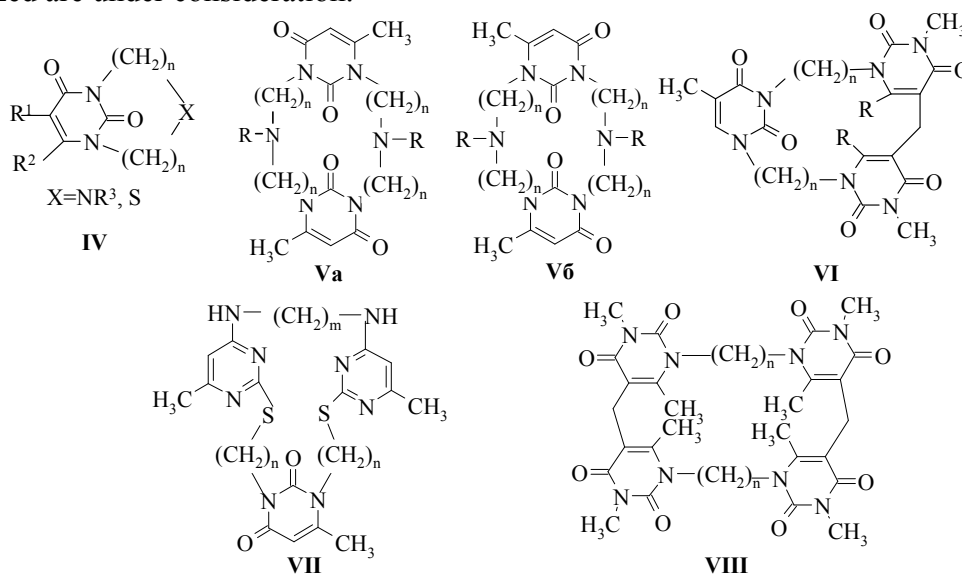
- [1] Kopusov A.Y., Netzel B.C., Yusubov M.S., Nemykin V.N., Nazarenko A.Y., Zhdankin V.V. // Chem. Comm. 2007, in press.
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DIRECTED PREPARATION OF PYRIMIDINOPHANES WITH DIFFERENT STRUCTURE

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Pyrimidinophanes, macrocyclic structures, being a different number of pyrimidine fragments connected with each other by hydrocarbon bridges are of interest due to their complexing, aggregative and biological properties. We have developed a strategy for a synthesis of pyrimidinophanes containing a different number of pyrimidine, in particular uracil, fragments connected with each other either via N atoms or via C atoms of the pyrimidine cycles, or by means of atoms of substituents on the pyrimidine cycles from practically the same initial substances such as N(1)-mono-(ω -bromoalkyl)-n(3)-methyluracils (**I**), N(1),N(3)-bis(ω -bromoalkyl) uracils (**II**) and α,ω -bis(3,6-dimethyluracil-1-yl)alkanes (**III**). Thus, reactions of **II** with aliphatic or aromatic amines or with Na₂S give macrocycles **IV**, reactions of **II** with N(1),N(3)-bis(ω -ethylaminoalkyl)uracils, obtained in turn from **II**, give isomeric macrocycles **Va** and **Vb**, reactions of **I** with thymine disodium salt followed by interaction of the products produced with paraform afford macrocycles **VI**, reactions of **II** with thiocytosine derivatives produce macrocycles **VII** and reactions of **III** with paraform result in macrocycles **VIII**. Pyrimidinophanes may be converted into amphiphile forms by quaternization or sulfonation of bridged heteroatoms or N atoms of the pyrimidine rings. The structure as well as aggregative, coordination and biological properties of the macrocycles synthesized are under consideration.



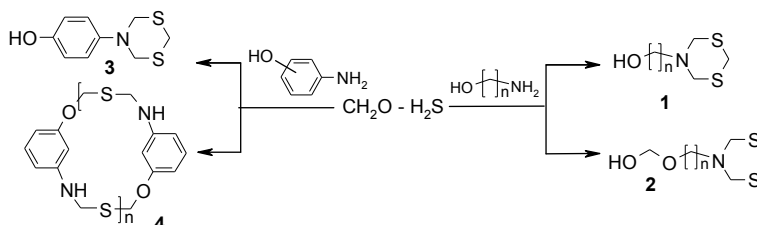
The work has been fulfilled under financial support of the Russian fund of fundamental investigations (project #07-03-00392) , programme #7 and programme#8 of the RAS presidium. Mr.Nicolaev A.E. is grateful to the domestic science assistance fund for the financial support.

MULTIMOLECULAR CYCLOCONDENSATION OF HETERO- AND BIFUNCTIONAL AMINES, H₂S AND ALDEHYDES

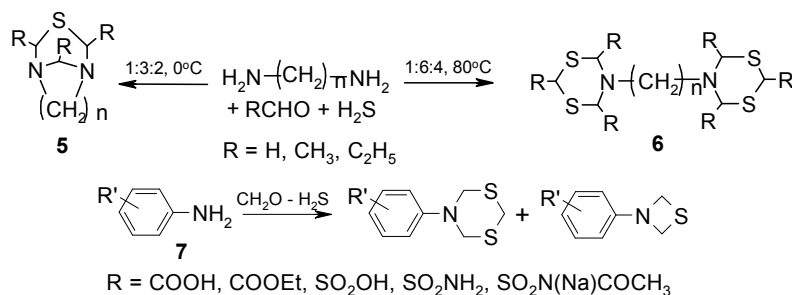
V.R. Akhmetova, G.R. Nadyrgulova, R.A. Vagapov, Z.T. Niatshina, R.R. Khairullina, R.V. Kunakova, U.M. Dzhemilev (Ufa, Russia)

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Cyclocondensation of methylamine, CH₂O and H₂S discovered by Wohl^[2] more than 100 years ago has become customary in preparative chemistry as a method to synthesize N-substituted 1,3,5-dithiazinanes^[3,4,5]. Recently during the investigations on multimolecular cyclocondensation of aliphatic aminoalcohols we have established that the reaction with participation of CH₂O-H₂S system first proceeds via NH₂ groups to form oxy(alkyl)1,3,5-dithiazinanes **1**, then following oxymethylation via OH-groups takes place. In case of aminophenols the cyclocondensation direction depends on the relative position of the functional group. Thus, *o*- and *n*-aminophenols form dithiazinanes **3** via NH₂ groups, while in *m*-aminophenole both functional groups undergo the action of CH₂O-H₂S reagent to afford azacrownthioesters **4** [6].



The report will present the data on investigation of regularities of the cyclocondensation of aliphatic diamines under conditions of conformational control, that allowed to obtain thiadiazabicyclanes **5** or *bis*-1,3,5-dithiazinanes **6** as well as the results of multimolecular cyclocondensation of amino acids **7**.



By the example of these reactions we made an attempt to determine the regularities promoting purposeful synthesis of N,S-containing heterocycles with functional groups.

¹ Wohl A., *Berichte*, **1886**, 19, 2344-2347.

² Collins D., Graymore J., *J. Chem. Soc.*, **1953**, 4089-4090.

³ Алеев Р.С., Дальнова Ю.С., Попов Ю.Н., Масагутов Р.М., Рафиков С.Р. *ДАН СССР*, **1988**, №4, 873-875.

⁴ Хафизова С.Р., Ахметова В.Р., Хакимова Т.В., Надыргулова Г.Р. *Изв. АН. Сер.хим.*, **2005**, №2, 423-427.

⁵ Ахметова В.Р., Надыргулова Г.Р., Хафизова С.Р. и др. *Изв. АН. Сер.хим.*, **2006**, №2, 305-308.

NEW HETEROCYCLIC SYSTEMS – THIOPHENE CIRCULENES AND HELICENES

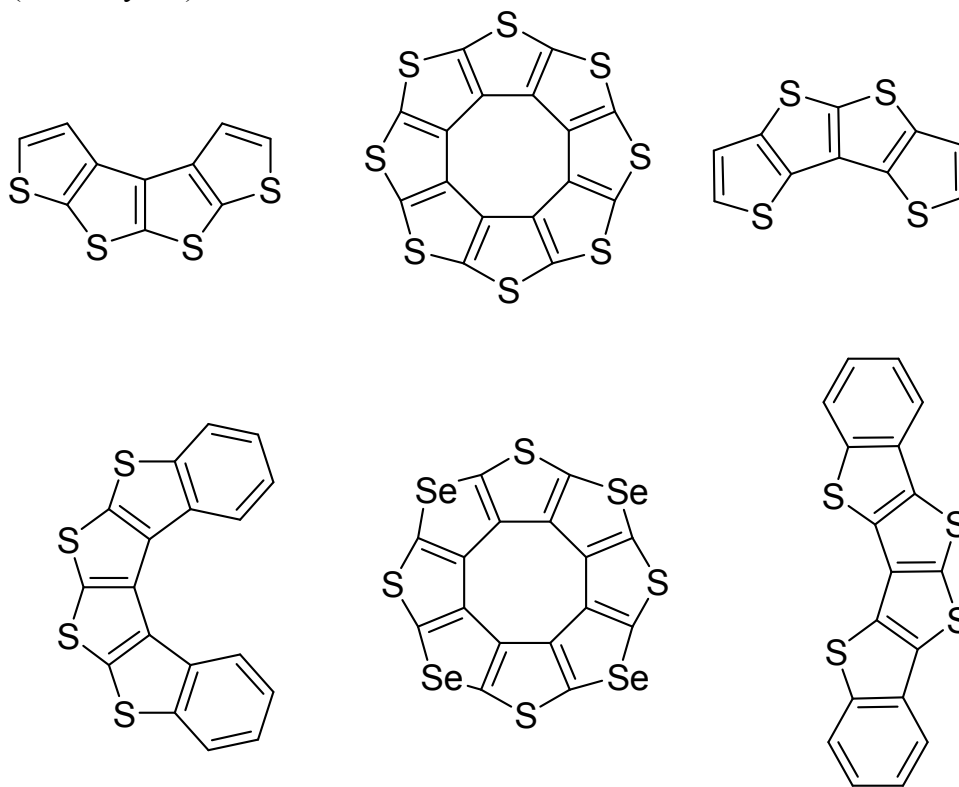
V.G. Nenajdenko, K.Yu. Chernichenko, S.S. Vshivenko, E.S. Balenkova
(Moscow, Russia)

E-mail: nen@acylium.chem.msu.ru

Creation of novel organic compounds and materials with a definite structure and specific properties is one of the central problems of modern organic chemistry. The most important task is synthesis of novel types of compounds, unknown earlier, their appearance may cause a qualitative advance in this field.

Condensed oligothiophenes attract a special attention recently. That is due to specific electronic properties of these aromatic systems that opens routes for using the materials on their basis in electronics, in particular, and in allied industries.

The report will consider the latest achievements in the synthesis of condensed oligothiophenes that open up opportunities of producing compounds of linear helicene and circulene (macrocyclic) series.

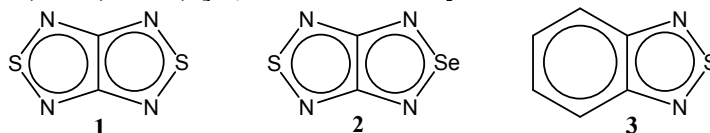


HETEROCYCLIC RADICAL ANION SALTS: PROMISING MOLECULAR MATERIALS

N.P. Gritsan, A.V. Zibarev, S.N. Konchenko, R. Mews, V.I. Ovcharenko
(Russia, Germany)

Construction and synthesis of new functional materials, in particular molecular magnetics and conductors, relate to the most actual tasks of modern chemistry.

Compounds **1-3** were chemically reduced to obtain salts of their anion-radicals with diamagnetic cations $[\text{Li}(12\text{-crown-4})_2]^+$, $[\text{Na}(15\text{-crown-5})]^+$, $[\text{K}(18\text{-crown-6})]^+$, $[\text{K}(\text{THF})]^+$, $[\text{Co}(\text{Cp})_2]^+$ и $[(\text{Me}_2\text{N})_2\text{CC}(\text{NMe}_2)_2]^{2+}$, characterized by EPR and RSA methods.

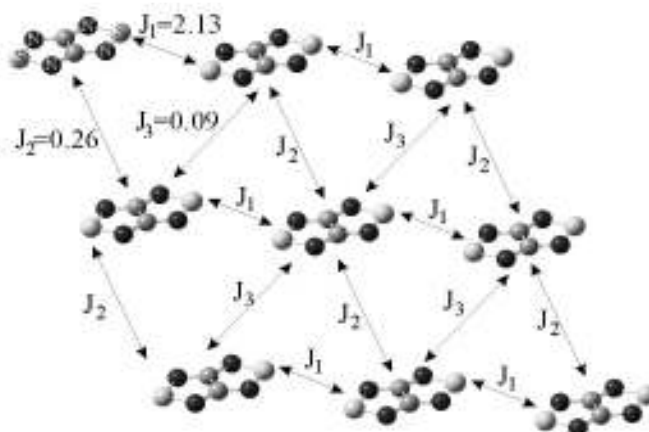


The experimental temperature dependence of magnetic susceptibility of the salts synthesized within an interval of 2-300K is well reproduced by phenomenological Bonner-Fischer theory suggested for end chains of exchange coupled paramagnetic centers and denotes antiferromagnetic ordering their spin systems at cryogenic temperatures. A variation of the exchange interaction energy in the salts is more than an order of magnitude. (Table)

The calculations of pairwise exchange interactions performed for real crystal packings by broken symmetry DFT (density-functional theory) method (spin-unlimited), and prove their three-dimensional character (the anion sublattice of $[\text{K}(18\text{-crown-6})][\mathbf{2}]$ salt and interaction in it have been shown)

Table.

Anion-radical salt	$-J$, cm^{-1}
$[\text{Na}(15\text{-crown-5})][\mathbf{1}]$	3.4, 1.1
$[\text{K}(18\text{-crown-6})][\mathbf{1}]$	1.2
$[\text{Co}(\text{Cp})_2][\mathbf{1}]$	7.7
$[\text{K}(18\text{-crown-6})][\mathbf{2}]$	1.7
$[\text{K}(\text{THF})][\mathbf{3}]$	54



The electrical properties of the salts, including those at low temperatures are under the investigation.

The authors are thankful for financial support to Siberian department of RAS (inter-discipline project № 25), RFFI (projects 06-03-32229, 06-03-32742, 07-03-00467) and to Deutsche Forschungsgemeinschaft (project 436 RUS 113/486/0-3 R).

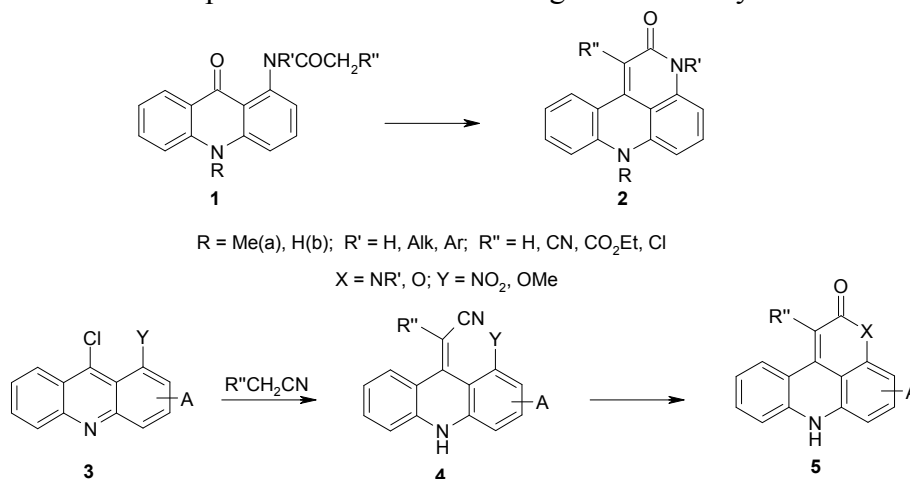
REACTIONS OF *peri*-CYCLIZATION AS A ROUTE TO 7H-PYRIDO- AND 7H-PYRANO[2,3,4-*kl*]ACRIDINE-2(3H)-ONES

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A large group of alkaloids possessing biological activity belongs to pyrido [2,3,4-*kl*]acridine series. Usually pyridoacridines are obtained by building an acridine nucleus, for example starting from quinoline derivatives. We have developed syntheses from compounds that have already have the acridine skeleton by means of intramolecular cyclization. Building a *peri*-annulated heterocycle is realized at the account of nucleophilic attack on the carbon atom at position 9 of the reaction center linked with δ -amino group, or by electrophilic attack on the heteroatom at position 1 of the functional group linked with position 9.

In the first case, 1-acetylamino-9-acridones **1**, containing unsubstituted or substituted acetyl group at the primary or secondary nitrogen atom, undergo cyclization. 1-Acetylamino-10-methylacridones **1a** are transformed into corresponding 7H-pyrido[2,3,4-*kl*]acridin-2(3H)-ones (**2a**) under the action of alkali in a polar aprotic solvent. 1-Acetyl(alkyl)aminoacridones **1b** with the NH-group in the nucleus are transformed to pyridoacridines **2b** in the presence of *n*-toluenesulfonic acid and potassium acetate at heating in acetic anhydride.



In the second case, *peri*-arrangement, necessary for formation of pyridoacridines **5** (X=NR'), is produced by the reaction of 1-nitro-9-chloroacridine **3** (Y=NO₂) with CH-acid followed by reduction of the nitro group in compound **4**. Generation of the hydroxyl group in position 1 brings to closure of the pyrone heterocycle. Thus, 1-methoxy-9-chloroacridines **3** (Y=OMe) after substitution of the chlorine by CH-acid residue and after heating in acid medium are converted into derivatives of 7H-pyrano [2,3,4-*kl*]acridin- 2(3H)-one (**5**, X=O) of the new heterocyclic system. Some properties of pyranoacridines were studied. There was demonstrated a possibility to introduce substituents (A) into the acridine nucleus of compounds **5** starting from corresponding chloroacridine **3**, that expands preparative potential of the method.

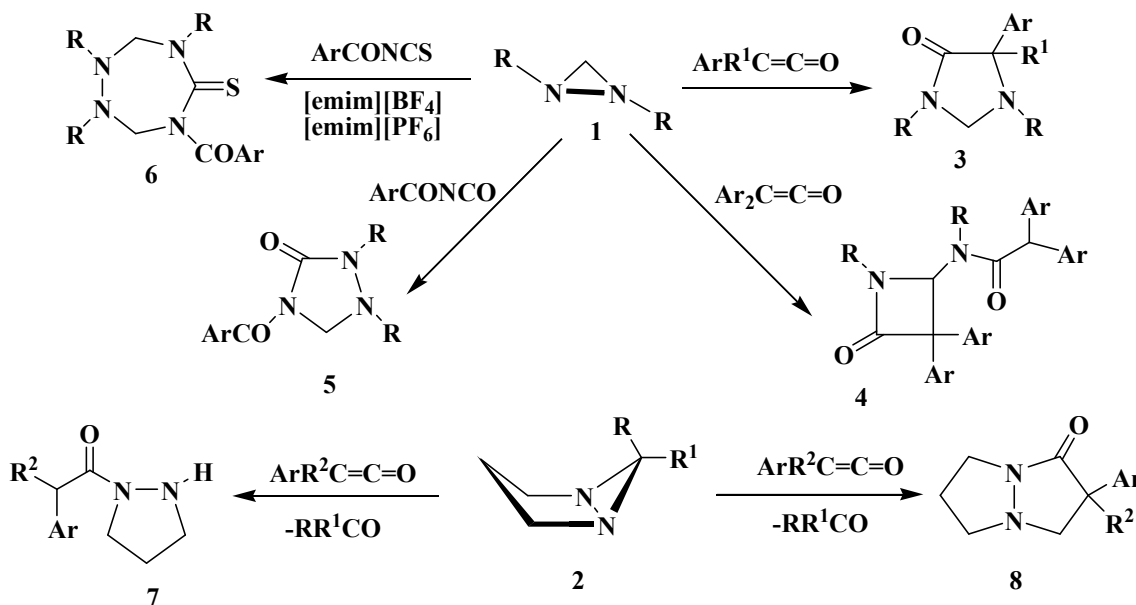
SYNTHESIS OF NITROGEN CONTAINING HETEROCYCLES BY TRANSFORMATION OF 1,2-DISUBSTITUTED DIAZIRINES WITH HETEROCUMULENES

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The chemistry of heterocyclic compounds has become one of the most developing branches of organic chemistry within recent tens years. Therefore development of a new strategy for construction of heterocyclic structures to allow new, easier and universal approaches to their synthesis remains issue of the day. The present work is devoted to the investigation of transformation of readily available 1,2-disubstituted diaziridines under the action of heterocumulenes in order to develop new approaches to producing nitrogen-containing heterocyclic compounds.

In the course of the investigation for the first time there was studied the interaction of two types of disubstituted diaziridines, namely *trans*-1,2-dialkyldiaziridines **1** and *cis*-1,5-diazabicyclo[3.1.0]hexanes **2**, with heterocumulenes (ketenes, isocyanates and isothiocyanates). It was shown that these reaction in fact lead to simple preparative 1-2-stage methods for producing a whole number of nitrogen-containing heterocycles (5-aryl-1,3-dialkylimidazolidin-4-ones **3**, representatives of β - lactams such as 4-acylaminoazetid-2-ones **4**, 4-aroyl-1,2,4-triazolidin-3-ones **5**, 4- benzoyl-1,2,6-trialkyl-1,2,4,6-tetrazeban-5-thiones **6**, 1-acylpyrazolidines **7** and 3-aryl-1,5-diazabicyclo[3.3.0]octan-2-ones **8**) which known synthesis methods are based on multi-stage procedures. The proposed mechanisms of the studied reactions were partly confirmed by quantum-chemical calculations within the frame of density functional theory.



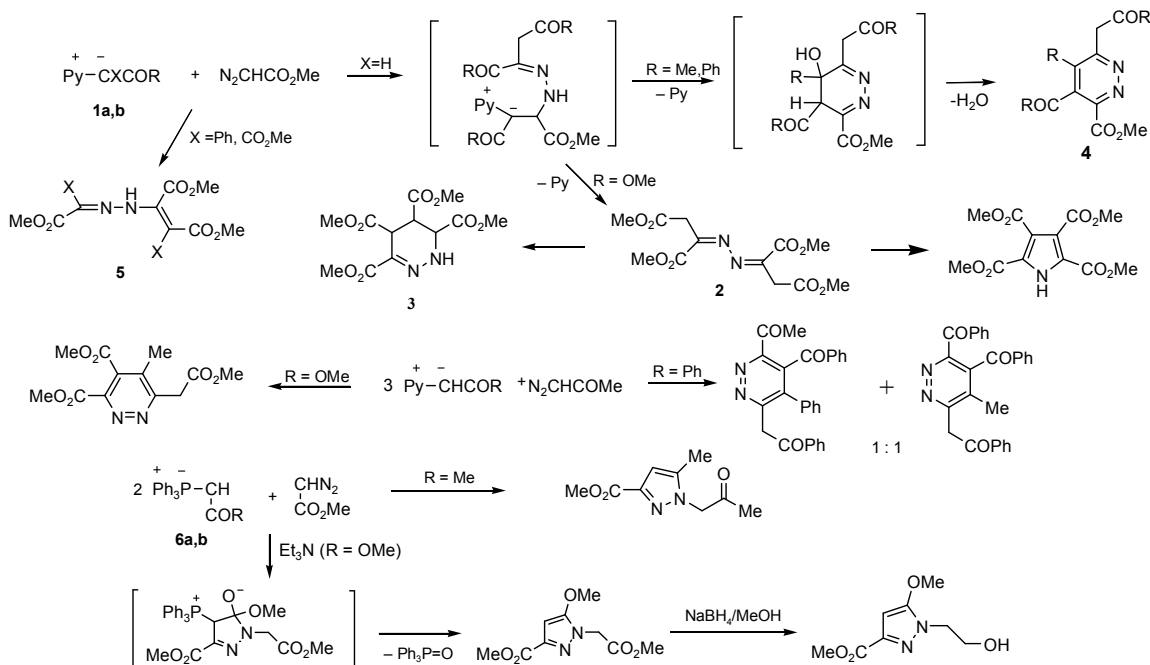
A NEW METHOD FOR THE SYNTHESIS OF AZAHETEROCYCLES BASED ON CASCADE REACTIONS OF NITROGEN- AND PHOSPHORUS-CONTAINING YLIDES WITH DIAZOCARBONYL COMPOUNDS

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A new approach developed for the synthesis of polyfunctional pyrazoles, pyridazines and tetrahydropyridazines is based on cascade transformations of diazo compounds with carbonyl-containing ylides of nitrogen or phosphorus [1-3]. So, a consecutive transformations of methyl diazoacetate and three molecules of ylide **1a** (R = OMe) results in diazaalkadiene tetracarboxylate **2**, which under the action of alkali is cyclized either in tetraester **3**, or at boiling in xylene in ester of pyrrole tetracarboxylic acid. The use of carbonyl derivatives of **1b** (R = Me, Ph) changes the cyclization reaction direction and pyridazines **4** become the main products. In case of disubstituted pyridinium ylides the reaction stops at the stage of interaction of diazoester with two ylide molecules to form compounds **5**. Also the reactions of pyridinium ylides with diazoacetone resulting in formation of substituted pyridazines were studied.

Unlike pyridinium ylides **1a,b** (X = H), less reactive triphenyl phosphonium ylides **6a,b** give products of the interaction of two ylide molecules with one molecule of diazoester that finally brings to the formation of pyrazole derivatives. Some chemical transformations of the obtained compounds were studied and in particular it was shown that the action of NaBH₄ in alcohol resulted in selective reduction of the ester group in alkyl N-substituent only.



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NEW ROUTE TO THE METHACYCLOPHANE SYSTEM

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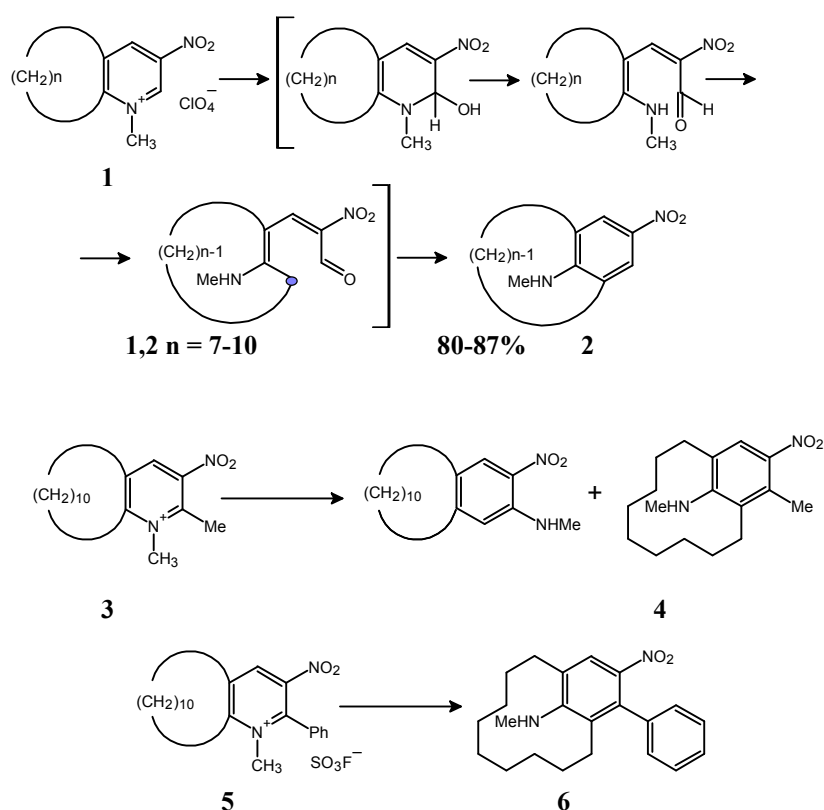
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The chemistry of cyclophanes has achieved a considerable progress within last three decades. An interest to the synthesis of strained metha-($n < 7$) and paracyclophanes ($n < 8$) is connected with investigation and development of the aromaticity theory [2].

The report is concerned the synthesis of methacyclophanes **2,4,6** with different length of the carbon chain by recyclization of salts of orthopyridinophanes **1,3,5** [3].



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