

EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF OZONE-RESISTANT TETRAFLUOROETHANE C₂H₂F₄ (REFRIGERANT R134a)

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New refrigerant R 134a is recommended to use as a working medium of refrigerating machines and thermocompressors instead of ozone- destructuring refrigerant R 12. To calculate thermodynamic cycle and heat exchanger sets it is necessary to have data about thermodynamic properties of refrigerant R 134a. The equation of state of R 134a in its virial form has been obtained:

$$Z = I + \sum_{i=1}^n \sum_{j=0}^m b_{ij} \frac{w^i}{\tau^i}$$

Based on this equation there has been developed a system of equations and calculated a table of thermodynamic properties of R 134a in saturation and in single -phase area within the temperature range $T = 240- 500$ K, and pressure $P = 0,01- 7,5$ MPa. The tables include density, compressibility, enthalpy, entropy, heat capacity, sound velocity, adiabatic exponent, throttling coefficient and vapour. The above tables include significantly more set of thermodynamic values than that usually.

PRECALCULATION OF BOILING POINTS OF FLUOROCOMPOUNDS BY METHOD OF STRUCTURAL ANALOGY

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Known methods of boiling points (T_b) precalculation provides typically the low precision of results. The solution of this problem is very actual for fluorocompounds which have numerous anomalies of physico-chemical properties. The precision of T_b estimation in the new-proposed method of structural analogy [1] is not worse than 1-2 K and have no dependence on chemical origin of compounds. Hence, the application of this method to fluorocompounds is highly interesting. The first step is the formation of two groups of structurally analogous compounds which are differ by the same fragments, namely $F \longleftrightarrow Cl$, $F \longleftrightarrow Br$, $Cl \longleftrightarrow Br$, $CF_3 \longleftrightarrow Cl$, $BrCF_2 \longleftrightarrow Br$, etc. One of them is reference (T_b values for all compounds are known) and the second is group under characterization (includes the compounds with unknown boiling points which must be precalculated). The following step is the application of non-linear three-parameter equation of general type (1) to establish the functional dependence between T_b (K) values of analogous compounds.

$$\lg T_{\text{кип}}(\text{II}) = a \lg T_{\text{кип}}(\text{I}) + b A + c \quad (1)$$

where A is the parameter which locate the position of each pair of analogues within corresponding taxonomic groups of compounds. Table 1 includes the information about Tb of four pairs of C2 freones (one of these groups is "exotic" bromofreones) and the results of eq. (1) application for the prediction of boiling points of other compounds which have no experimental Tb data at present.

Table 1. The correlation of boiling points of Br <—>Cl structural analogues and precalculation of these constants for some bromofreones.

Структурный аналог/ Structural analogue	T _{кип} , °C (эксперим.)/ T _b , °C experimental	Характеризуемое соединение/ Compound being characterized	T _{кип} , °C (эксперим.)/ T _b , °C experimental	A	T _{кип} , °C (рассчитанн.)/ T _b , °C precalculated
ClCH ₂ CH ₂ F	53.0	BrCH ₂ CH ₂ F	71.6	2	71.5
ClCH ₂ CHFCl	73.8	BrCH ₂ CHFCl	96.6	3	96.8
CF ₃ CHCl ₂	27.6	CF ₃ CHClBr (галотан/ halotan)	50.2	5	50.0
CF ₃ CF ₂ Cl	- 38.7	CF ₃ CF ₂ Br	- 22	6	- 21.9
Коэффициенты (1)/ Coefficients of eq. (1): a = 1.0385, b = 2.8858×10 ⁻³ , c = - 0.078663, <ΔT _b > ≈ 0.2 K					
Характеристика новых соединений группы бромхладонов/ Characterization of new compounds					
CH ₃ CFCl ₂	31.9	CH ₃ CFClBr	нет	3	50.5
CH ₃ CHFCl	- 11.0	CH ₃ CHFBr	нет	2	1.5
CF ₃ CFCl ₂	3.6	CF ₃ CFClBr	нет	6	25.3

Литература: 1. И.Г.Зенкевич. *Ж. физ. химии*. 70 (1996) 33-38.

References: 1. I.G.Zenkevich. *J. Phys. Chem. (Rus)*. 70 (1996) 33-38.

A NEW APPROACH TO THE SYNTHESIS OF 2-AMINO-5- (PERFLUOROALKYL- AND FLUOROPHENYL)-1,3,4-THIADIAZOLES

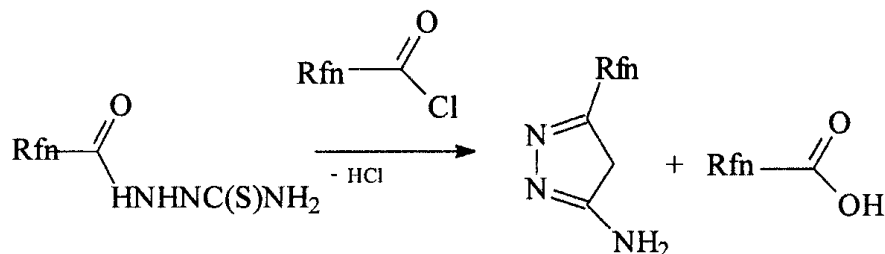
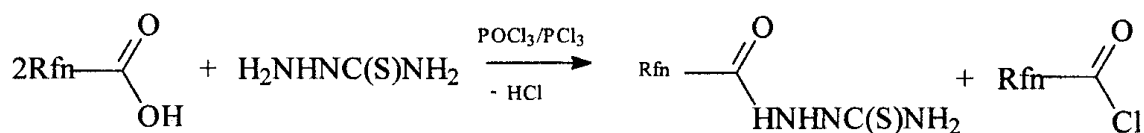
K.I. Eryomin, V.S. Znamensky, A. V. Golovanov,

V.I.Krutikov, A.N. Lavrentiev

Recently compounds with three heteroatoms in the ring have been intensively investigated. 2-Amino-5-substituted 1,3,4-thiadiazoles belong to this class of compounds. The interest to these compounds is based on wide spectrum of their pharmacological activity. The derivatives of 1,3,4-thiadiazole are used in industry as oxidation inhibitors, coloring agents, complexing agents with metals, and in agriculture as herbicides. Compounds containing fluor in their structure are of special interest.

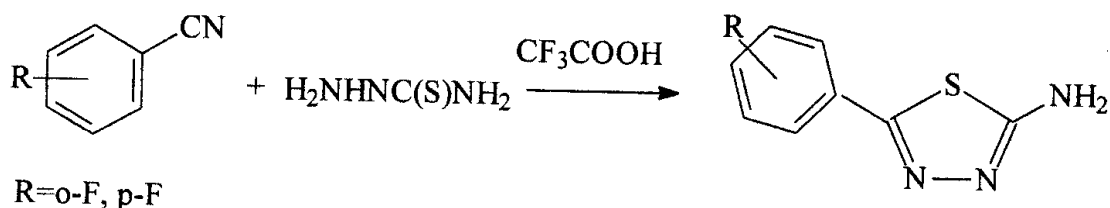
To widen the series of biologically active compounds, we suggested a new one-pot method of synthesis of 2-amino-5-perfluoroalkyl-1,3,4-thiadiazoles (n = 1,3,4,6,8) and 2-amino-5-(2-fluorophenyl)- and 2-ammo-5-(4-fluorophenyl)-1,3,4-thiadiazoles.

In the course of the present work it was found that heterocyclization of perfluoroalkyl acids with thiosemicarbazide using chlorinating agents (PCl₃ and POCl₃) proceeds in one step with high yield of the desired products. The reaction mechanism probably involves the initial conversion of an acid into its chloride followed by the formation of acetylthiosemicarbazide as an intermediate complex which further undergoes cyciodehydration in excess of the acid chloride, according to the scheme:



Rf = perfluoroalkyl C₁, C₃, C₄, C₆, C₈

2-Fluorophenyl /4-fluorophenyl-1,3,4-thiadiazoles have been obtained from the corresponding 2/4-fluorobenzoic acids nitriles in the medium of trifluoroacetic acid, according to the reaction:



The obtained compounds are crystalline substances, whose structure was confirmed by ¹H, ¹³C, ¹⁹F NMR data, and individuality - by TLC.

SYNTHESIS AND SPECTRAL INVESTIGATION OF FLUOROCONTAINING 6-ARILAMINOURACILES

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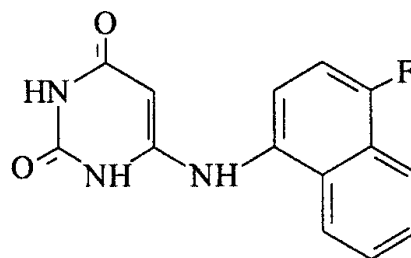
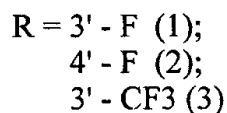
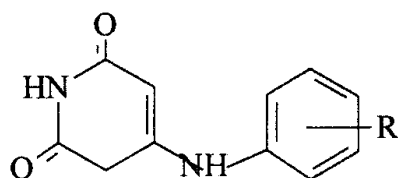
In continuation of our earlier studies in the field of biologically active arilaminouraciles, some F-containing analogies have been synthesized. 6-(3'-Fluoro-phenylamino)-uracile (1), 6-(4'-fluorophenylamino)-uracile (2), 6-(3'-trifluoromethyl-phenylamino)-uracile (3) and 6-(4'-fluoronaphtyl-1-amino)-uracile (4), shown on Scheme 1,2, were obtained by heating of 6-chlorouracile and the corresponding F-containing aromatic amine in aqueous medium.

<IMAGE3_3.GIF" height = 172 width = 443Scheme2

All the compounds are high-melting (m.p.>300°C) white crystalline substances, practically insoluble in water and poor-soluble in ordinary organic solvents. The attempt to carry out the similar interaction between 6-chlorouracile and pentafluoroaniline was unsuccessful even after 50-hour heating in the sealed ampule at 120°C.

PMR spectra demonstrate groups of signals typical for this class of compounds, d : 1H singlet at C₅ 4.2-4.8; 1H singlet of exocyclic NH - 8.5 and two singlets of heteroaromatic NH - 10, 11 of pyrimidine system as well as groups of aromatic protons signals at 6.9, 8.2

¹³C NMR spectra are typical as well, d signals at 77, 151, 152, 164 typical for the pyrimidine ring and the aromatic carbons group at 110-140; at the same time some signals splitting caused by interaction with paramagnetic F-nuclei was observed.



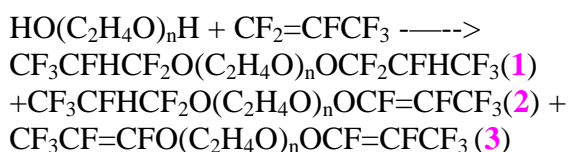
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DEVELOPMENT OF THE FLUORO-MODIFIED COMPRESSION OILS

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The method of synthesis of the new fluoro-modified compression oils was proposed. The method is found on the nucleophilic addition of a -olefins (hexafluoropropene) to polyoxaalkylenglicols (Mm 402, 502).

The interaction between hexafluoropropene and polyoxaalkylenglicols yields oligoether (1) and secondary products - olefines (2,3) by scheme as follows:



The compounds (2,3) with present the sign of the water don't occur.

The optimal process parameters were find. NMR 1H, 19F and IR spectroscopy estimated the structure.

The infra-sound structure-metric method without destruction of substance was elaborated for express-diagnostic of the reaction proceed completeness.

The antifriction properties of the modified oils (K_f, D G) were investigated. The cationic polymerization of 2-decene (C₁₀H₂₀) catalyzing BF₃, and initiating H₂O-HF-HBF₄ at 40-80 °C for 1-2 h was carried out. After treatment of the reaction mixture was obtained the polymer as foundation for ozone-soluble industrial oils.

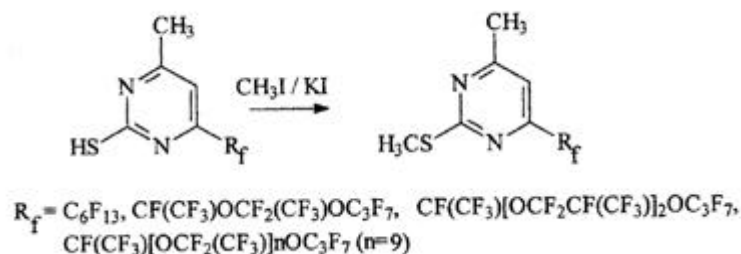
The kinematics factors of viscosity at different temperature were find. The technology scheme of continuous polymerization 2-decene was proposed.

S-METHYLATION 6-PERFLUOROALKYL(ALKOXIALKYL)-2-MERCAPTOPYRIMIDINES

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It is known, that the S-methyl derivatives of pyrimidines possess own high physiological activity. In continuation of our investigations we synthesised the series 6-perfluorosubstances 2-methylthio-4-methylpyrimidines.

The S-alkylation of 2-mercaptopyrimidine derivatives prepared by cyclization of fluorinated unsymmetrical β -diketones in the presence of alcohol and hydrochloric acid was carried out in alkaline solution of methyl iodide at 40-50° C for 2-3 h.



After extraction ether and distilled off solvent yield of product was 88-90%. The compounds were amorphous crystals, exclusive of pyrimidines with substituted perfluorinated fragment (n=9).

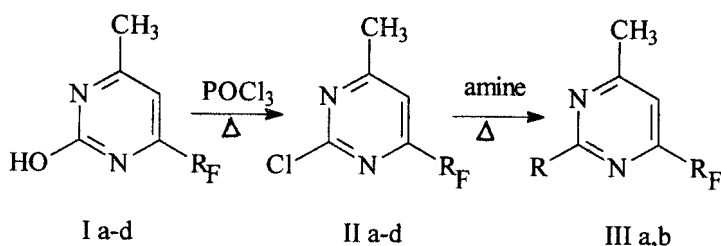
The IR spectra of synthesized compounds are typical for such structures. There are absorption bands in the region 810-740 and 530-525 cm^{-1} due to S-Me, stretching vibrations. The fungicidal activity of S-methylperfluoropyrimidines were showed.

REACTIONS OF 6-PERFLUOROALKYL(ALKOXYALKYL)-2-HYDROXYPYRIMIDINES

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Fluorinated pyrimidines are interested by their wide spectrum of biological activity. We are carried out the synthesis of series derivatives 6-perfluorosubstituted pyrimidines, possessing the atom of chlorine or alkylamino-group in 2-position of ring.

The 2-hydroxypyrimidine derivatives (Ia-d) have been prepared from urea and perfluorinated 1,3-diketones. These pyrimidines (Ia-d) were used as starting materials to prepare the compounds (IIa-d, IIIa,b) according to the scheme as follows:



$R_F = a C_6F_{13}, b C_8F_{17}, c CF(CF_3)OC_3F_7, d CF(CF_3)OCF_2(CF_3)OC_3F_7$ (II);

$R_F = a C_6F_{13}, R = NHBu$ (IIIa); $b C_8F_{17}, R = N(Et)_2$ (IIIb)

The chlorination of hydroxy-group in 6-perfluorinated pyrimidines were carried out by their refluxing in the excess of phosphoryl chloride at presence of hydrochloric acid during 5 h. The yield of 2-chloropyrimidines (IIa-d) achieved 90-92%. The IR spectra of (IIa-d) demonstrated the presence of absorption band at 700 cm^{-1} due to C-Cl stretching vibrations.

We carried out the aminolysis of 2-chloropyrimidines (IIa,b) with primary and secondary amines in aqueous ethanol at heating for 6 h. 6-Perfluorosubstituted 2-alkylaminopyrimidines (IIIa,b) was prepared (yield 80%, oil). The IR spectra of the substituted fluorinated pyrimidines (III)

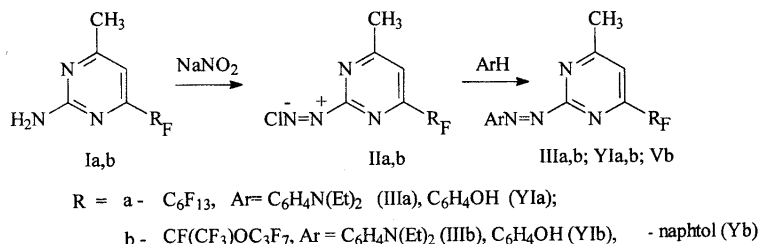
showed very strong absorption bands in the region $1350-1050\text{ cm}^{-1}$ due to C-F stretching vibrations, absorption bands in the region $1700-1515\text{ cm}^{-1}$ due to vibrations of pyrimidine ring, stretching vibrations of the type N-H (IIIa) were found in the region $3380-3200\text{ cm}^{-1}$ and stretching vibrations of CH_3 -group - $2965-2760\text{ cm}^{-1}$.

SYNTHESIS AND REACTIONS OF DERIVATIVES 6-PERFLUOROPYRIMIDYL DIAZONIUM

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The diazotation of 2-amino-4-methyl-6-perfluorinated pyrimidines (Ia,b) was carried out. It was obtained by means of guanidine carbonate and fluorinated unsymmetrical β -diketones cyclization.

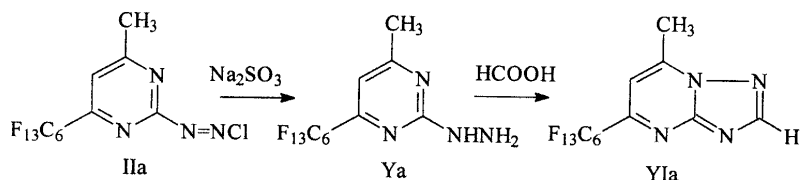
The 2-diazonium salts of 2-amino-6-perfluoropyrimidines (IIa,b) were obtained from the corresponding pyrimidines (Ia,b) by diazotation in aqueous alcohol solution of nitrite sodium at $0-2^\circ\text{C}$ for 2 h. The 2-pyrimidyl diazonium salts (IIa,b) were stable into fluorochlorocarbones. The IR spectra of the substituted fluorinated 2-pyrimidyl diazonium salts (IIa,b) showed absorption bands in the region $2350-2210\text{ cm}^{-1}$ due to $\nu\text{-N=NCl-}$ vibrations.



The 2-azopyrimidines (III, IV, V) were obtained by coupling with a N,N' -diethylaniline (IIIa,b) (pH 5, yields 55%, 60% corresponding), phenol (IVa,b) (pH 9, yields 57%, 63%) and β - naphthol (pH 9, yield 55%).

The composition and construction of the compounds (III-V) were estimated by IR and UV spectroscopy and elemental analysis.

The reduction of the 2-diazonium salt(IIa)with sodium sulphite in acid medium permitted us to prepare corresponding 2-hydrazinoderivative (Ya). 6-: Perfluorohexil-2-hydrazino-4-methylpyrimidine (Va) was converted into the s-triazolo[1,5- α]-3-methyl-7-perfluorohexilpyrimidine (VIa) by treatment with formic acid for 12h, yield 54%. The construction of the compound (VIa) was estimated by spectral methods.

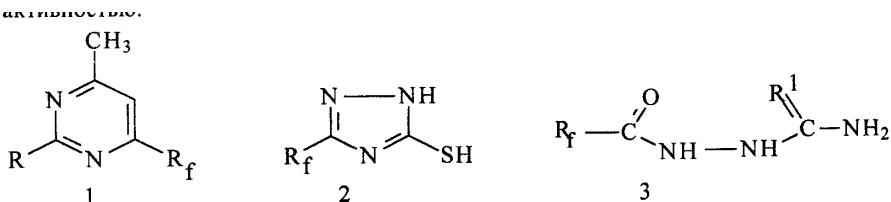


THE FUNGICIDIC ACTIVITY OF SERIES PERFLUORINATED AZINES AND AZOLES

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The fungicidal activity of perfluorinated derivatives of pyrimidines, 1,2,4-triazoles and some perfluoroacylthiosemicarbazides and perfluoroacylaminoguanidine with reference to *Bacillus mucilaginosus* was studied. It was found all tested substances own bacteriostatic action. The fluorinated pyrimidines (1a,b,d,e) and triazoles (2a,c,d) with mercapto- and methylthiogroups in 2 and 5 position of ring and also perfluoroacylsemicarbazides (3a,c) manifested the most bacteriostatic activity. Probably it is attributed to by presence into molecule the atom of sulphur. The substances activity is depended on length and structure of perfluorinated fragment. The compounds (1 d,e) have optimal length of fluorofragment (C=6-8). The SCH₃ group availability cause high fungicidal activity of tested products. The considerable increase of length of perfluoro-fragment leads to decrease of bacteriostatic activity. Into result the substances (If, R=NH₂, OH, SH) own low activity.



$R_f = a C_6F_{13}, b C_8F_{17}, c CF(CF_3)OC_3F_7, d CF(CF_3)OCF_2(CF_3)OC_3F_7$
 $e CF(CF_3)[OCF_2CF(CF_3)]_2OC_3F_7, f CF(CF_3)[OCF_2(CF_3)]_nOC_3F_7 \quad (n=9)$
 $R = NH_2, OH, SH, NH(n-Bu), SCH_3$ (1); $R^1 = NH$ (3)

The quantity constant of biological activity (λ) not depending of compound concentration and characterizing individual properties of product was introduced. The functional dependence of one-size diameter of the zone of suppression of the growth of culture bacterium (δ) from concentration and biological activity (λ) was defined.

SPECIFIC FEATURES OF INTERACTION OF FLUORINATED CARBONYL COMPOUNDS WITH SULPHENYL CHLORIDES

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Aliphatic and arylaliphatic ketones usually easy react with alkyl and arylsulphenyl chlorides without any catalysis and acceptance of HCl giving monothiolating compounds. Even low active polyfluorosulphenyl chlorides react with carbonyl compounds under weak heating. We show that 1,1,1-trifluoroacetone (I) and ethyltrifluoroacetylacetate (II) don't react with sulphenyl chlorides both in polar and unpolar solvents and without them. Thiolation of I and II by benzenesulphenyl chloride take place only in presence of organic bases.

Trifluoroacetone gives the only three thiolating product triphenyltrithioortotrifluoropiruvate, but reaction of II with benzenesulphenyl chloride in presence of base give products of mono- or bis-thiolation in different conditions.

SYNTHESIS OF FLUOROCONTAINING 2-HYDROXYIMINO-, 2-ARYLHYDRAZO SUBSTITUTED 1,3-DI-, TRICARBONYL COMPOUNDS AND THEIR REACTIONS WITH DINUCLEOPHILES

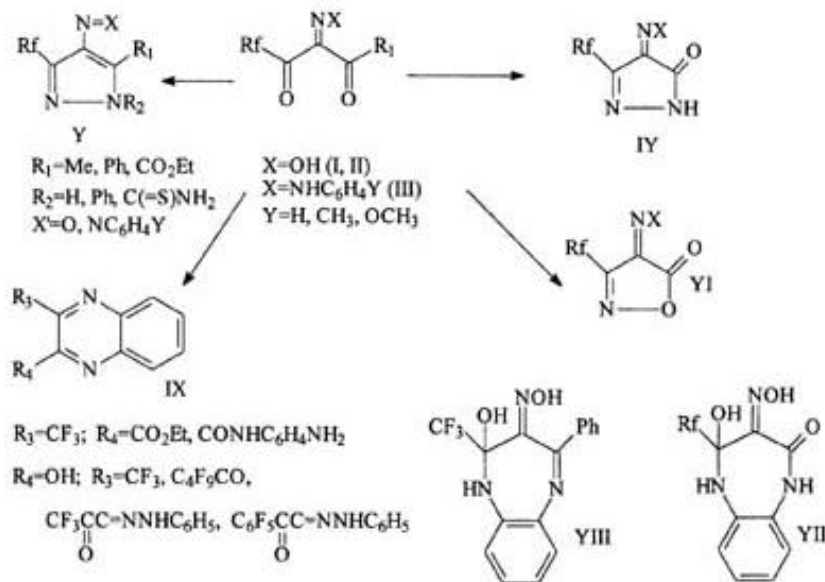
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2-Hydroxyimino-1,3-keto esters ($R_f=CF_3, C_4F_9$, $R_1=OC_2H_5$) (I) and 1,1,1-trifluoro-2-hydroxyimino-4-phenyl-2,4-butanedione (II) have been prepared by the nitrosation of the corresponding 1,3-dicarbonyl compounds with $NaNO_2$. The coupling of 1,3-diketones ($R_f=CF_3, H(CF_2)_2$, $R_f=CH_3$), 1,3-keto esters ($R_f=CF_3, C_4F_9$; $R_f=OC_2H_5$) and 2,4-diketo esters ($R_f=CF_3, C_6F_5$, $R_f=CO_2C_2H_5$) with aryldiazonium chlorides leads to the arylhydrazones (III).

It has been shown that oximes (I) had reacted with hydrazine hydrate to form 3-fluoroalkyl-2-hydroxy-4-hydroxyimino-pyrazolidone-5 (IV) with $R_f=CF_3$ can be dehydrated to 2-hydroxyimino-pyrazolinone-5; (II) in this reaction gives 4-nitrosopyrazole (V); arylhydrazones of (VI). 1,3-Diketones, 2,4-diketo esters and 1,3-keto esters (III) yields 3-fluoroalkyl(aryl)-5-methyl-(ethoxycarbonyl)4-arylazopyrazoles (V) and 3-fluoroalkyl-4-arylhydrazopyrazolinone-5

Reaction of 1,3-keto esters arylhydrazones with hydroxylamine leads to 3-fluoroalkyl-4-aryl-hydrazoimxazolinone-5 (VI). Arylhydrazones of 1,3-diketones with phenylhydrazine and semicarbazide gives 1-phenyl-(thiocarbonyl)-substituted pyrazoles (V). Interaction of (I) with ortho-phenylenediamine in diethyl ether leads to 3-hydroxyimino-4-hydroxy-4-fluoroalkyl-2H-1,5-benzdi-azepinone-2 (VII), a (II) - 2-hydroxy-2-trifluoromethyl-3-hydroxyimino-4-phenyl-1H-1,5-benzdi-azepine (VIII); in methanol (I)-(III) gives the substituted quinoxalines (IX).

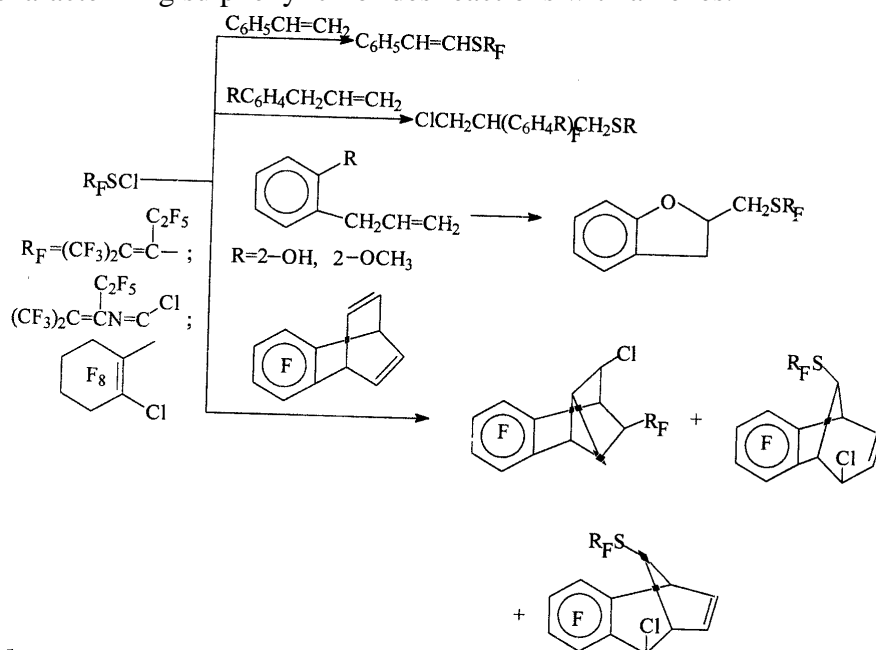


POLYFLUORINATED α, β -UNSATURATED SULPHENYL CHLORIDES - REAGENTS OF NON-ADDITIVE SULPHENYLATION OF ALKENES

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For the first time it was found that when polyfluorinated α , β -unsaturated sulphenyl chloride interact with alkenes under ordinary conditions the products of substitution, rearrangements, cyclization and non-stereoselective addition to double bond are formed instead of stereospecific trans-addition characterizing sulphenyl chlorides reactions with alkenes.



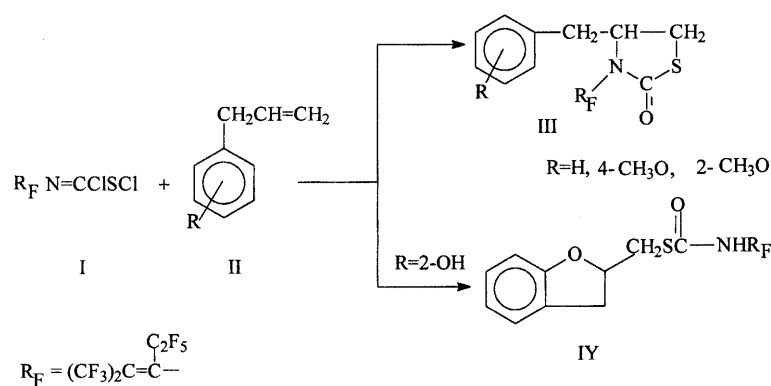
Thus there have been found reagents containing bivalent sulphur which may be qualified as strong electrophiles.

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STIMULATED HETEROCYCLIZATION IN REACTIONS OF N-PERFLUORO-2-METHYL-2-PENTEN-3-YL-IMINOCHLOROMETHANE SULPHENYL CHLORIDE WITH ALKENES

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We have realized heterocyclization in reactions N-perfluoro-2-methyl-2-penten-3-yl-iminochloromethane sulphenyl chloride (I) with alkenes which was completed by nucleophilic groups of electrophile or substrate and promoted by $\text{LiClO}_4\text{-CH}_3\text{NO}_2$ system. When sulphenyl chloride (I) interacts with allyl benzenes (II; $R=\text{H}, 4\text{-CH}_3\text{O}, 2\text{-CH}_3\text{O}$) in $\text{LiClO}_4\text{-CH}_3\text{NO}_2$ system the principal course of reaction is heterocyclization completed by nitrogen atom of reagent with formation of thiazolidinones (III, $R=\text{H}, 4\text{-CH}_3\text{O}, 2\text{-CH}_3\text{O}$) (yield - 60%), whereas in CH_3NO_2 without salt the yield of these heterocycle is no more than 5%. In reaction of sulphenyl chloride (I) with allyl phenol (II, $R=2\text{-OH}$) in $\text{LiClO}_4\text{-CH}_3\text{NO}_2$ system heterocyclization is completed by hydroxy group of unsaturated compound with formation of dihydrobenzofuran (IV)



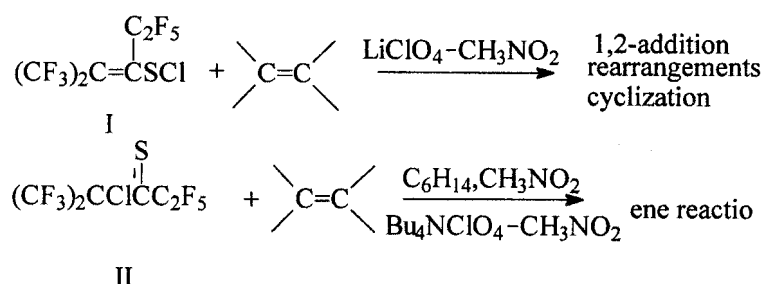
The authors are grateful to the Russian Foundation for Fundamental Research (grant no. 96-03-32402a) and the Competitive Centre of fundamental natural sciences of St.Petersburg University (grant no. 95-0-9.4-36) for financial support.

TWO FORMS OF INTERACTION OF PERFLUORO-2-METHYL-2-PENTEN-3-YL SULPHENYL CHLORIDE WITH ALKENES

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It has been found that perfluoro-2-methyl-2-penten-3-yl sulphenyl chloride reacts with alkenes in form of sulphenyl chloride (I) (realization of 1,2-addition, rearrangements, cyclization) or in form of 2-chloroperfluoro-2-methylpentane-3-thione (II) (realization of ene reaction). These reaction courses are controlled by reaction conditions: first course takes place in $\text{LiClO}_4\text{-CH}_3\text{NO}_2$ system, second - in C_6H_{14} , CH_3NO_2 and $\text{Bu}_4\text{NCIO}_4\text{-CH}_3\text{NO}_2$ system.



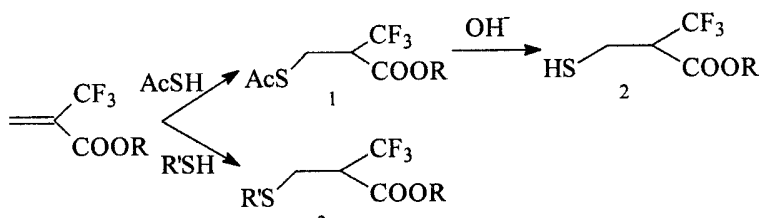
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SYNTHESIS OF FLUOROSULFURCONTAINING CH-ACIDS

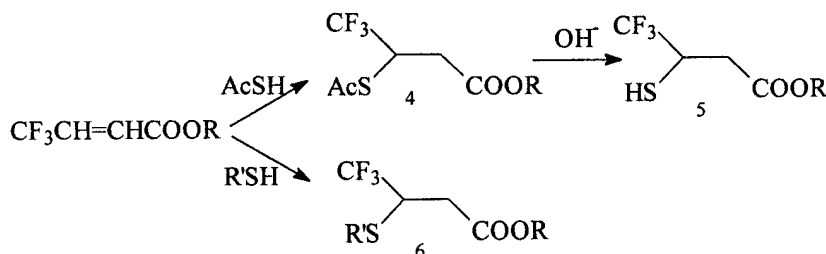
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Derivatives of 2- or 3-polyfluoroalkylcarboxylic acids including the various sulfurcontaining groups in the p-position are unknown today. At the same time they are convenient objects for the research of mutual effects of polyfluoroalkyl and sulfurcontaining groups on the CH-acidic properties of F, S- containing carboxylates. The 2- and 3-trifluoromethylacrylates were the initial compounds for the synthesis of fluorosulfurcontaining CH-acids. 2-Trifluoromethyl-propenoates interact with the thiolic compounds in the mild conditions giving the vicinal F, S - containing CH-acids 1-3:



Synthesis of the heminal fluorosulfurcontaining CH-acids 4 - 6 was realised by the thiolation of 3-trifluoromethylpropenoates. The interaction of reagents occurs only under the rigid conditions and as a rule in the presence of the catalyst.



Thus CF₃-group in the α -position activates, but in the β -position sharply inactivates the double bond C=C of the propenoates in the reactions of thiolation. It follows from this that the thiolation's rate is controlled by the polarity of the double .

SELECTIVE DEHALOGENATION OF POLYFLUOROAROMATIC COMPOUNDS.

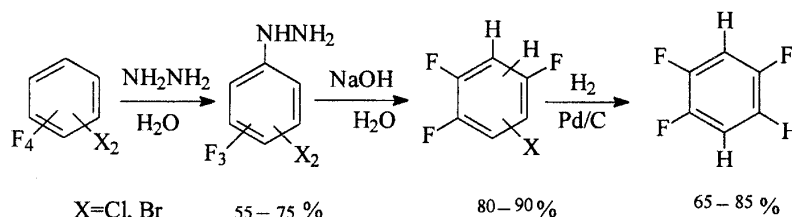
1. PREPARATION OF 1,2,4-TRIFLUOROBENZENE AND ITS DERIVATIVES

V. Zabolotskih, A.S. Kochanov, V. V. Gogoleva, A. V. Tiunov, V.F. Zabolotskih

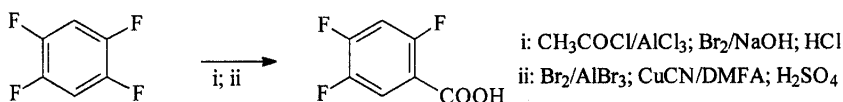
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The technology development and large scale preparation of hexafluorobenzene via "Halex" fluorination of hexachlorobenzene with potassium fluoride lead one to consider the problem of preparation of aryl fluorides on the basis of the by-products mentioned above "Halex" process. We are proposed the suitable method for the preparation of 1,2,4-trifluorobenzene by using the reaction of dichlorotetrafluorobenzenes with hydrazine hydrate, as the selective reducing dehalogenating agent.

We have shown that dichlorotetrafluorobenzenes (isomer's mixture m:o:p = 65:20:15) react with hydrazine hydrate to give the corresponding dichloro-tetrafluorophenylhydrazine derivatives. After treatment by NaOH this hydrazine derivatives give 1,2,4-trifluorochlorobenzenes, the gas-phase catalytic hydrogenation of which yield to the selective preparation 1,2,4-trifluorobenzene. Similar transformation can be carry out with dibromotetrafluorobenzene.



The obtained 1,2,4-trifluorobenzene was converted into 2,4,5-trifluorobenzoic acid by usual reactions.

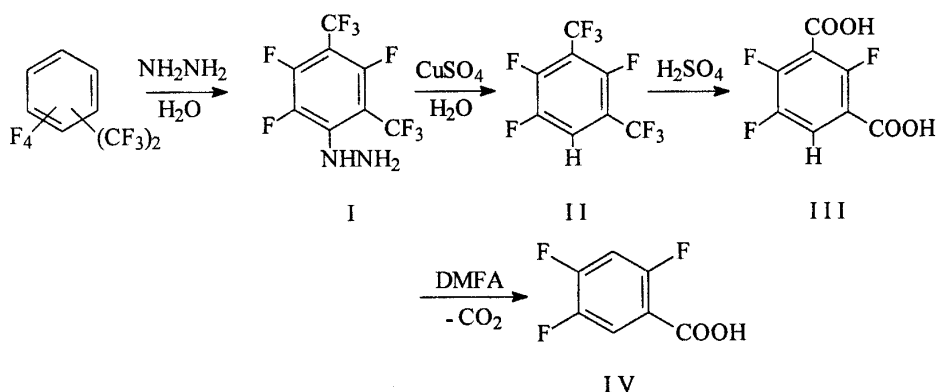


SELECTIVE DEHALOGENATION OF POLYFLUOROAROMATIC COMPOUNDS. II. PREPARATION OF 2,4,5-TRIFLUOROBENZOIC ACID

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It is known, that, when hexafluorobenzene was available via "Halex" fluorination hexachlorobenzene, the isomeres of perfluoroxylens are obtained as byproduct and can be isolated alongside the perfluoro(ethylbenzene) by the technology developed from Perm department RSC "Applied Chemistry". We have studied the ways suitable for preparation 1,2,3-trifluorobenzoic acid by using the reaction perfluoroxylens with hydrazine. We have shown that under the intereaction between of perfluoroxylens and hydrazine hydrate the only meta-isomer reacts to give 2,3,5-trifluoro-4,6-bis(trifluoro-metyl)phenylhydrazine (I), which can be converted into (II) with the substitution NH_2NH -groups in benzene ring by the hydrogen atom using the decomposition in the cupric sulphate solution. In this case the presence of perfluoro(ethylbenzene) in the reaction mixture is not reflect on the selectivity running of a process.



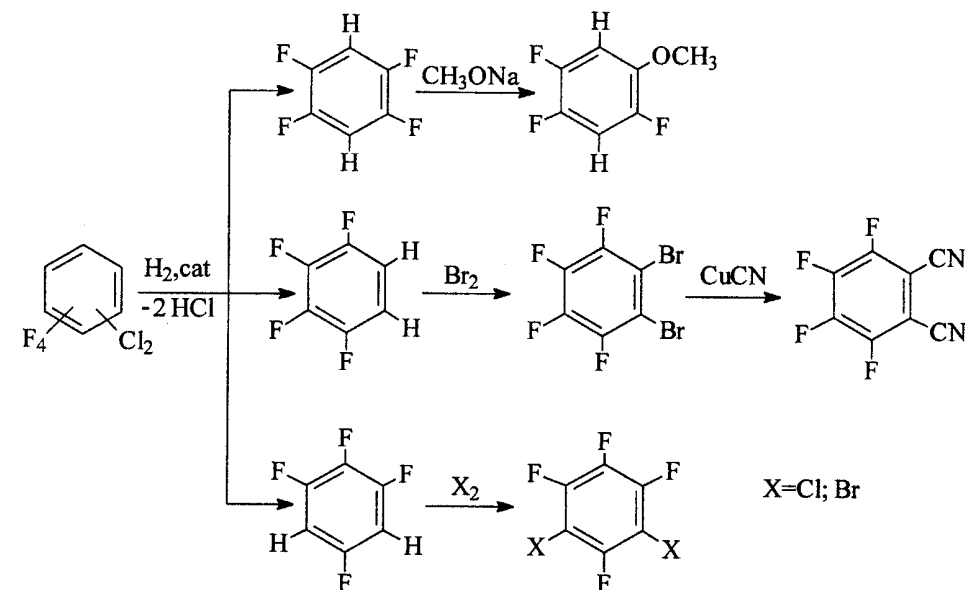
The consequent hydrolysis of the trifluoromethyl groups xylene (II) was used for the preparation 2,4,5-trifluoroisophthalic acid (III). After this we have carried out the selective decarboxylation of only one carboxyl group from (III) to obtain 2,4,5-trifluorobenzoic acid (IV), widely used in the syntheses of medicines.

SELECTIVE DEHALOGENATION OF POLYFLUOROAROMATIC COMPOUNDS. III. PREPARATION OF TETRAFLUOROENZENES AND THEIR DERIVATIVES

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With a view to preparation of tetrafluorobenzenes we have studied the gas-phase reaction of catalytic hydrogenation of dichlorotetrafluorobenzenes, which are basic by-products from "Halex" fluorination of hexachlorobenzene.

We are examined the influence of various parameters (reaction temperature, reagent ratio, contact time) on yield. The defluorination process as by-reaction is reduced to a minimum (trifluorobenzenes content less 0,5%). The tetrafluorobenzenes (isomers mixture) are formed with high yield (95%) and are separated through rectification.



The reaction of tetrafluorobenzenes with electrophilic and nucleophilic reagents results in the formation of various arylfluorides, used in the syntheses of biologically active compounds.

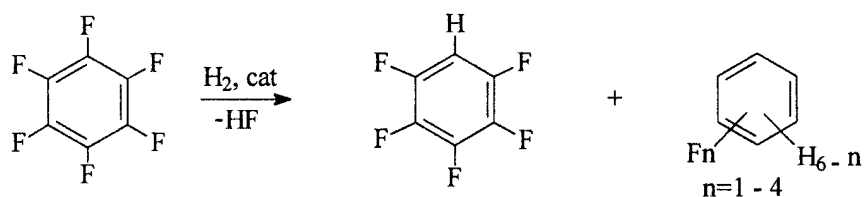
SELECTIVE DEHALOGENATION OF POLYFUOROAROMATIC COMPOUNDS.

IV. PREPARATION PENTAFLUOROGENE BY CATALYTIC HYDROGENATION OF HEXAFLUOROGENE

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Hexafluorobenzene is either of two main products which is obtained whereby large scale technology of "Halex" fluorination hexachlorobenzene performed by Perm Department RSC "Applied Chemistry". To extend the range of this technology we have studied the catalytic hydrogenation of hexafluorobenzene with the aim of preparation of pentafluorobenzene.

We are shown, that gas-phase catalytic hydrogenation hexafluorobenzene gives pentafluorobenzene combined with other polyfluorobenzenes to more highly extent defluorination including fluorobenzene. Under optimum reaction conditions (temperature, contact time, reagents ratio) pentafluorobenzene is formed with selectivity 90%.



Pentafluorobenzene can be singled out of the reaction mixture with high purity.

SELECTIVE DECHLORINATION OF POLYCHLOROFLUOROAROMATIC COMPOUNDS. PREPARATION OF 1,3,5-TRIFLUOROBENZENE

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It is known that polychlorofluorobenzene (I) are formed, when hexachlorobenzene interacts with potassium fluoride. The fraction, containing trichlorotrifluorobenzenes, consists of 65-75% symmetric 1, 3,5-trichloro-2, 4,6-trifluorobenzene, contents of the rest isomers forms 25-35% in the amount.

It is shown, that under the gas-phase catalytic hydrogenation along with the reaction of dechlorination proceeds the reaction of defluorination, that results in the formation of considerable amounts of difluorobenzenes, besides the target trifluorobenzenes. Degree of defluorination forms from 50 to 95%.

However, when carrying out the reactions of dechlorination under the milder conditions, such as in the liquid phase using various solvents trifluorobenzenes succeed in obtaining with yield of about 80% under the complete conversion of the starting trichlorotrifluorobenzenes.

Isolation of the target 1,3,5-trifluorobenzene is rather easy, since of the whole set of the formed reaction products (trifluorobenzenes and difluorobenzenes) this isomer is the most easily boiling (b.p. =75-76°C), 1,3-difluorobenzene (b.p. =82°C) and 1,3,4- trifluorobenzene (b.p. =88 °C) have the closest boiling temperatures.

1. Vorozhtsov N.N.//J.V.C.S, 1970, No. I, p. 52-63

SOME DATA ON 125-HALON EFFICIENCY IN EXTINGUISHING IN PREMISES

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According to restrictions on application of bromohalons imposed by the Montreal Protocol, the necessity arose to search their replacements for using in gas total flooding systems.

As alternatives for bromohalons the non-ozone depleting agents closed to them by physical properties and high operational characteristics, have been considered: halon 125 (C₂F₅H), halon 31-10 (C₄F₁₀), halon C-318 (C₄F₈), halon 227 (C₃F₇H), halon 218 (C₃F₈), halon 23 (CF₃H), pentafluoroethyl iodide (C₂F₅I), and SF₆ gas. Laboratory tests showed that halon 125 seems to be the most promising with respect to its characteristics as well as manufacturing opportunities.

Fire extinguishing efficiency was estimated in the room measured 5x4x2,5 m, of volume V 50 m³ during extinguishing a combined fuel charge (fire sources of Class A and Class B).

Halon 125 was discharged from a gas total flooding unit installed at a corner of the room. The unit was the balloon having a locking head with electric starter. The head had the distributing device providing uniform distribution of an extinguishing agent inside the room. The pressure inside the balloon was 4,0 MPa. The discharge time of halon 125 liquid phase varied over the range of 10-17 s. The extinguishing was considered as efficient if the extinguishing time $t_{ext} < 30 \pm 5$ s. In tests it was from 17 to 80s.

Six experiments were carried out. They showed that in extinguishing fires of Class B (benzene) the specific flow rate of halon 125 was $0,7 \text{ kg/m}^3$. That agreed with standard fire extinguishing concentration ($Q_N = 0,53 \text{ kg/m}^3$), taking into account the coefficient of non-uniformity of halon 125 distribution, determined by sampling was equal to 1,2. For the fires of Class A (wood stack) the specific flow rate was $0,8 \text{ kg/m}^3$, that corresponded to $Q_N = 0,62 \text{ kg/m}^3$. The presence of HF in combustion products was detected in the tests. It was found that in reducing an extinguishing time (the time from start of halon discharge to fire suppression) the amount of HF tends to decrease.