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STRUCTURAL AND NONLINEAR DIELECTRIC PROPERTIES INFLUORIDE SrTiO₃ OR BaTiO₃ CERAMICS

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Advanced ceramics are making news across industry, right around the world. Electrical and electronic ceramics currently dominate applications. Barium titanate (BaTiO₃) and strontium titanate (SrTiO₃) has a couple of properties that make them attractive in memory devices. For example, the solid solution B_{1-x}Sr_xTiO₃ is commonly used as a capacitor in DRAMS (1-4). The samples used in this study are oxyfluoride ceramics derived from SrTiO₃ or BaTiO₃. They were obtained at low temperature ($t_{\text{int}} < 1000^{\circ}\text{C}$) from ATiO₃-MF₂-LiF mixtures (A=Sr, Ba, M=Ca, Sr,Pb), air -Fired at 950°C. X-ray diffraction analysis were carried out to control the purity and to identify the different phases. The ceramic microstructure was automatically characterized by a scanning electron microscopy observation performed on fractured samples. Dielectric measurements (ϵ'_{r} , ϵ''_{r} and $\tan \delta$) were performed as a function of temperature ($120\text{K} < T < 470\text{K}$) and frequency ($20\text{Hz} < f < 109\text{HZ}$). The room temperature frequency dependencies of ϵ'_{r} and ϵ''_{r} show a piezoelectric resonance for SrTiO₃ derived ceramics in the range $3 \cdot 10^8$ - $5 \cdot 10^8$ Hz and a dielectric relaxation at about $7 \cdot 10^6$ Hz for BaTiO₃ related materials.

FUEL TANKS FABRICATED FROM PELP WITH FLUORINATED SURFACE

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In the last few years some automobile firms (such as FORD, GAZ) have attempted to fabricate fuel tanks and other reservoirs from PELP (polyethylene of low pressure) instead of those made of steel with lead-tin coating. In many cases it is also expedient to use such reservoirs for storage and transportation of various organic solvents and food products aspects to improve include lower cost price, potential advantages concerning safety, more freedom in choosing forms of a tank, reduction of weight, resistance to corrosive attacks. The chief drawback of PELP is its high permeability to petrol, diesel and some organic solvents. This disadvantage can be overcome by applying the technology of gas fluorination of internal surface of tanks. The modification of an internal surface of reservoirs is conducted for 10-200 min with a mixture of molecular fluorine and inert gas (helium, nitrogen) at room temperature with subsequent removal of the unreacted fluorine and reaction products.

Notable reduction of permeability is obtained through formation of fluorinated surface layer due to substitution reaction when the atoms of fluorine replace the atoms of hydrogen. The fluorinated surface layer is very similar in structure and properties to fluorine polymers.

Table. The results of long-term storage of variety of fuels in the reservoirs made of PELP with fluorinated and untreated surface layer (the wall of the reservoirs is 1,5 mm thick-, the surrounding temperature is 20°C)

Вид обработки Manner of treatment	Топливо Type of fuel	Доля оставшегося топлива от его начальной массы (в масс. %) при хранении в течение / Proportion of fuel left from the initial weight (%) after storage period of		
		10 сут.(days)	30 сут.(days)	90 сут.(days)
Без обработки Untreated sample	Бензин А-76 Petrol	96,5	90,0	71,6
Фторирование Fluorinated sample	А-76	99,5	98,7	96,0
Без обработки Untreated sample	Дизельное топливо Diesel fuel	—	91,0	77,0
Фторирование Fluorinated sample		—	99,7	99,0

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HETEROPHASE FLUORINATION OF RUBBERS

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Fluorination of rubbers goes much faster than fluorination of polyolefines (reaction rates are higher by 1- 2 orders of magnitude), This is because there are many unsaturated bonds in rubbers, and the coefficient of a reactant's diffusion tends to be rather large, which makes it harder to control the process. In this work, we have studied in detail basic properties of heterophase fluorination of different types of rubbers (i.e. ethylene-propylene, butadiene-nitril, isoprene, butyl, silicon, and natural rubbers). We have applied a mixture of molecular fluorine and inert gas to the samples, and have found out the optimal conditions for the fluorination. This technique has proved to be effective, and can improve essentially many features of the original materials, such as insufficient wear resistance, migration of ingredients, chemical resistance, etc. (by a factor of 2-5), without afflicting the mechanical properties. The most interesting result is a major improvement of the physical and chemical characteristics of fluorine rubber SRF-26 after the fluorination of the sample's surface. In vinylidene-fluoride atoms of fluorine replace units of this rubber, atoms of hydrogen, and this increases the chemical resistance of the substance, and improves its antiadhesion properties. For example, the effort required to pull apart the Filling of the vacuum bolt after pumping out for 24 hours at 250 C is 10 kg/cm for the original sample, but decreases to 0.1 kg/cm for the fluorinated one. In dynamic experiments, me have seen that the chemical resistance to also goes up dramatically (from 30% of the total mass for the original sample to 3 - 5% for the fluorinated one). The residual deformation of 80% at 150 C is accumulated for 48 hours for the original sample, but it takes as long as 55 days for the fluorinated one. Thus, useful properties of original rubbers can be largely improved by the suggested technique of surface fluorination. This makes it possible to produce high-quality materials which can turn out to be even better than usual fluorine rubbers for a number of applications (in particular, as far as the ratio "cost to properties" is concerned)

*The work has been supported by the Russian Fund for Fundamental Research, code No. 95-03-08389a.

STRUCTURE AND COMPOSITION OF A SURFACE LAYER IN POLYMER MODIFIED BY HETEROPHASE FLUORINATION

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As a result of heterophase fluorination of polymers, a special surface layer is formed, whose chemical contents usually varies in the direction perpendicular to the surface, The closer to the surface the more fluorinated it is. Physical and chemical properties of fluorinated polymers are affected by various characteristics of the surface layer, such as its effective thickness, chemical structure and the gradient of the chemical composition across the layer, the stability, and the compatibility of a modified surface layer (via an interface layer) with the bulk. In this work, heterophase fluorination of polyolefines and fluoropolymers has been studied experimentally, The chemical composition of the obtained materials has been determined by methods of electron spectroscopy, infra-red spectroscopy, elementary chemical analysis, and gravitometry, and then the whole set of experimental data has been used to evaluate the thickness of the modified layer, A surface and an interface layer of fluorinated polyolefines, typically, have rather varied molecular design", containing methylene vinyl-fluoride, and vinylidene fluoride fragments. We have suggested an approach to describing such systems, based on an analogy with statistical and block-copolymers and layered polymers. Chemical structure of a surface layer has been shown to be similar to statistical fluorine-copolymers. Meanwhile, an interface layer is the same as in a block copolymer where fluorinated fragments are adjacent to the surface layer, whereas parts of the original polymer appear deeper in the bulk.

The compatibility between the bulk of the fluorinated polymer and its surface and interface layers has been estimated using the parameters of solubility. This compatibility is crucial to provide stable properties of such polymers when in practical use. It is known that most pairs of polymers obey the inverse proportionality between the thickness of the interface layer (or the interface layer, for the systems in question) and the difference between the solubility parameters of the two polymers. Neither molecular composition nor structure of the fluorinated layer itself is uniform. This is because, initially, most polyolefines have partly amorphous and partly crystalline structure. Therefore, under certain conditions, the most fluorinated polymer segments may be accumulated on the surface, leading to the decrease in the surface energy.

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FORMATION AND PHOTOREACTIONS OF FREE RADICALS IN FLUORINATION OF POLYSTYRENE

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It was established that the appearance of perfluorocarbon radicals as a result of the low-temperature (77K) photolysis of fluorinated polystyrene (PS) enhances the photosensitivity of polymer.

The quantum yield of radical formation increases by two to three orders of magnitude by comparison with that for the radicals of unfluorinated PS. It is known that peroxy radicals in the common PS perform as photosensitive centers and undergo various photo-chemical reactions, in particular, photodisso-ciation with the cleavage of C-C and C-H bonds. Fluorination of PS extinguishes the phenyl chromophores due to saturation of double bonds in aromatic rings by the fluorine. That is why the peroxy radicals of fluorinated PS didn't prove to be photosensitive.

High reactivity of radical species produced during the photolysis of fluorinated. PS is revealed in reactions of recombination and oxidation at 77K. UV or γ -radiation may be used to activate the fluorine-containing radicals during the direct fluorination of polymers.

THE BIORESISTANCE OF FLUORINATED POLYMERS

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The problem of increasing of bioreistance of polymer materials and products (and the inverse problem of accelerated biodestruction is crucial for units and parts of equipment, which is maintained in damp and warm climate, and also which is stored for a long time. The ways of solving it, in general, do not differ much from traditional methods of increasing physical and chemical resistance of polymer materials, but at the same time have some special features. High bioreistance polymers containing fluorine makes us think that heterophase fluorination of polymers' surface is one of the prospective direction towards increasing their stability to microorganisms.

Полимер Polymer	Вид обработки Kind of processing	Биообращение, балл Biocovering, point	Биомасса колонии, мкг/см ² Bioweight of colony, mkg/sq. Cm
ПММА / PMMA	исходный/initial	3	1,9
ПММА / PMMA	фторированный/fluorinated	1	0,2
ПЭНП / PELD	исходный/initial	2	1,1
ПЭНП / PELD	фторированный/fluorinated	0	0,0
БК / BR	исходный/initial	2	1,3
БК / BR	фторированный/fluorinated	0	0,1

Various kinds (more than 10) of microscopic fungi, that were pieces of equipment under operating conditions, and also of fungi borrowed from the collections of cultures of Russian Academy of Sciences were used for estimation of bioreistance of initial samples and the samples, processed by mixing molecular fluorine and helium, polymethylmeth-acrylate (PMMA), polyethene of low density (PELD) and butylrubber (BR). Sample films and sheets, inoculated by spores were incubated in the vapor tritium water at 30°C and relative humidity of air 90%. The estimation of bioreistance after 28 days of incubation was carried out visually using scale and gravimetry according to quantity of mass, formed on a sample when it is covered with fungi (see the table, the results are averaged over 10 different types of microorganisms**).

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THE FLUORINATED SULFOVINYL ETHERS FOR HIGH PERFORMANCE OF ION EXCHANGE MEMBRANES

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The most wide-spread method of obtaining vinyl ethers is thermodestruction fluoroanhydrides perfluoroalkyl (alkoxyalkyl)carbon acids in unprotonic solvent with Na₂CO₃ at 60-140°C. However, generally accepted method of synthesis to obtain sulfovinyl ethers CF₂=CFOC₂F₄Q, where Q=SO₂F, COF proved to be unacceptable because of cyclization with appearing heterocyclic sulfons and ketons.

The purpose of the present paper is to study the possibility of purification of hafnium tetrafluoride from the transition metal impurities by the sublimation method. The "colouring impurities" are the limiting ones for hafnium tetrafluoride used for the production of fluoride glasses and optical fibres on its basis. The fluorides of iron, nickel, chromium, manganese, copper and cobalt refer to this type.

A technique has been developed to, determine ,the transition, metal impurities in the samples of hafnium tetrafluoride by the method of atomic-emission spectral analysis with preconcentration of impurities on the carbon collector. The content of impurities of iron, copper and nickel in the starting hafnium tetrafluoride is at the level of $1 \cdot 10^{-1}$ - $1 \cdot 10^{-2}$ mass %, and of chromium, manganese and cobalt, at the level of $5 \cdot 10^{-3}$ - $5 \cdot 10^{-4}$ mass %.

Hafnium tetrafluoride was purified by the method of sublimation with the subsequent heterogeneous and homogeneous desublimation of the purified vapours. ZrF₄ was evaporated at the temperature of 900-950°C in the inert gas flow. It is shown that the method of purification, of hafnium tetrafluoride with homogeneous desublimation of the purified vapours is the most promising one. The content of the transition metal impurities in ZrF₄ after a one-fold sublimation decreased by two-three orders of magnitude.

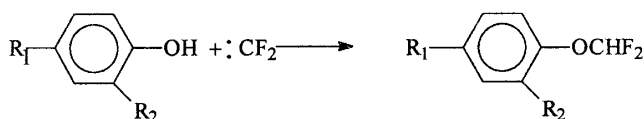
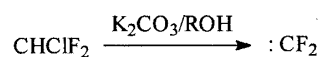
CHLORODIFLUOROMETHANE AS A CONVENIENT REAGENT FOR DIFLUOROMETHYLATION OF VEGETATIVE PHENOLS

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The existing methods for difluoromethylation of phenols by chlorodifluoromethane provide intermediate formation of difluorocarbene under action of the strong basis such as metal sodium, concentrated solutions of alkalis [1].

We have improved process of difluorocarbene generation in this type of reaction, having applied heterophase reactionary system of K₂CO₃/alcohol for dehydrochlorination. The difluoromethylation occurs at passing gaseous freon-22 through this system at the presence of corresponding phenol at the temperature of 70°C during 1- 3 hours. It is suggested that the interaction proceeds as follows:



R=CH₃CH₂CH₃;

R₁=H, CH₂CH=CH₂, CH=CHCH₃, CH₂OH, CH(OH)CH₂CH₃, C(O)H, C(O)CH₃;

R₂=H, OH, OCH₃

The difluorocarbene generation under action of alkoxide-ion formed in conditions of interphase transfer of proton occurs in rather soft conditions. It has allowed to enter into the difluoromethylation reaction such labile compounds as natural phenols. The reactions proceed solely on phenolic hydroxyl groups of substrate (according to the data NMR ¹⁹F) and result in formation of difluoromethyl ethers with good yields.

Freon-22 has been used also for difluoromethylation of oligomer phenols such as industrial lignin's representing waste of chemical processing of wood from various productions. The fluorocontaining lignins have been tested as modifying agents of rubber. It has been found that the insignificant additive of such lignin component (1 % on weight) increases the cohesion strength of crude rubber mixes.

The use of chlorodifluoromethane for synthesis of fluorocontaining phenolic compounds and the modification of technical lignins can be of interest as a method of production of new biologically active substances and perspective materials without negative effect on environment.

1] L.M. Yagupolsky. Aromatic and heterocyclic compounds with fluorocontaining substituents (in Russ.).- Kiev: Naukova Durnka, 1988.- 320 p.p.

ETHYLENE AND PERFLUOROETHERS COPOLYMERS. SPECIAL FEATURES OF DISSOLUTION AND FILM FORMATION

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Fluoroelastomer - based film forming materials resistant to polar and nucleophilic agents are of great interest in practice. The synthesis of ethylene and perfluoroethers copolymers (EPFE) is shown to be a promising route to meet these challenges. Copolymers of the (CH₂-CH₂)_x-CF(R)-CF₂ have been prepared, where R is:

O-CF₂-CF₂-CF₃ EPFE-1

CF₂-O-CF₂-CF₂-CF₃ EPFE-2

O-CF₂-CF(CF₃)-O-CF₂-CF₂SO₂F EPFE-3

O-CF₂-CF₂-(OCF₂)₄OCF₃ EPFE-4

Chemical structure of the copolymer unit is shown to enable copolymer dissolution in only low-molecular fluorinated media/ Casted films exhibit however time dependence of the geometry which makes then impracticable. Dynamic light scattering examination has been performed on molecular organization of copolymer macrochains in the solution. The fact being taken into account, that the solution structure closely correlates to the behavior of casted films.

Copolymer macromolecules have been shown to dissolve into the thermodynamically best solvent (hexafluorobenzene) mainly in the form of associates. The presence of these in solution has been detected at even lowest

concentrations. Thermodynamic incompatibility of hydrocarbon and perfluorinated units of the copolymer chain is suggested to be an incentive. Possible mechanisms of associate formation have been studied and means of disintegration thereof proposed. Composite solutions that yield EPFE films with good physico-mechanical properties proposed have been developed on the basis of the mechanisms assumed.

ETHYLENE AND PERFLUOROETHERS COPOLYMERS STRUCTURE AND SORPTION BEHAVIOUR

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Film-forming fluoropolymers with high resistance to corrosive media up to high temperatures are promising candidates for tread coatings. It should be noted that ultrathin films of fluoropolymers have also found use in permselective membranes. Regular examination of the correlation between polymer unit structure and sorption behavior enables specific applications to be forecast. Data on the interaction of film-forming materials with low-molecular substances (as environmental factors) are sure to contribute to both practice and science.

The data for copolymers obtained of ethylene and perfluoro-alkyl-vinyl ethers like $(\text{CH}_2\text{-CH}_2)_x\text{-CF(R)-CF}_2$ are available from the present work. Commercial perfluorinated and polyfluorinated copolymers (based on vinylidene fluoride and tetrafluoro ethylene) were also studied to be compared with. The combination of thermodynamically incompatible hydrocarbon and perfluorinated sequences in the linear chain results in a molecular organization dissimilar to that of perfluorinated analogs. It is naturally followed by the change in physico-mechanical properties of polymer films - solubility, resistance to nucleophilic media, diffusive permeability. So, the copolymers obtained are insoluble in polar low-molecular liquids and withstand a long-term exposure to nucleophilic media.

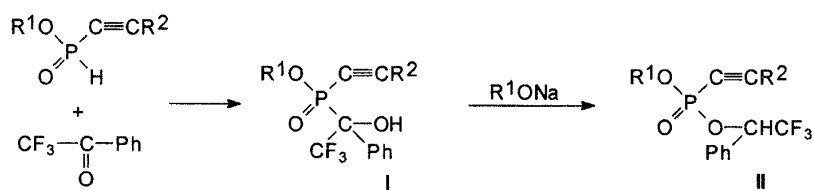
The effects of the length of methylene sequences, side chain length and flexibility and also available functionalities on sorption behaviour and copolymer permeability are also studied as compared to a series of model gas and liquid mixtures. E.g., by the separation of gas mix He/N₂ the copolymer of ethylene and perfluoro-propene-vinyl ether offered selectivity $\alpha=43.4$ capacity being 25.3 barr.

REACTIONS OF 2, 2, 2 -TRIFLUOROACETOPHENONE WITH MONOESTERS OF ALKYNYLPHOSPHONOUS ACIDS

Yu.G. Trishin, M. V. Vorobiov, V.I.Namestnikov

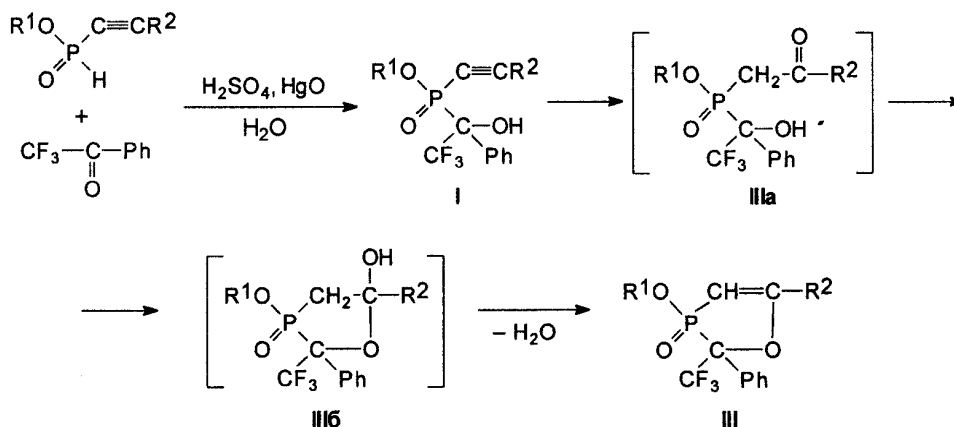
St.Petersburg State Technological University of Plant Polymers

Reactions of α -fluorocarbonyl compounds with monoesters of α, β -acetylenic phosphonous acids for the first time were investigated on an example of 2,2,2-trifluoroacetophenone. It was found that structure of final products in these reactions is defined by nature of a catalyst. In absence of the catalyst O-alkyl(alkynyl)phosphonites are added to 2,2,2-trifluoroacetophenone with formation of acetylene 1-hydroxy-1-phenyl-2,2,2-trifluoroethylphosphates (I). In presence of the catalysts of basic nature (sodium alcoholate) initially forming phosphinates are undergone rearrangement which leads to obtaining of mixed esters of alkynylphosphonic acids (II).



$\text{R}^1 = \text{Me, Et}; \text{R}^2 = \text{Me, } t\text{-Bu, Ph}$

In Kucherov's reaction conditions (catalyst $\text{-H}_2\text{SO}_4, \text{HgO}$) as result of interaction of O-alkyl(alkynyl)phosphonites with 2,2,2-trifluoroacetophenone the unique phosphorus-oxygen containing heterocyclic compounds — Δ^4 -1,3-oxaphospholenes (III) with trifluoromethyl substituent in position 2 of the ring were synthesized.



The reaction proceeds via intermediate formation of 1-hydroxy-1-phenyl-2,2,2-trifluoroethylphosphinates (I), ketophosphinates (IIIa) and cyclic semiacetals (III b).

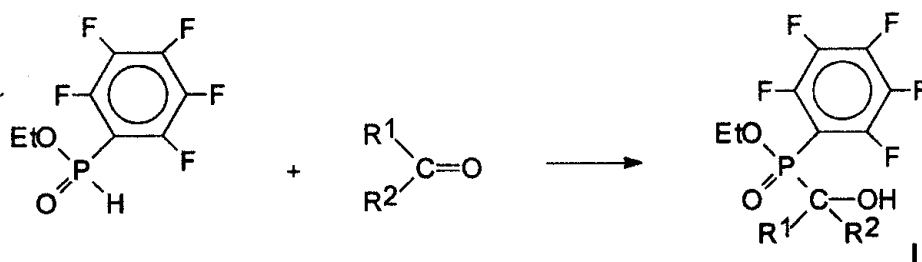
INTERACTION OF O-ETHYL(PENTAFLUOROPHENYL)PHOSPHONITE WITH CARBONYL COMPOUNDS AND AZOMETHYNES

V.I.Namestnikov, Yu.G.Trishin, M.V.Vorobiov,

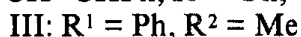
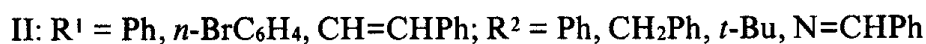
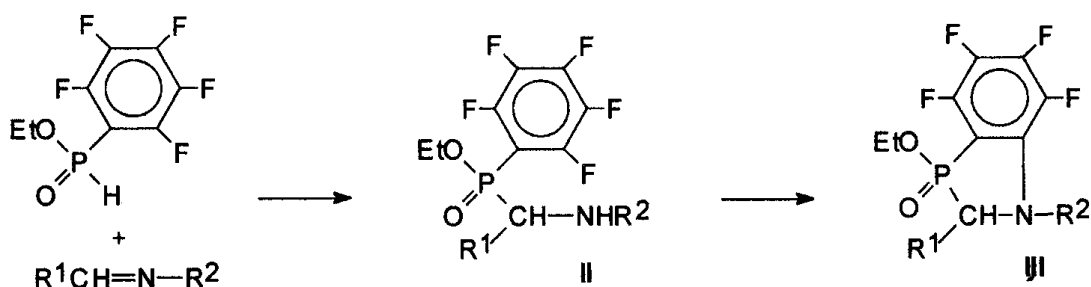
St.Petersburg State Technological University of Plant Polymers

Chemistry of O-ethyl(pentafluorophenyl)phosphonite which is able to be a synthone for obtaining of wide range of phosphorus-fluoro containing compounds is practically not studied.

We established that this fluorinated hydrophosphoryl compound is easily added to aromatic aldehydes, chloral, alkylaromatic and cycloaliphatic ketones with formation of appropriate O-ethyl(pentafluorophenyl) (1-hydroxyalkylphosphinates (I) — crystalline substances which were given off with yields 70 - 90%.



The interaction of O-ethyl(pentafluorophenyl)phosphonite with azomethynes proceeds more intensively than with carbonyl compounds and leads, as a rule, to O-ethyl(pentafluorophenyl)(1-N-R²-aminobenzyl)phosphinates (II) (yield 70-95%).



Reaction with N-methylbenzalamine, containing the most nucleophilic and the least space-blocked nitrogen atom in studied range of azomethynes, does not stop at phosphinate of type (II) formation stage, but finishes with intermolecular nucleophilic substitution of fluorine atom in o-position to phosphorus atom. As a result, in this circumstance the substituted 3-oxotetrafluorobenzod[1,3]-azaphospholine (III) is obtained, which is the first representative of condensed heterocyclic system of such a structure.

TFE-POLYMERIZATION INITIATED BY FLUORINATED CARBON

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Fluorinated carbons, prepared by fluorination of various forms of carbon (carbon blacks, cokes and graphite), were found to be able to initiate fluorinated vinyl monomers' polymerization and telomerization processes and TFE-polymerization in particular [1]. No assumptions have been made about the mechanism of polymerization, nature of initiating centers.

Fluorinated graphite, CF_x , (State Institute of Applied Chemistry, St. Petersburg) where x is close to 1 was used. Polymerization was carried from gas phase without any solvent at TFE pressure less than 760 Torr, and at temperatures 0-95°C. Experimental results show that:

1. Polymerization rate slowly increases with time on initial nonstationary stage and changes negligibly (quasi steady state stage) during long period;
 2. Polymerization rate is proportional to TFE pressure up to atmospheric; Polymerization rate value is extremely high at near-room temperatures. At temperatures close or higher than 90°C a dramatic drop of the rate is observed in two cases -
 - a) if one starts polymerization at temperatures close to 90°C or higher, or
 - b) if to increase temperature to 90°C during quasi steady state stage;
 4. Polymerization behavior depends on pre-history of the CF sample. A simple treatments allow to change polymerization kinetics;
 5. Initiating and propagating active centers are sensitive to hydrocarbons and oxygen exposure. Treatment of CF_x , with hydrocarbons from gas phase on any stage leads to sufficient decrease of polymerization rate, treatment with oxygen leads to acceleration of polymerization.
- The results of experimental study of TFE-polymerization mechanism and kinetics at different conditions will be discussed.

1. Krespan, C.G.; Petrov, V.A.; U.S. Patent 5,459,212(1995) to DuPont

THE KINETICS OF THE THERMAL DECOMPOSITION OF DIFLUOROCHLOROMETHANE ON A FRESH QUARTZ SURFACE

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The process of thermal decomposition of difluorochloromethane (DFCM) in temperature range from 923 to 1073 K on a fresh quartz surface in the presence and absence of additives of molecular chlorine and oxygen has been studied.

It was established that thermal destruction of DFCM in all cases investigated occurs at the first order respectively to DFCM. The activation energy of thermal destruction of DFCM in case of the process on a fresh quartz surface turned out to be by 5-66 kJ lower than the energy determined in previous studies which were carried out in reactors pretreated by DFCM decomposition products during a long time.

Introduction of chlorine additive into DFCM subjected to thermal decomposition on a fresh quartz wall leads to decreasing the activation energy by 29 kJ and to increasing the decomposition rate in 2 times as compared to the process of decomposition of pure DFCM under similar conditions.

Based on the results of thermal decomposition study of DFCM in the presence of chlorine additive, it was established that the order of reaction on chlorine is 0.75 and the rate of decomposition process increases approximately in 1.8 times with increasing the ratio surface / reactor volume in 2.5 times.

In case of thermal decomposition of pure DFCM the decomposition rate of DFCM also grows, but

to a lower degree (in 1.5 times). It is noted that introduction of oxygen into DFCM influences the rate of decomposition process as well as introduction of chlorine. Moreover, in both cases there occurs the elevated content in decomposition products of difluorodichlormethane and 1,2-dichlorotetrafluoroethane.

It was established that under conditions studied there occurs a high yield of tetrafluoroethylene. Based on the results, it was concluded that under conditions studied radical chain mechanism of thermal destruction of DFCM takes place. The mechanism of the process has been proposed.

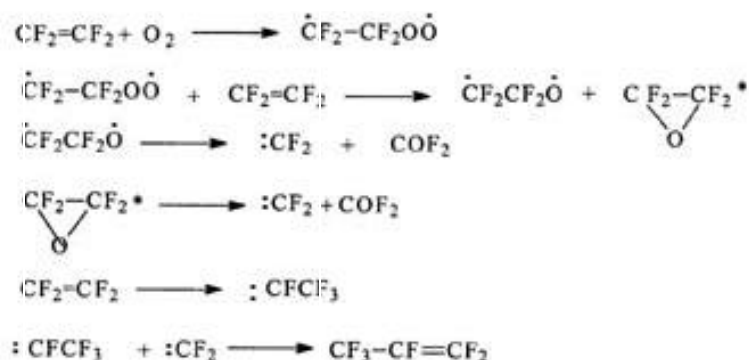
THE PYROLYSIS OF TETRAFLUOROETHYLENE AT PRESENCE OF OXYGEN

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The process of pyrolysis of tetrafluoroethylene at 800°C in the presence of gaseous oxygen to give hexafluoropropylene has been studied.

The influence of oxygen concentration upon the process selectivity according to hexafluoropropylene and upon tetrafluoroethylene conversion is determined

On the grounds of experimental data it is ascertained that the use of oxygen addition in the amount of 1-5 vol. % with respect to tetrafluoroethylene allows to increase TFE conversion by 30 per cent in comparison with TFE pyrolysis without oxygen. The process selectivity by hexafluoropropylene increases by 20-35 per cent. The results received conform to the mechanism expected:



The use of oxygen in the amount less than 1 vol. Per cent is insufficient for the formation of the amount of peroxide biradicals $\dot{\text{C}}\text{F}_2-\text{CF}_2\dot{\text{O}}\text{O}$ required, with the use of more quantity of oxygen (more than 5 vol. per cent) under conditions of pyrolysis the break-down of the starting tetrafluoroethylene occurs that is being confirmed by the presence of such components as carbon dioxide, hexafluoroethane, carbonyl fluoride in the reaction products.

FLUORINATION OF FULLERENE POWDERS AND FULLERENE FILMS

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The notion of fullerene structure as a tree dimensional analog of aromatic compositions make it possible to treat the chemistry of fullerenes as a new promising lead in organic chemistry. Fluorinating of fullerenes has its great scientific and applied interest due to the unique properties of carbon clusters, and possibility of their industrial applications for creating new lubricants, coatings and films, polymers, and other materials with new properties.

In the presented paper we report the work which has been done in order to compare different

methods of fluorinating and chose the most effective one.

We investigate the process of obtaining fullerene fluorides using as the fluorinating agents the following compositions: pure molecular fluorine, mixture of pure molecular fluorine with HF, and cobalt fluoride. Our experiments show that the most effective and technological is fluorinating by means of molecular fluorine in gas-phase-diffusion system. The created method enable to fluorinate powders of fullerite (fullerene in solid state) as well as films deposited on substrate using different methods.

ESCA and Mass-spectroscopy were used to investigate chemical and molecular compositions of obtained fullerene fluorides. Those methods show the dependence of molecular composition of obtained fullerene fluorides on temperature, pressure and time of fluorinating. The obtained fullerene fluorides easily hydrolyzed with formation of $C_{60}F_n(OH)_m$ composition, that is proved by ESCA.

For the first time the film of fullerene fluorides was obtained by means of gas-phase fluorinating of fullerene film deposited on sapphire substrate using thermal diffusion in vacuum.

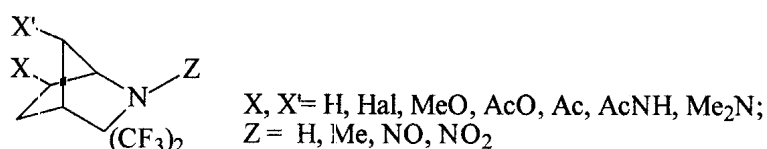
The work has been supported by Russian Scientific Technical Program "Fullerenes and Atomic Clusters", project N 95103.

THE SYNTHESIS AND ANALGETIC ACTIVITY OF SOME FLUORINE-CONTAINING 2-AZABICYCLO[2.2.1]HEPTANES

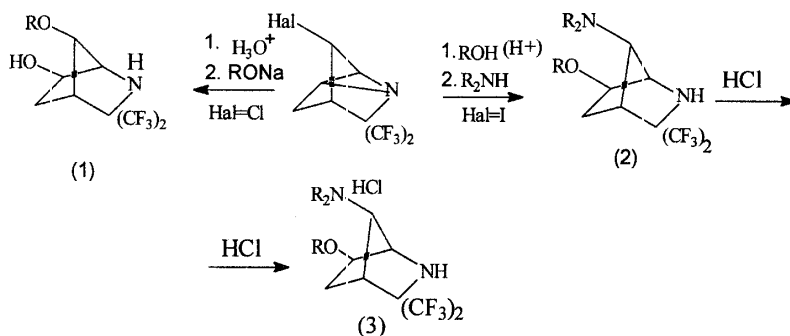
V.M. Nagaev, V.S. Dobryanskii, A.F. Yelejev, T.A. Klimova, V.K. Kurochkin, G.A. Sokol'skii, and S.S. Khokhlov

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For further searching for non-narcotic analgesics of a new structural type, we produced and biotested tens of different N- and C- substituted 2-azabicyclo[2.2.1]-heptanes with general formula depicted below /1/:



The biological activity of these substances was assessed in experiments with laboratory male mice using the "hot plate" techniques /2,3/. Only several synthetic substances were revealed to display a pronounced antinociceptive activity without any signs of the narcotic effect, such as substances 1-3 produced from earlier described azanortricyclanes /1/ by towing pathways (R=Me):



Pharmacological activity of substances 1-3 may be illustrated by comparison of lethal (LD50, i.m., mg/kg) and effective (ED50, i.m., mg/kg) doses:

Substance	LD50	ED50	LD50/ED50
1	>1000	96,8	>10

2	>1000	45,0	>22
3	>1000	88,4	>11

Basing on these results, we are thus able to conclude that this structural type substances are promising for the design of new effective drugs.

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3. V.V. Gatsura, Metody pervichnogo farmakologicheskogo issledovaniya biologicheskii aktivnykh veshchestv (Methods of Primary Pharmacological Study of Bioactive Substances), 1974, Moscow: Meditsina, pp.39-41.

DEHYDROFLUORINATION OF 1-VINYL- AND 1-PROPENYL-2-PERFLUOROALKYL-2,3,3-TRIFLUOROCYCLO BUTANES

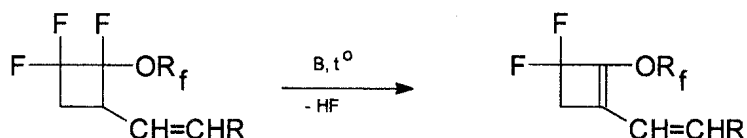
A.A. Glazkov, E.N. Ushakova, A.V. Ignatenko, S.P. Krakovsky

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The products of cycloaddition of perfluoroalkylvinyl ethers and some dienes, containing equal quantity of cis- and trans- isomers in respect to the cycle have been recently obtained [1].



In this communication some properties of these cycloadducts were studied. Cis- and trans- isomers were separated by means of HELC. Dehydrofluorination of these cycloadducts under the action of different bases was studied.



$R = CF_3CF_2CF_2; CF_3(OCF_2CF_2)_n, n=3,4$

$R = H, CH_3$

$B = NH_3, Et_2NH,$,

Elimination of HF was found to proceed at 1,2-positions of the cycle. Cis-isomer was shown to be more active than the trans- one.

1. A.A. Olazkov, A.V. Ignatenko, S.P. Krukovsky, V.A. Ponomarenko. Bull. Acad. Sci. USSR, Div. Chem. Sci., 27, 10, p.2137-2141 (1988)

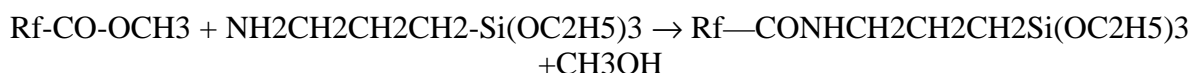
FLUOROORGANOSILICONE COMPOUNDS FOR THE PROTECTION OF HISTORICAL BUILDINGS FROM HARMFUL ENVIRONMENTAL IMPACTS

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At present a lot of Moscow architectural monuments and arts sites made mainly of white stone are in urgent need of being protected from harmful environmental impacts. This objective can be attained by their treatment with original compositions that would generate a protective layer on their surface to prevent moisture, acidic impurities and industrial contaminants penetrating limestone pores.

For this purpose there was synthesized a number of fluoroorganosilicone compounds via the following mechanism



Rf= CF₃CF₂CF₂O(CF₃)CF₂PO(CF₃)-, CF₃O(CF₂CF₂O)CF₂- and others

Their structure was confirmed by NMR and IR spectroscopies. A drastic decrease in their water absorbability is observed upon the treatment of limestone samples with 5% solutions of the synthesized fluoroorganosilicone products in an organic solvent. A hydrophobic effects (Eh) of generated coating was 80-90% in 8 hours with a full plunging of the samples into water/

$$Eh = \frac{W_0 - W_1}{W_0} \times 100\%$$

W₀ - /sample water absorbability before the treatment

W₁ - /sample absorbability after hydrophobization

Contact angles of the pre-treated limestone surface wetting with water, methylene iodide, glycerine and decline were identified as 131-138°, 100-120°, 120- 140°, and 110-120°, respectively. The contact angle values of the above liquids with the pre-treated limestone surface gave way to calculating free surface energies ys ranging from 2.8 to 4.0 dyne/cm and testifying to a weak interaction of the hydrophobized surface with those liquids, This is indicative of a high hydro- and oleophobic abilities of the protective layer produced on the basis of the synthesized compounds. Hydro- and oleophobicization degrees result from the Rf structure, method of coating, density of the generated protective layer, and nature of the material being treated.

A financial support to the effort was given by the JSC Moscow Committee on Science and Technologies Ltd. founded by the Moscow Government.

DIMERIZATION OF 1,3-HEXAFLUOROBUTADIENE AT HIGH PRESSURE

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1,3-Hexafluorobutadiene /HFB/ is known to yield a wide range of products, i.e. dimers of various structure, trimers and polymers [1], if maintained for a long while at 100 - 300°C and under autogenous pressure.

The present papers sets a goal of studying the impact of high pressure on HFB thermal transformations.

Experiments were performed on a cylinder-piston apparatus. A Teflon ampoule (1.5 ml) that served as a reactor was filled with liquid HFB (99.5%) at -15°C in argon atmosphere. The experiment time varied in the interval of 1 to 24 h. The reaction mixture was analyzed by gas

liquid chromatography, and the product identification was carried out on a VG 7070E mass spectrometer.

High pressure applied led to the generation of HFB dimers in the yield of above 95% for 1 - 2 hours. This is two orders of magnitude faster than under autogenous pressure.

The processing of the experimental results has shown:

1. The HFB transformation proceeds with a prevailing dimer generation via a 2+2 mechanism.

Yet, the generation of trimers and polymers in a total amount exceeding 50% is observed once T is over 130°C and P is above 1,000 MPa.

2. Dimerization has the second order along the reaction course.

3. A ratio of cis- and trans-isomers of HFB dimers almost does not alter with T and P. It remains unchanged in the range of 1-1.07 at 80- 130°C and 600 -1,500 MPR.

The effect of pressure $\Delta V_o \pm = -35 \text{ cm}^3 / \text{mol}$ was calculated by the equation

$$\ln K_p / K_o = - \frac{\Delta V_o^\pm P}{RT(1 + b * P)}$$

where $b = 9.2 * 10^{-5} \text{ bar}^{-1} / 2$

Activation energy $E_a = 57 \text{ kJ/mol}$ (13.6 kcal/mol) was calculated from the data obtained at $P = 600 \text{ MPa}$ by the Arrhenius equation.

HFB dimers undergo polymerization yielding a solid transparent polymer in the presence of a radical initiator at 1,000- 1,500 MPa and 160 -200 ° C. In this process cis-isomer displays a higher reactivity than trans-isomer.

REACTION OF POLYPERFLUOROALKYLENE OXIDES, CONTAINING PEROXY GROUPS, WITH PERFLUOROALKYL- AND PERFLUOROOXAALKYL VINYL ETHERS AT HIGH PRESSURE

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The reaction of polyperfluoroalkylene oxides containing peroxy groups (I) with perfluoroalkyl- and perfluorooxaalkylvinyl ethers (IIa-b) were studied at high pressure.

$\text{I CF}_3\text{O}(\text{CF}_2\text{O})_x(\text{CF}_2\text{CF}_2\text{O})_y - \text{A} - (\text{CF}_2\text{O})_x(\text{CF}_2\text{CFO})_y - \text{A} - (\text{CF}_2\text{O})_x(\text{CF}_2\text{CF}_2\text{O})_y\text{CF}_3$,
A - are peroxide bonds distributed randomly along the chain:

$\text{CF}_2\text{OO CF}_2\text{CF}_2\text{O}; \text{CF}_2\text{OO CF}_2\text{O}; \text{CF}_2\text{CF}_2\text{OO CF}_2\text{CF}_2\text{O}$,

M_n (I): MW= 1400-3000

Ratio $(\text{CF}_2\text{O}) : (\text{CF}_2\text{CF}_2\text{O})$ in (I) is from 13/1 to 23/1 The active oxygen content is from 0,45 to 1,53 wt %

II a) $\text{CF}_2 = \text{CF}[\text{O CF}_2\text{CF}(\text{CF}_3)]_m\text{O}(\text{CF}_2)_6\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF} = \text{CF}_2$, $m + n = 2$

b) $\text{RfOCF} = \text{CF}_2$, $\text{Rf} = -\text{CF}_2\text{CF}_2\text{CF}_3$; $-(\text{CF}_2\text{CF}_2\text{O})_3$; $-(\text{CF}_2\text{CF}_2\text{O})_4\text{CF}_3$

Cleavage of the initial perfluoroalkylene oxides (I) was carried out by heating (170-210°C) under pressure (100-1000 MPa).

The amount of perfluorovinyl ethers was from 10 to 30% of the polyperfluoroalkylene oxide (I) weights. This resulted in branched

perfluoropolyethers with various molecular weights or cross-linked perfluoropolyethers.

HEXAFLUOROPROPYLENE AND CHLOROTRIFLUOROETHYLENE COPOLYMERIZATION AT HIGH PRESSURE. COPOLYMER PROPERTIES.

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Literature almost lacks the data on kinetic features of hexafluoropropylene (HFP) and chlorotrifluoroethylene (CTFE) copolymerization and their copolymer properties. The objective of this effort was to produce copolymers with a HFP content close to 50%, to study their properties, and to determine HFP and CTFE copolymerization constants and their dependence on pressure and temperature.

Experiments were conducted on a cylinder-piston high pressure apparatus at pressure up to 1,000 MPa and temperature below 150°C. The reaction was initiated by oxygen (0.02 - 0.1 weight %). A Teflon ampoule (1.5 ml) that served as a reactor was filled with a liquid reaction mixture at -75°C and in argon atmosphere. The experiment lasted for 1 to 24 hours.

Solid white copolymers produced had different thermal stability and rupture strength. Copolymers solubility changed in a broad range resulting from their composition. CTFE-enriched copolymers dissolved in fluorinated solvents at heating and copolymers with an approximate 50% HFP content dissolved even in carbon tetrachloride.

The experiments have shown that the application of high pressure gives a ten-fold and even hundredfold increase to the polymerization rate versus experiments under atmospheric pressure. This allows to synthesize HFP-enriched polymers during a few hours. The Table lists "copolymer composition-initial mixture composition" curves obtained and calculated copolymerization constants (r_1 and r_2).

Temperature	Pressure	r_1	r_2
120° C	600 MPa	23±2	0.003±0.002
120° C	1,000 MPa	13±2	0.004±0.002
150° C	1,000 MPa	6±1	0.003±0.002

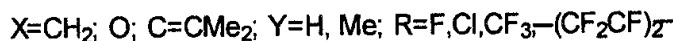
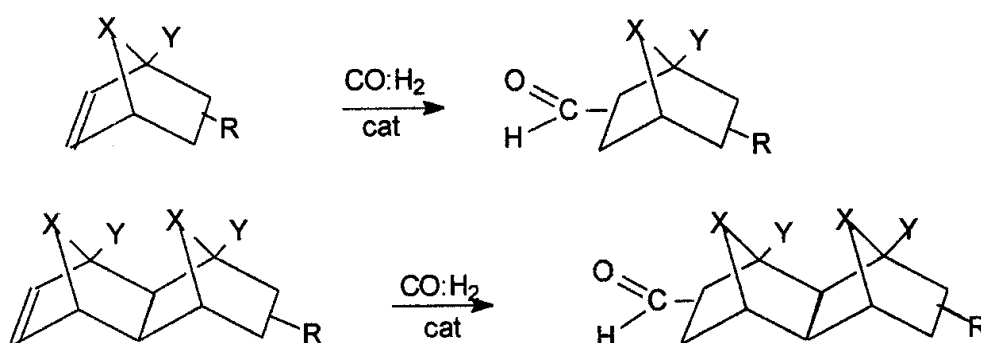
As seen from the tabulated data the copolymerization constant r_1 drops with the pressure and temperature applied in the experiment. Such change in r_1 means that the constant k_{12} characterizing the interaction of the radical $R_f-C_2F_3Cl$ with the HFP double bond increases with pressure and temperature faster than the constant k_{11} that is responsible for the CTFE polymerization rate. In other words, pressure and temperature facilitate HFP entering the copolymer molecule.

Conclusion: The high-pressure method is promising in the synthesis of copolymers, particularly when the reactivity of one of the monomers is much lower than that of the other. In this case not only the identification of the copolymerization reaction is achievable but a growth of the passive monomer shares in a copolymer as well.

RHODIUM CATALYZED HYDROFORMYLATION OF FLUORO NORBORNENES AND ANALOGOUS COMPOUNDS

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Leninsky Prospect, 29, Moscow, Russia, Fax: (095) 230-22-24*

The research is dedicated to the study of the hydroformylation of fluoro norbornenes and their derivatives:



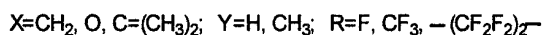
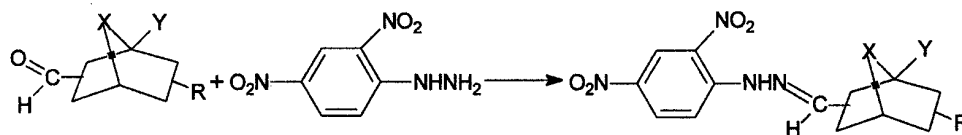
The reaction in question makes possible the formation of fluoro bicycloaldehydes. The hydroformylation of norbornenes and their derivatives including those having different combinations of X, Y, and Z radicals, in presence of rhodium acetylacetonato dicarbonyl and PPh₃, has been performed. The optimization for the reaction parameters elucidated the yield of desire products between 81 % and 97 %.

A special feature of the reaction is that the exo- direction of formyl group insertion takes place independently of the nature of its relative position at the norbornene ring.

SYNTHESIS OF FLUORO BICYCLOHYDRAZONES

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It is well known that many of the hydrazones act as tubercular - static preparations exhibiting a combined activity. Our interest is of investigation of the properties of several bicyclohydrazones. Different derivatives of bicyclohydrazones have been synthesized through the fluoro bicyclo aldehydes and 2,4 -dinitrophenylhydrazine.



The bactericidal activity and the human peripheral blood lymphocytes behaviour have been revealed for a series of synthesized fluoro bicyclohydrazones. All of them are distinguished for their weak static activity and produce the immune - depressing attack. The optimization for the reaction conditions has been elucidated, the spectral and physico - chemical characteristics of the fluoro bicyclohydrazones are described.

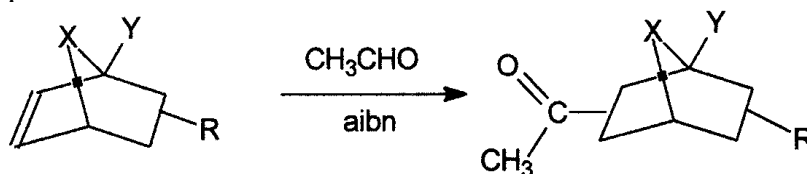
SYNTHESIS OF FLUORONORBORNANEMETHYLKETONES

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The results of study of acetic aldehyde radical insertion into double bond of the fluoronorbornene are the objective of this presentation.

It is known that the norbornene and acetic aldehyde interaction in the presence of azo isobutyronitrile when heating in autoclave, give rise to the formation of exo-2-norbornanemethylketone. Previously it was shown that catalytic hydroformylation of fluoronorbornenes yields eminently the exo - formyl derivatives regardless of the nature of fluoro radical.

Under severe conditions, fluoro norbornenes are susceptible to the acetaldehyde radical insertion according to the equation:



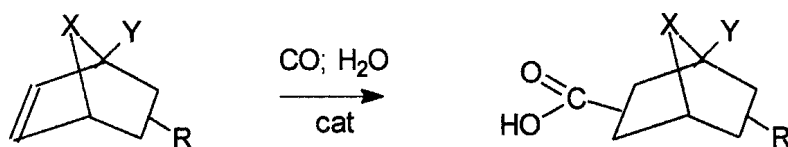
In distinction from the formyl group catalytic insertion, a peculiarity of the acetyl group radical insertion appears to give endo- (10%) and exo- (90%) derivatives as revealed from NMR ¹H and ¹⁹F spectra.

The reaction mechanism, spectral and physico -chemical characteristics of the synthesized compound are under discussion.

CARBONYLATION OF FLUORO NORBORNENES

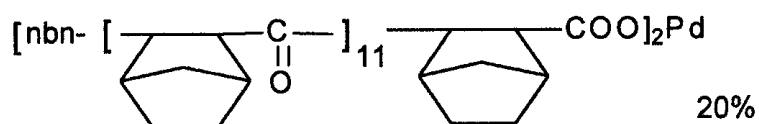
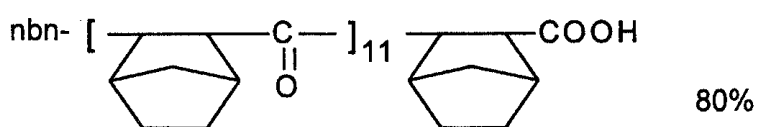
*I.I.Kerov, V.A.Yashkir, G.A.Korneeva, I.I.Krylov, K.V.Slmnsky
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Experimentally it has been found that fluoro norbornenes and their derivatives hydroxycarbonylation gives corresponding fluoro bicyclo carboxylic acids in the presence of dioxane - water solution of PdCl₂-PPh₃-HCl



Analogous fluoro bicyclo carboxylic acids were synthesized by the aldehyde oxydation with KMnO_4 in alkaline solution. According to the NMR ^1H , ^{19}F data, the insertion of the carbonyl group into the norbornene fragment undergoes to give exo - product independently of the nature of R.

As opposed to fluoro norbornenes, the fluoro - free norbornene hydrocarboxylation is attended with alternating co-polymerization of norbornene and CO providing the formation of the oligomer (yield -75%) along with norbornanecarboxylic acid (yield -20%). On evidence derived from NMR ^{13}C data, IR and ESCA analysis, the oligomer has the structure:



The optimization for the operating conditions, the physico - chemical characteristics of the synthesized compounds are described.