

THE SYNTHESIS AND SOME CHARACTERISTICS OF PARTLY FLUORINATED ALCOHOLS ON THE BASIS OF TETRAFLUOROETHYLENE AND HEXAFLUOROPROPYLENE (REVIEW)

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In this review the approaches of partly fluorinated alcohols on the tetrafluoroethylene and hexafluoropropylene basis are analyzed. New experimental data regarding telomeric alcohols involvement into reactions with unsaturated compounds and hetero-organic derivatives are discussed. Oxidation processes and reactions in strong acid mediums of telomeric alcohols are analyzed. Also in this review you will find the trends of practical using of telomeric alcohols. The questions regarding partly fluorinated alcohols toxicity and some of their derivatives are discussed here.

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2. Partly Fluorinated Alcohols as Effective O-nucleophilic reagents, their application for creation of fluorine containing semi-products and materials on their base.

On the basis of alcohols interaction with tetrafluoroethylene and hexafluoropropylene in the liquid phase in the presence of radical sources universal complex obtaining technology of semi-products (poly-fluorinated alcohols, the most important components of fluoroorganic materials production) was developed and is functioning successfully. They can be parent materials for production of many fluorocontaining materials, used in engineering industry and medicine. In connection with this the functionalization of telomeric alcohols like $H(CF_2CF_2)_nCH_2OH$, $n = 1-5$ widens the production fields of new perspective fluorine materials. Below you will find some directions of its realization.

Thus on their basis new materials with important chemical and physical characteristics are created. These researches opened excellent features of a number of new emulsions regarding their ability to storage, sterilization and rheology. As time goes by they will become a basis of alternative replacement of industrial liquids and they will find a wide range of application.

Poly-fluorinated alcohols are more acidic compare to hydrocarbons analogues, that results in reduction of their nucleophilic properties (table 2) [56].

Table 2. Constants of some fluoroalchols acidity at 25 °C [56].

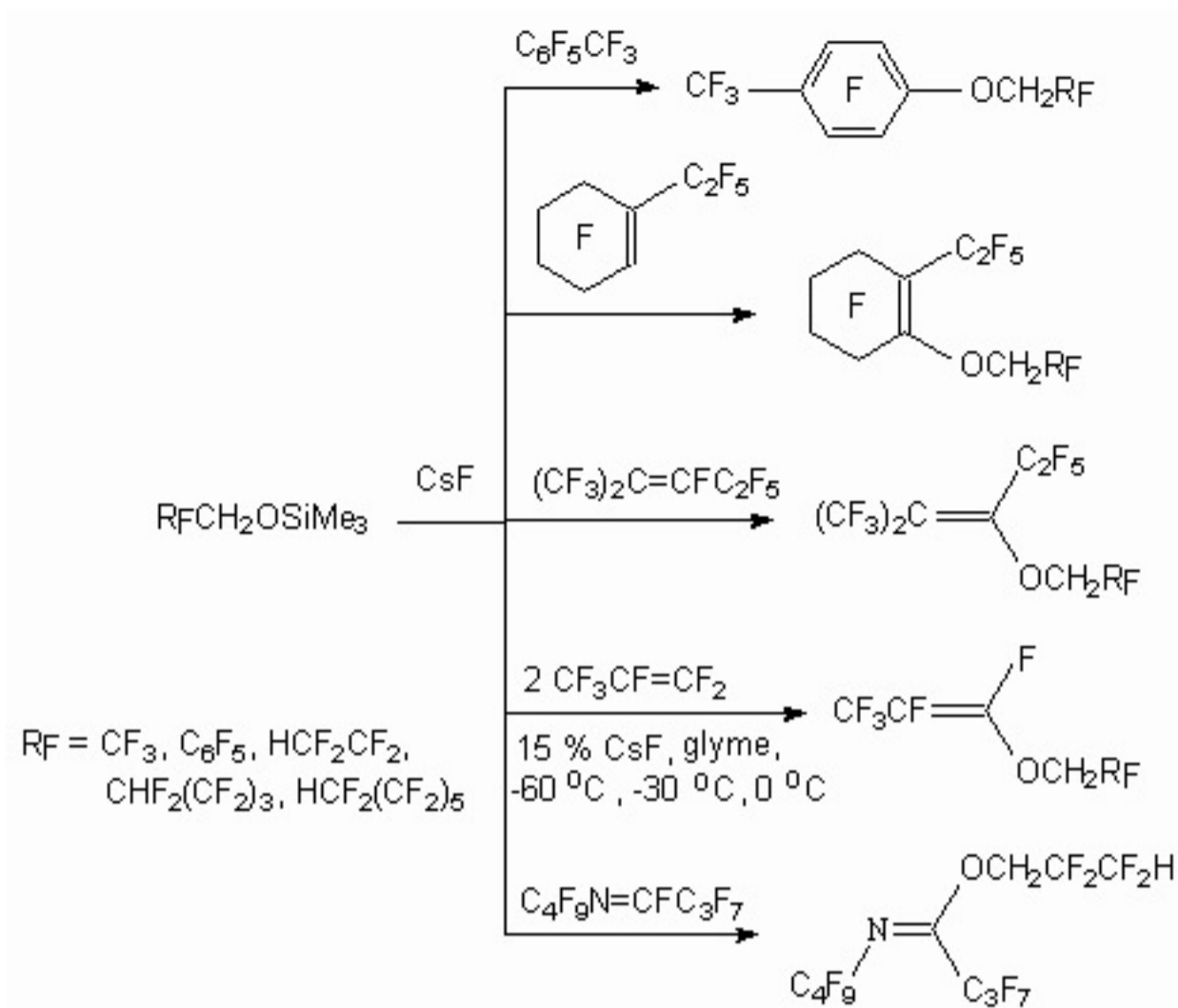
ROH	pKa	ROH	pKa ^a
$((CHF_2)_2C(OH)_2$	9,11	$CF_3CF_2CH_2OH$	12,39
$(CF_3)_2CHOH$	9,39	CF_3CH_2OH	12,40
$(CF_3)_2(CH_3)COH$	9,93	$(CF_3)(CH_3)CHOH$	12,70
$(CF_3)(CH_3)C(OH)_2$	10,57	$(CF_3)(CH_3)_2COH$	13,13
		$C_3F_7CH_2OH$	11,4

^a [57].

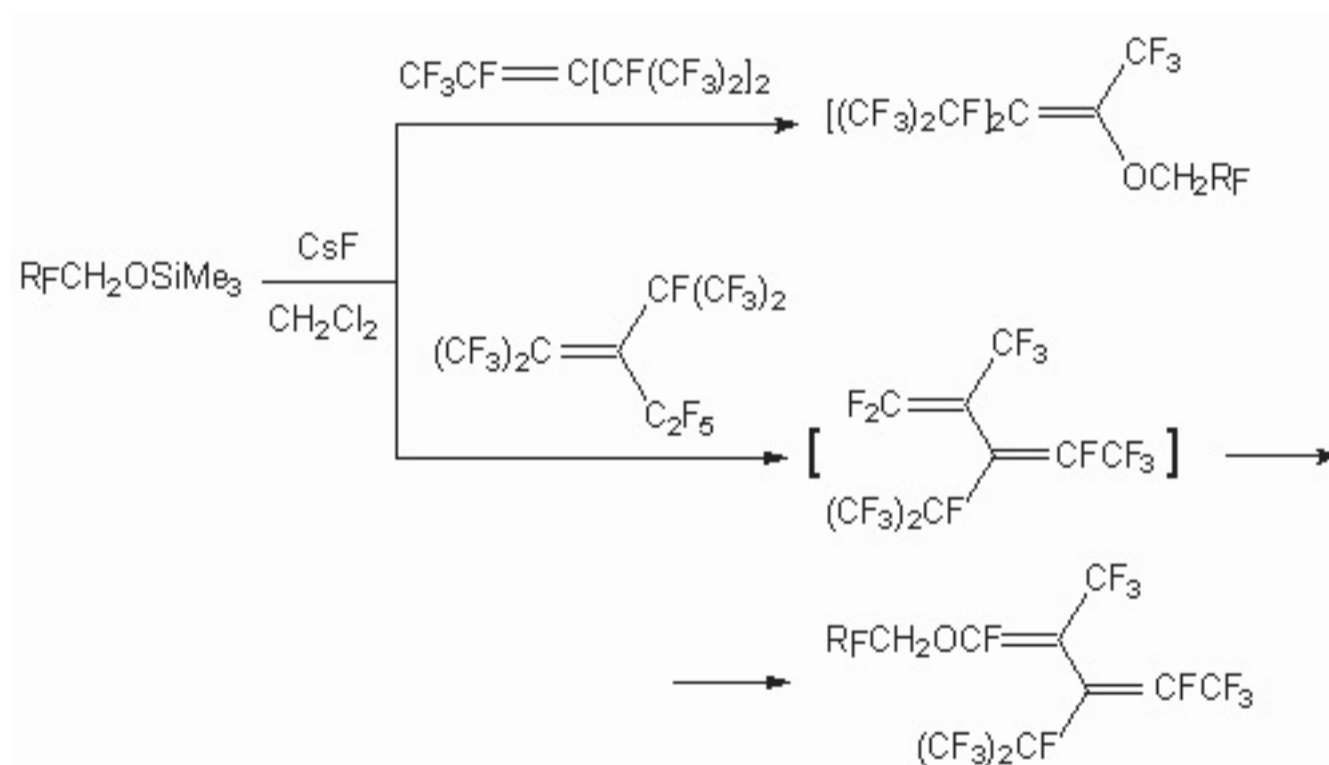
The peculiarity of telomeric alcohols chemical behavior is their higher acidity and reduced reaction ability as nucleophilic reagents. Nevertheless, they were used in nucleophilic replacement and addition reactions. For example , 2,2,3,3-tetrafluoropropanol reacts in autoclave with tetrafluoroethylene in the presence of NaOH in dioxane at 60°C during two hours, producing $CHF_2CF_2CH_2OCF=CF_2$ with the yield of 42 % [58].

2.1. The interaction of trimethylsilyl ethers of partly fluorinated alcohols and unsaturated compounds - the way of wide application field dialkyl ethers synthesis.

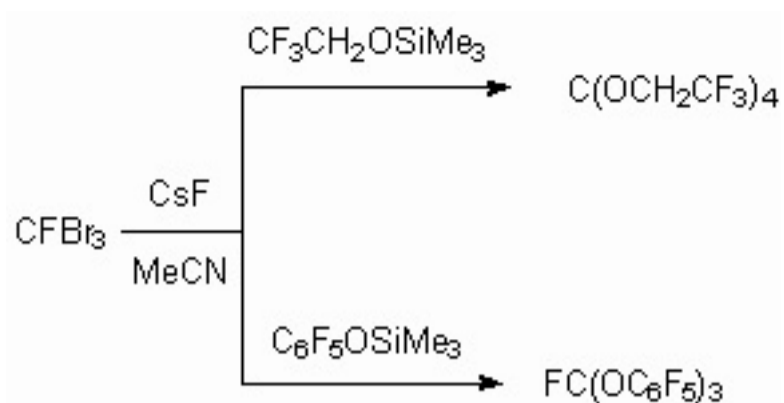
One of the approaches of partly fluorinated alcohols activation as O-nucleophiles was their trimethylsilyl ethers use in the process carrying out conditions in the presence of fluoride-ion source. Cesium fluoride is rather effective source. Thus, this method is used for forming of C-O and C-N bonds in highly fluorinated systems [48,49]. This method is successfully used instead of olefins reactions with alcoholates of alkali elements.



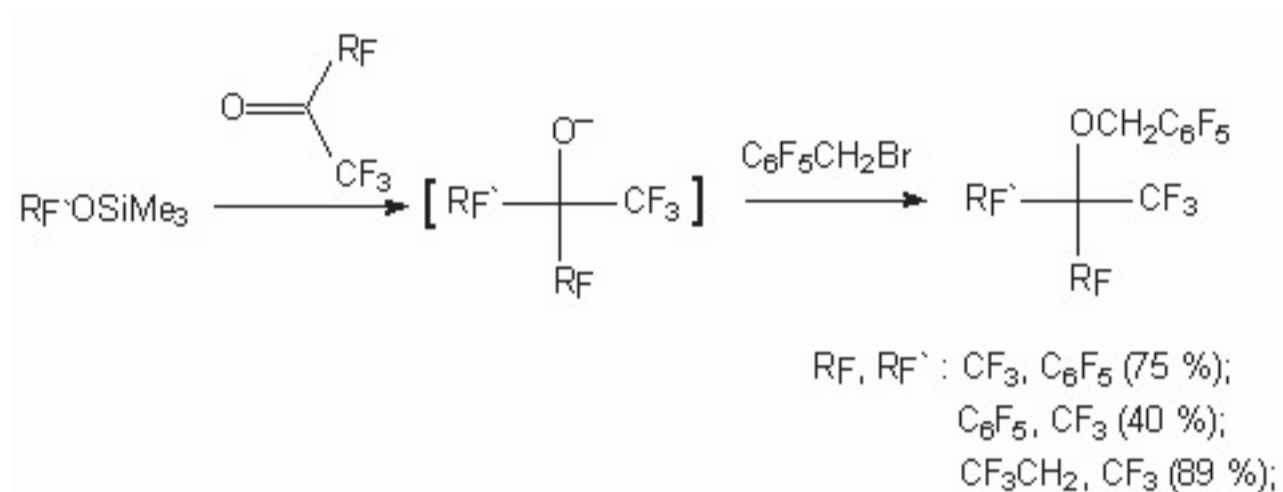
The alcohols' reaction $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{OH}$ ($n = 1-3$) with hexafluorobenzene and octafluorotoluene in the presence of CsF, Et₃N or pyridine results in formation of replacement products of fluorine atoms in benzene ring [61]. In case of trimethylsilyl ethers of telomeric alcohols reaction with mixture of isomeric trimers of hexafluoropropylene two butadiene derivatives are formed.



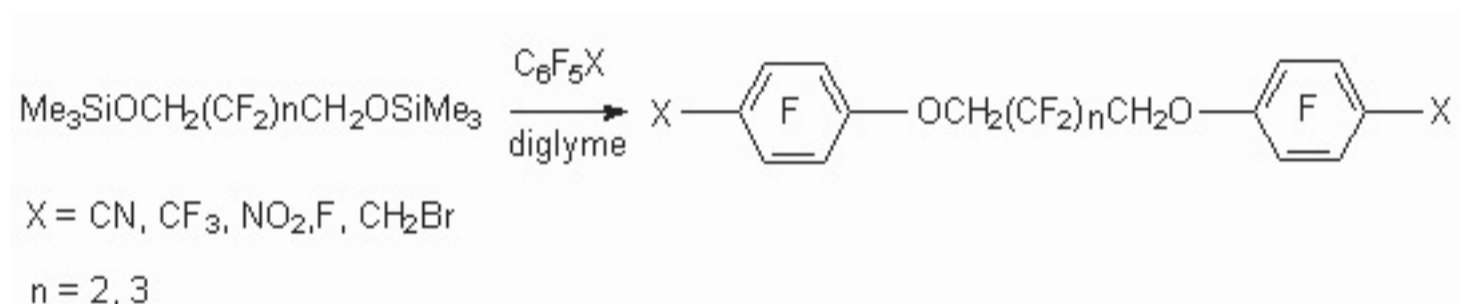
For reactions with pentafluoropyridine, pentafluorosubstituted benzenes like C₆F₅X (X = CN, CF₃, Cl, F), 1,4-diiodotetrafluorobenzene in the conditions of catalysis using fluoride-ion the following trimethylsilyl ethers of fluorocontaining alcohols are used: (CF₃)₂CHOSiMe₃, (CF₃)₃COSiMe₃, CH₃C(CF₃)₂OSiMe₃, PhC(CF₃)₂OSiMe₃, C₇F₁₇CH₂CH₂SiMe₃, CF₃CH₂OSiMe₃, CF₃C(CH₃)₂OSiMe₃, (CF₂CH₂OSiMe₃)₂, CF₂(CF₂CH₂OSiMe₃)₂ [62]. Likewise such ethers are introduced into reaction with tribromomethane.



Reactions with fluorocontaining ketones were put into practice, resulting in formation of perfluorinated alcohols, which are transferred into corresponding perfluorinated ethers [62].

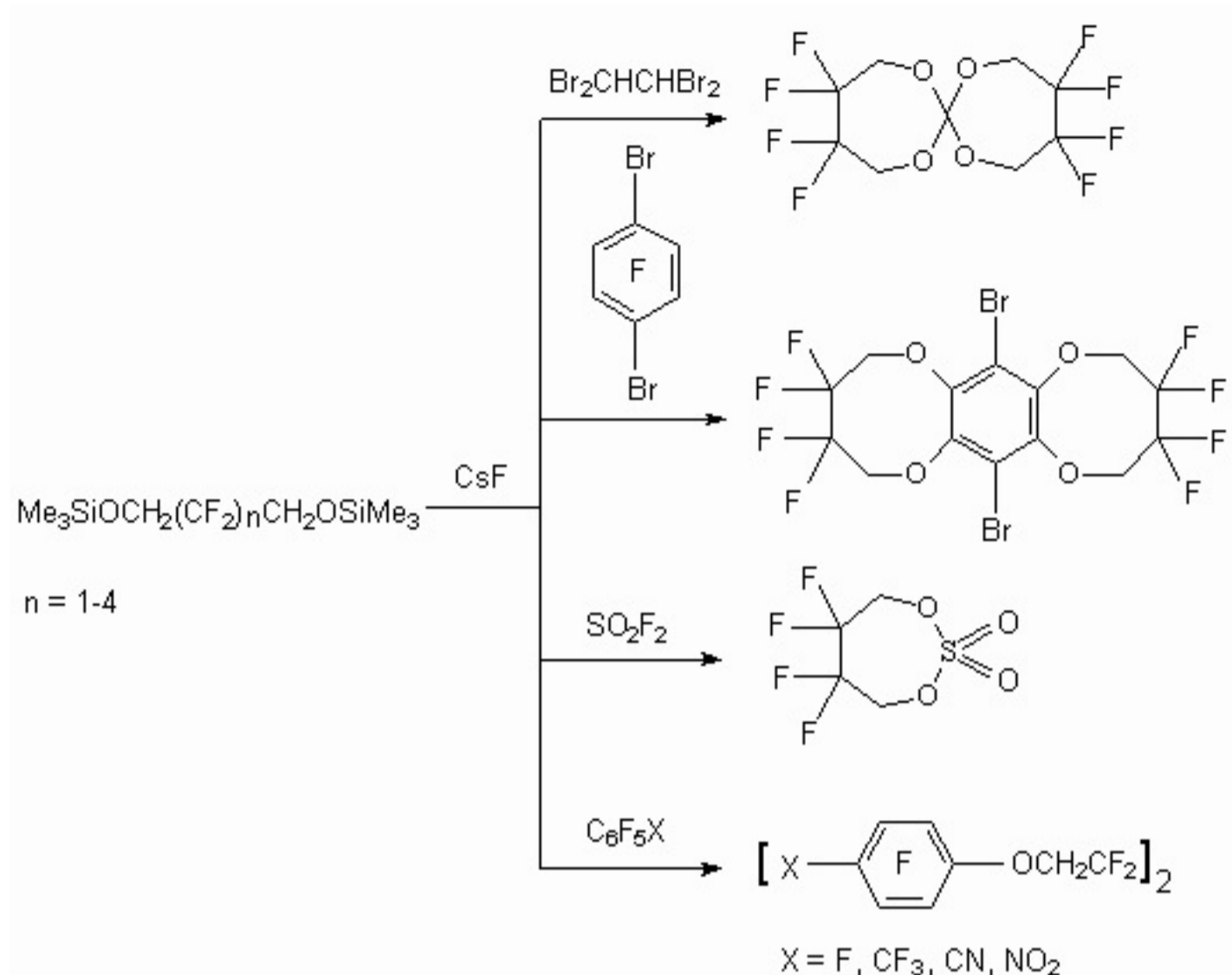


The reactions of bifunctional trimethylsilyl ethers of telomeric alcohols with polyfluorinated benzenes and pentafluorobenzylbromide in diglyme produce replacement products of fluorine atoms in benzene ring and bromine of CH₂Br group [63].

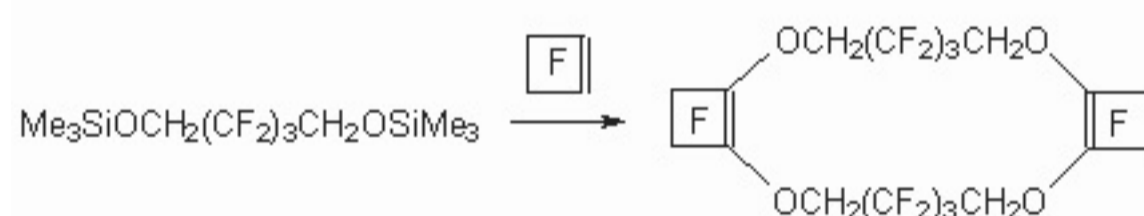


These compounds are liquids with freezing points -20 °C and boiling points 330-350 °C and they can be used as dielectric heat transfers with wide application field.

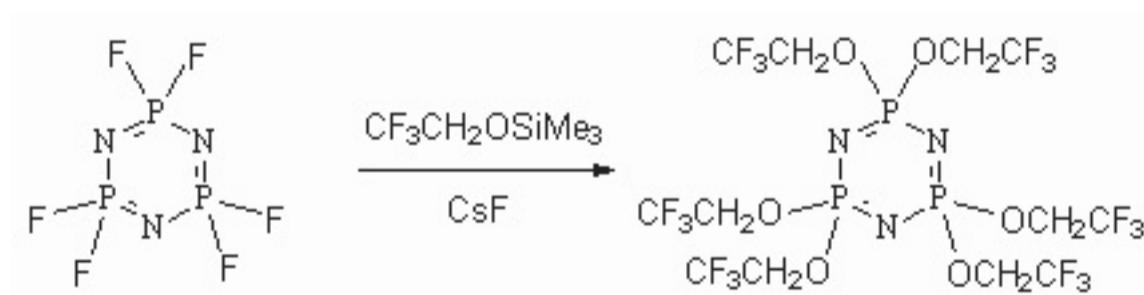
Compounds, possessing movable halogen atoms, also react in such reaction with formation of halogen atoms replacement products, besides this the formation of heterocyclic compounds exists [64].



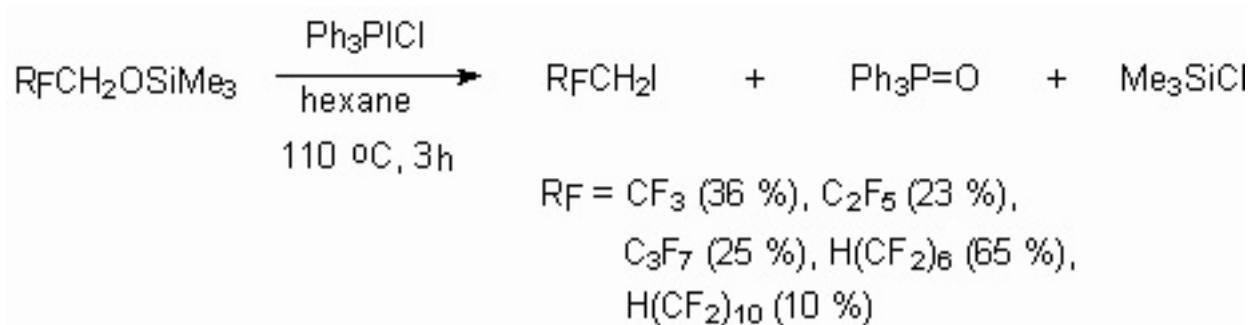
In the case of perfluorocyclic olefins the replacement of both fluorine atoms takes place at multiply bond with formation of polycyclic compound. It should be noted, that cycles like these can act as complex formers like crown ethers, for example with fluorine anion [65].



This method doesn't have any limits for practical purposes. Thus compounds, having movable fluorine atoms at phosphorus atom, are introduced into the reaction [66].

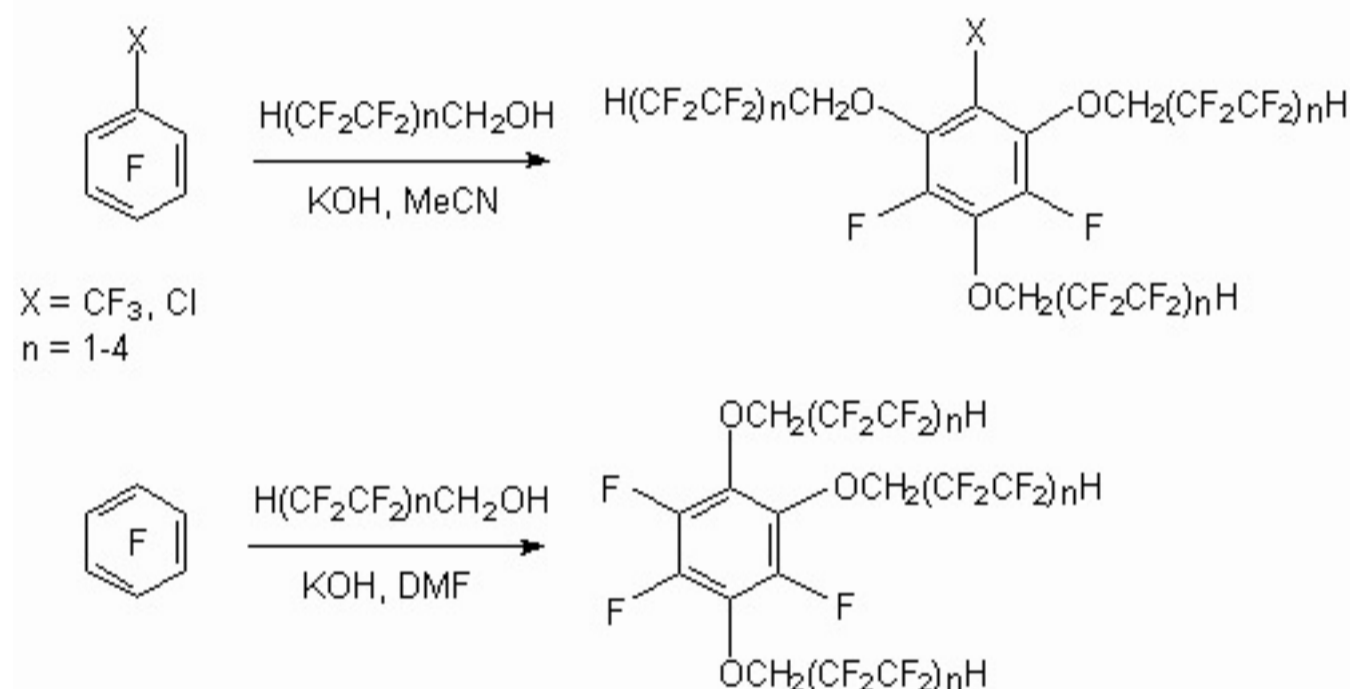


Polyfluoroalkoxytrimethylsilanes react with compounds of quinquivalent phosphorus with formation of polyfluoroalkyl iodides [67]. This is an interesting variant of transfer from telomeric alcohols to polyfluoroalkyl iodides. The key moment of this reaction is the formation of stable triphenylphosphine oxide.



2.2. Reactions of polyfluoroaromatic compounds with telomeric alcohols and creation of new fluorine materials on their basis.

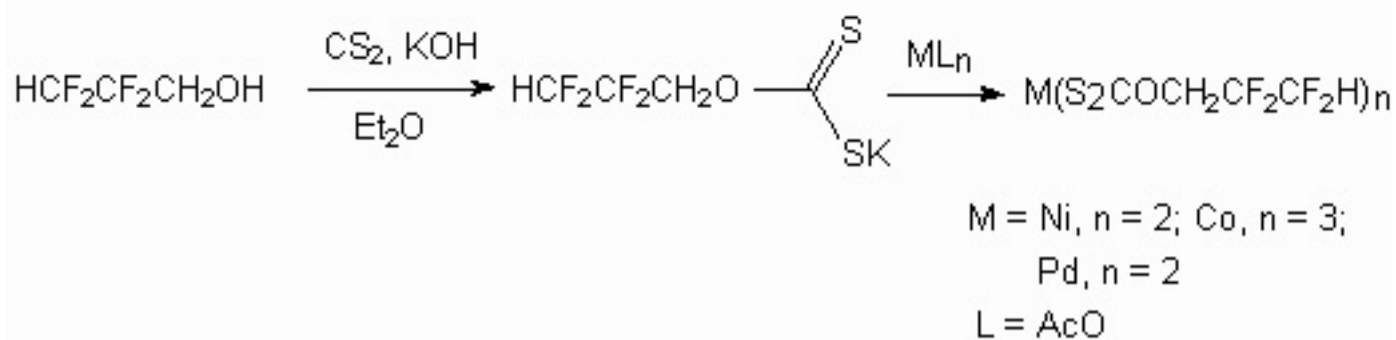
The reactions of telomeric alcohols with polyfluoroaromatic compounds in the presence of KOH results in formation of di- and tri-substituted products, which can be used as high temperature (more than 350 °C) liquids, used as lubricants, heat transfers and hydraulic liquids [68]. The demand of high temperature lubricants, which at moving details processing increase the mechanisms' function life due to their low constant of friction, is rather high. Along with this they can be used as lubricants for rolling mills of both steel and other metals. Another field of application is for oil equipment and oil lines, because such lubricants are not washed off with organic compounds compare to mineral oils.



Partly fluorinated alcohols reacts with other benzene polyfluoro derivatives: with 2,3,4,5,6-pentafluorostyrol /NaH [69], decafluoroazobenzene/CsF [70], deca-fluor-*m*-dimethylbenzene/NaH [71] with formation of replacement products of benzene ring fluorine atoms.

2.3. The interaction of telomeric alcohols and hetero-organic compounds.

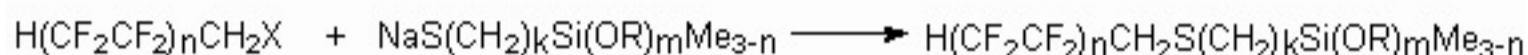
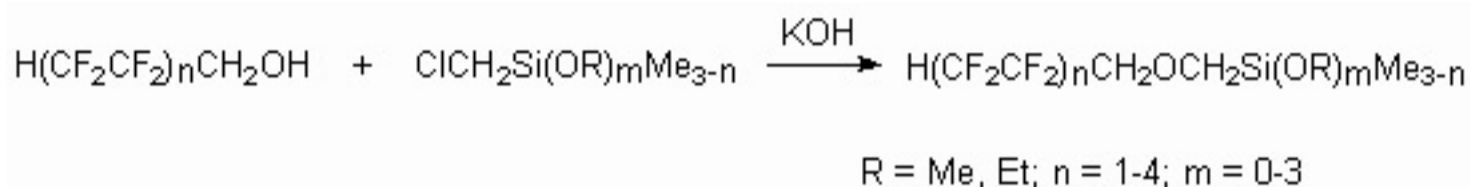
Technologically available 2,2,3,3-tetrafluoropropyl alcohol is used for synthesis of volatile xanthogenates of metals [72]. Thus the reaction of this telomeric alcohol with *carbon bisulfide* in absolute diethyl ether at 0 °C in the presence of KOH results in formation of potassium salt of 2,2,3,3-tetrafluoropropylxanthogenate, which later under the influence of nickel, cobalt, palladium salts produces corresponding salts.



Telomeric alcohols can be used in the following perspective directions. First of all, they can be used for flotation of gold and silver containing minerals. [73]. Thus at flotation of clay- silica ores the use of such telomeric alcohols allows to increase the gold yield at the rate of 8.9% and silver yield at the rate of 21.7% compare to use of potassium xanthogenate

Potassium 1,1,2,2-tetrafluoroethylxanthogenate was used at flotation of sulphide ores as collector for flotation separation of polymetallic concentrates [74].

Polyfluoroorganosilicon monomers form oil and water repellent bio-resistant coatings on the surface of different materials. Their production is based on the interaction of trihydroperfluoroalkane alcohols like $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{OH}$ or polyfluorohalogenalkanes like $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) with silicium compounds [75].

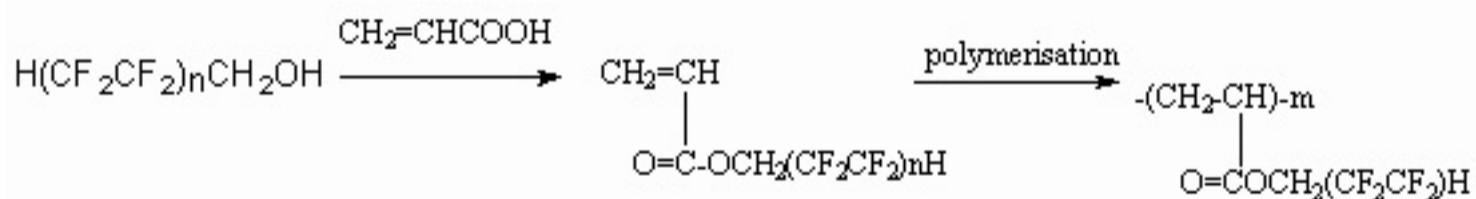


$\text{X} = \text{Cl}, \text{Br}$

From the last compounds were obtained corresponding siloxanes having useful technical characteristics .

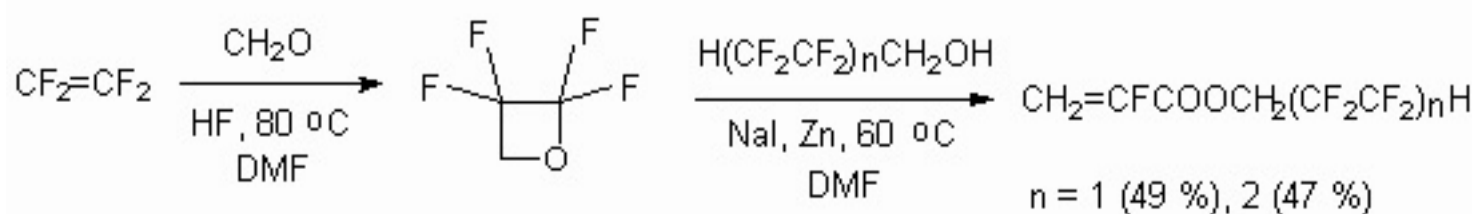
Deeply fluorinated di-epoxides are obtained at the reaction of alcohols like $\text{HCH}_2(\text{CF}_2)_n\text{CH}_2\text{OH}$ ($n = 3, 8$) with epichlorohydrin in the **basic** media in the presence of tetrabutylammonium hydrosulphate as catalyst [76].

It turned out, that fragment $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{O}$ in the polymer composition can call changes of its properties. Thus, modified polymethylmethacrylate especially co-polymer 1,1,3-trihydrotetrafluoropropyl-2-fluoroacrylate with 1,1,5-trihydrooctafluoroamylacrylate possess the properties of light guide [77].

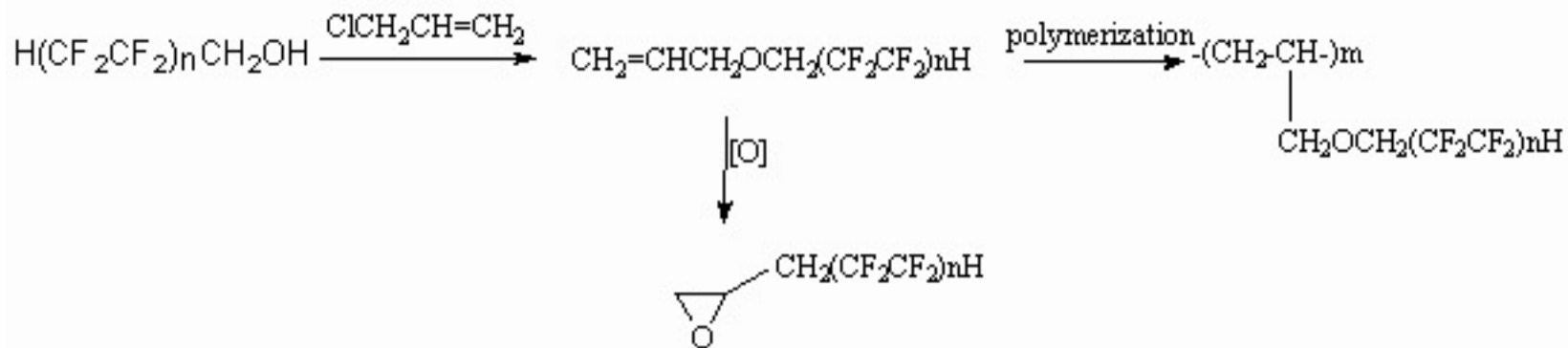


The polymer light guide index of refraction is rather low, the melt flow index for light reflecting cover applying is 10-30 g/10 min at 190 °C. They can be used for light guides production.

The obtaining of acrylic acid polyfluorinated esters can be carried out either by interaction of acrylic acid with telomeric alcohol in the presence of acid (for example, meta-toluenesulpho- acid), or by using of Prince reaction [78-80].



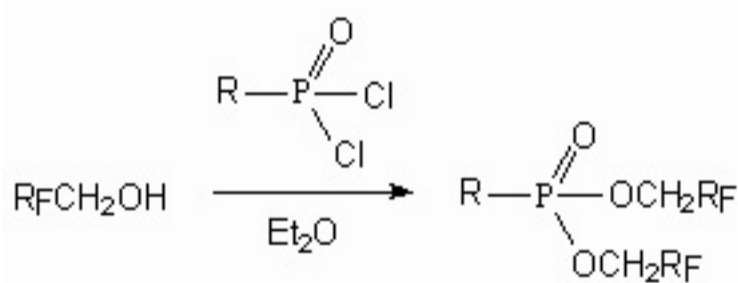
Fluorine anhydride α -fluoroacryl acid, which is transferred into esters by reaction with telomeric alcohols, is obtained using interaction of 2,2,3,3-tetrafluorooxetane, halides of alkali metals and dehalogenating agent in aprotic bipolar solvents in the presence of radical polymerization inhibitor [78-80].



Polymers α -fluoroacrylates noticeably exceed their meta-acrylic analogues in many operating parameters. Fluorine introduction into polymer ester part resulted in improvement of block organic glass properties and first of all in heat resistance and impact resistance. Excellent optical properties of such fluorine modified polymers in combination with high heat resistance, flexibility and water-resistance allow to use them in fiber optics. Refraction index of such polymers equal to 1.36 - 1.50 allows to use them as materials of light guide body and reflective cover [81-89]. They can be used as materials for optical storage devices of optical disks [84,90].

CH ₂ =CYCOOR		k ₀ , %	n _D ²⁰	a _n , kJ/m ²
Y	R	optical transmission		impact elasticity
F	CH ₂ CF ₂ CF ₂ H	91	1,398	95
	CH ₂ (CF ₂ CF ₂) ₂ H	90	1,379	77
	C(CF ₂) ₂ CF ₂ CF ₂ CF ₃	90	1,330	60
Me	CH ₂ CF ₂ CF ₂ H	91	1442	71
	CH ₂ (CF ₂ CF ₂) ₂ H	91	1,400	50
	C(CF ₂) ₂ CF ₂ CF ₂ CF ₃	90	1,346	62

Bis(fluoroalkyl)alkylphosphonates are obtained with the yield of 28-69 % at treatment of Cl₂P(O)R using telomeric alcohols in the presence of triethylamine [91]. Such compounds are used as hydraulic liquids.



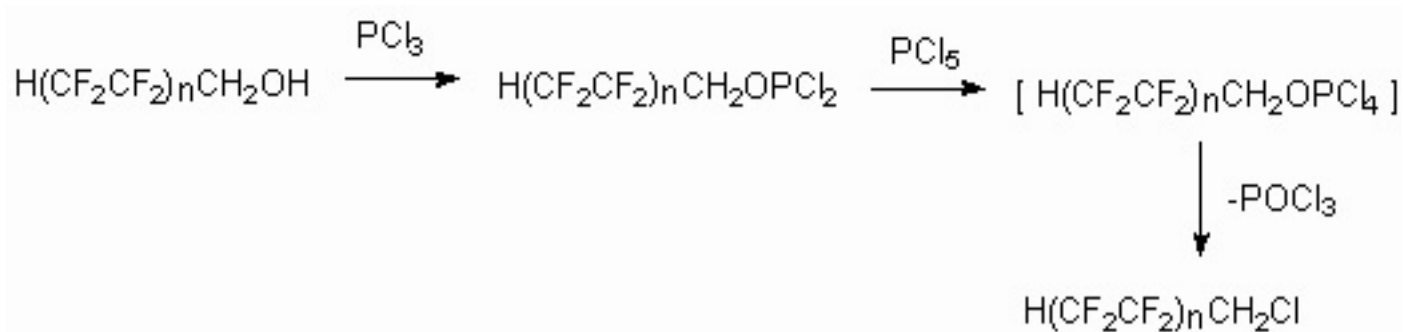
RF = CF₃CH₂, HCF₂CF₂CH₂, C₂F₅CH₂,

C₃F₇CH₂, (CF₃)₂CH

R = Me, Et, Pr, iPr

The reaction of phosphorus trichloride with alcohols like R_FOH (R_F = HCF₂CH₂, H(CF₂)₂CH₂, H(CF₂)₄CH₂, CF₃CH₂, C₂F₅CH₂, C₃F₇CH₂, (CF₃)₂CH, C₆F₁₃CH₂CH₂, CF₃Me₂C, (CF₃)₂MeC, CF₃CH₂CH₂) results in formation of phosphorus derivatives like (RFO)₂P(O)H with the yield equal to 42-89 % [92]. These compounds are more thermally stable compare to hydrocarbon analogues.

The important moment of telomeric alcohols interaction with phosphorus compounds was the synthesis of polyfluorohalogenalkanes - fluoroorganic semi-products [75]. Thus the polyfluorohalogenalkanes obtaining method by action of PCl₃ , PCl₅ (or PBr₅) onto telomeric alcohols was developed.

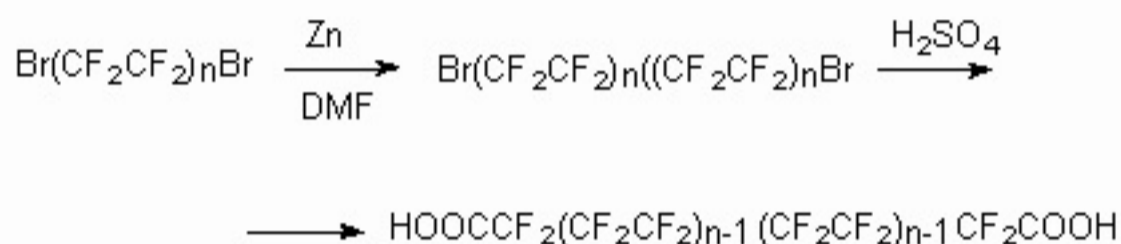


The transformation of telomeric alcohols $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{OH}$ ($n = 1-5$) into other semi-products, out of which important materials for techniques and medicine can be obtained, is an important way of fluorine containing materials synthesis.

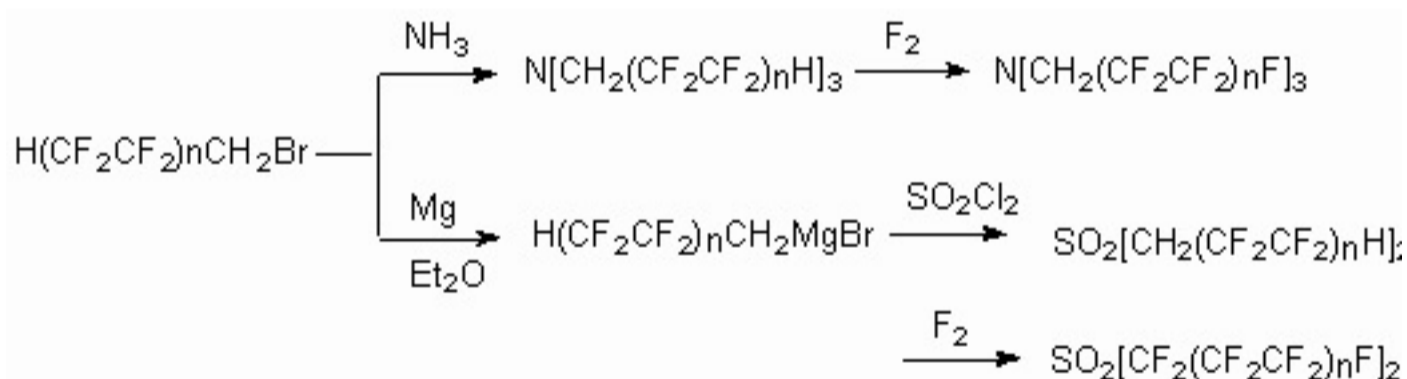
The use of telomeric alcohols' $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{OH}$ ($n = 1-5$) oxidization processes under the influence of halogens for creation of the new generation of blood substitutes and perfluorinated dicarboxylic acids.



$n = 8$ - new generation of artificial blood substitutes

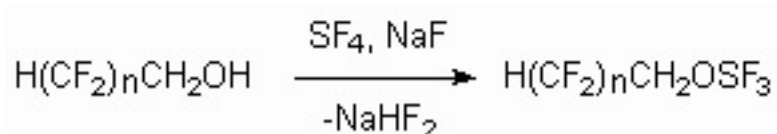


Later these semi-products are subject to transformation into hard-to-reach compounds, which now are in stable demand.

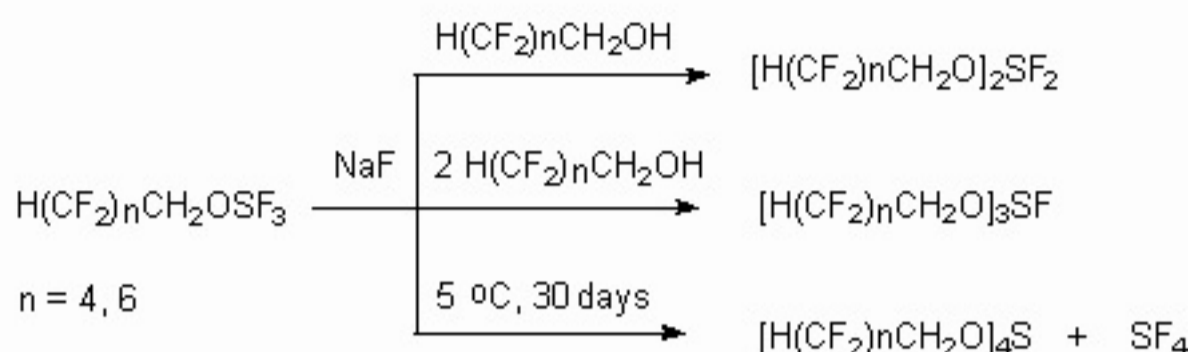


These compounds can be used as high temperature dielectrics, heat transfers, high parameters hydraulic liquids for electric machines, airplanes and aircrafts hydraulic systems. As these compounds are incompressible they can find their application as hydraulic liquids for robotics and they can be effective lubricating oils for machines' and mechanisms assemblies.

In few cases the introduction of $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{O}$ group into molecule essentially influences the stability of organic molecule. Thus, the authors of works [93,94] for the first time have put into practice the synthesis of stable organic compounds of tetravalent tetracoordinated sulphur. Such model compounds with trihydropolyfluoroalkoxyl group turned out to be rather stable compounds.

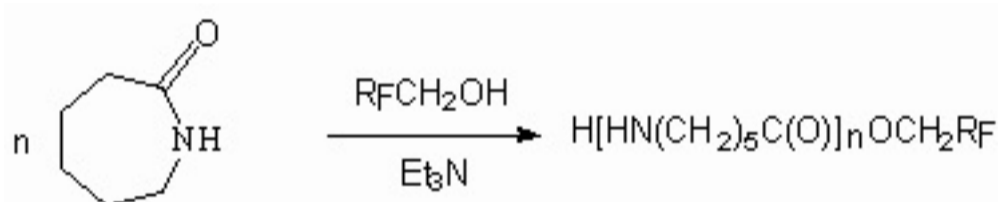


$$n = 2, 4, 6, 8$$



Sulforanes possess polyfluoroalkylating properties, react with nucleophilic reagents, act as fluorinating and dehydrating reagents [95-98].

It is stated [99,100], that carrying out ϵ -caprolactam reaction with 1,1,3-trihydroperfluoropropanol in DMF and trimethylamin results in formation of esters (ϵ -aminocaproic acid oligomers with the yield equal to 36% (during 4 hours at 220-260 °C). Poly-fluorinated esters (ϵ -aminocaproic acid oligomers can be used as metals' protection material against corrosion, as anticorrosion hydrophobic coats for protection of articles surface against aggressive medias, they also might be perspective regards antiviral activity. They are easily put on different surfaces in the form of varnishes.

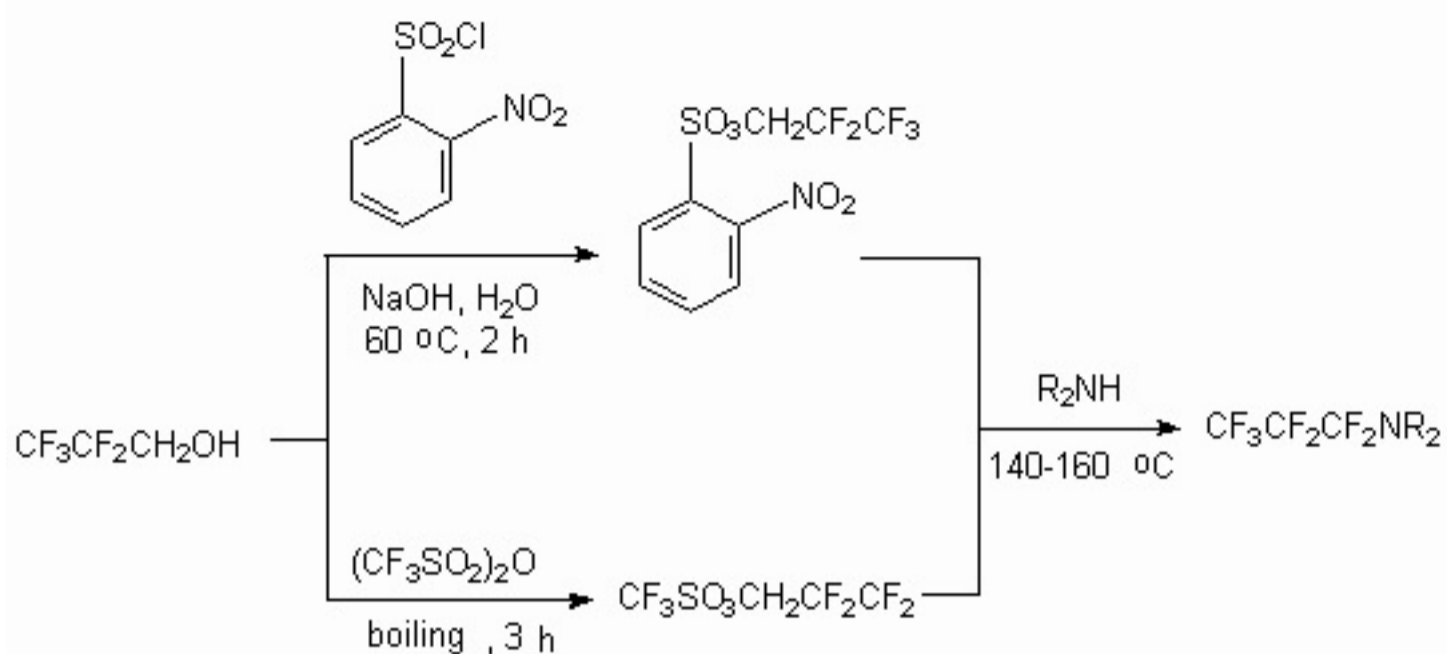


As the length of telomeric alcohol carbon chain increases the yield of dehydrofluorination and polymerization by-products increases also. Thus for $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{OH}$ prolonged inductive period (more than 60 minutes) is observed, the oligomer yield for the period of 4 hours is 61% at fractional conversion equal to 74%. In this process the solvent is used as catalyst. Copper acetate appeared to be more effective as catalyst.

The authors of work [101] showed the opportunity of associative interactions of polycaproamide with telomeric alcohols $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{OH}$ ($n = 1,2$). Polycaproamide forms homogeneous solutions at 15 °C ($n = 1$, during 18 min, $n = 2$, during 37 min) with concentration of polymer equal to 0.1-3 %. At heating up to 50-80 °C the concentration rises up to 15 %, and at boiling point of alcohol - up to 25 %. Such polycaproamide modified by telomeric alcohols reveals higher thermal stability and can be recommended for use in compositions with lowered flammability, in mechanical rubber articles with higher aggressive resistance and resistance to gasoline and also for obtaining articles with higher wearing qualities.

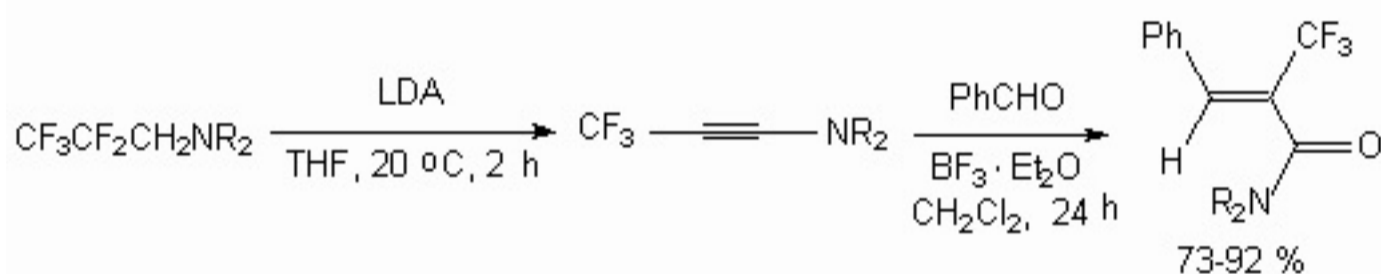
Ketones and aldehydes are subject to oxidization according to Baeyer-Villiger type using hydrogen peroxide in the presence of catalyst in the media of fluorinated alcohols $\text{R}^1\text{R}^2\text{R}^3\text{COH}$ ($\text{R}^1\text{-R}^3 = \text{C}_n\text{F}_{2n+1}$, H, $n = 1-6$) . Thus, the mixture of cyclohexanone, 1,1,1,3,3,3-hexafluoropropan-2-ol and *para*-toluenesulfonic acid under action of hydrogen peroxide at 60 °C during 65 min produce ϵ -caprolactam with 99 % yield [102].

Telomeric alcohols are used for obtaining of different derivatives due to the fact that the transformation of alcohol group take places. Thus, using sulfoesters they were turned into trialkylamines with high stereoselectivity and high effectiveness [103].

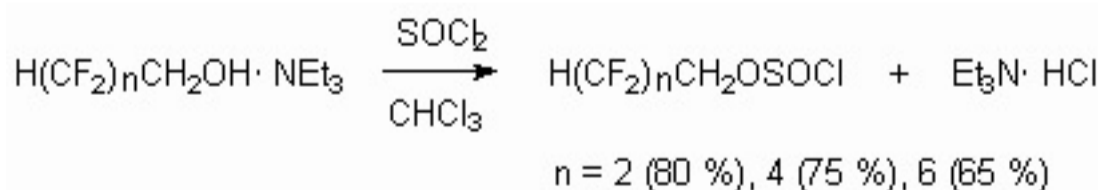


$\text{NR}_2 = \text{Bu}_2\text{N}$ (150-160 °C, 6 h) (48%); (60 °C, 1 h) (93%);
 BnNMe_2 (150-160 °C, 4 h) (86%);
 piperidine (boiling, 1 h) (79%);
 $i\text{Pr}_2\text{NH}$ (boiling, 24 h) (45%);
 Bn_2NH (boiling, 24 h) (49%)

Such amines at action of bases transform into α -(trifluoromethyl) β -unsaturated amines.



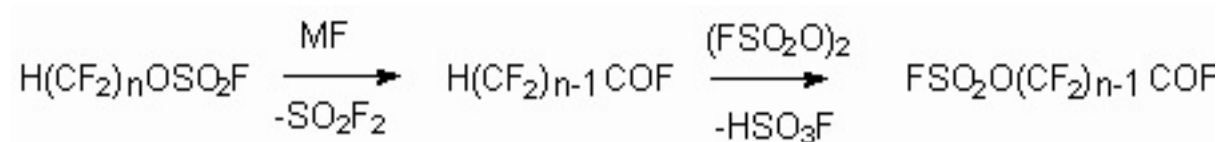
Polyfluoroalkylchlorosulphites synthesis out of available for industry telomeric alcohols by their treatment with sulfuryl chloride and thionyl chloride was worked out [23]. The reaction doesn't run when without catalysts, but goes in the presence of tertiary amines (triethylamine, urotropine and others). It is stated, that initially complexes of structure $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{O}^-\text{NHEt}_3$ are formed (heat of formation for $n = 1$ complex is 19.8 kJ/mol, for $n = 2 - 21.6$ kJ/mol). At treatment of last mentioned with thionyl chloride the yield of polyfluoroalkylchlorosulphites $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{S}(\text{O})\text{Cl}$ reaches more than 80 % at conversion of alcohol more than 92 % [23]. The constants of reaction speeds are determined, that reactions run according to the second order. The reaction is carried out in the media of inert solvent (CHCl_3 , CCl_4). To depress the formation of *bis*-polyfluoroalkylsulphite it is necessary to use the 1.5-2.5 mol of thionyl chloride excess.



Polyfluoroalkylchlorosulphites in contrast to non-fluorinated analogues are resistant compounds up to 100 °C. The rate constant of decomposition reaction is determined as first order. The authors explain this as particularities of internal molecule associative interactions of CH_2 group hydrogen atom with chlorosulphite group oxygen, which makes difficult the attack of electrophilic carbonic atom of chlorine, that usually results in destruction with extraction of sulfurous anhydride and formation of chloroalkane. Telomeric alcohols' reaction with sulfuryl chloride the corresponding polyfluoroalkylfluorosulphates, which are new polyfluoroorganic syntones are obtained [75].

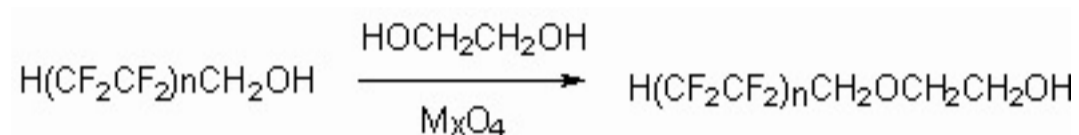
Fluorosulphates are colorless easy movable resistant to liquid hydrolysis ($n < 8$) or solid compounds ($n > 8$) stable at prolonged storage. Their most important characteristic is turning into fluoroanhydrides ω -

hydroperfluorocarboxylic acids at treatment using metal fluorides. This is used as obtaining method of poly-fluorinated carboxylic acids [104].



The further hydrogen replacement for FSO₂O group results in formation of ω-(fluorosulfonyloxy)perfluoroacylfluorides, the initial semi-products for production of ion-exchange membranes [105].

Polyfluoroalkylchlorosulphites and polyfluoroalkylchlorosulphates are used as alkylating reagents for monomers' production, as hydraulic liquids, heat transfers and surface active materials. It is stated that, reaction of fluorinated telomeric alcohols with alcohols is catalyzed by metal oxides of 2-nd and 3-d groups and proceeds through formation of glycols and polyfluoroalcoholates of metals. The reaction products are used for monomers' production and peroxides initiators. [106].



$n = 1-5$

The reaction rate increases twice at change from telomeric alcohols $n=1,2$ to telomeric alcohols $n=3-5$.

Polyfluoroalkylchlorosulphites easily react with KF, LiCl, KBr, KI with formation of corresponding polyfluoroalkylhalogenides with the yield of 75-90 %. The interaction of polyfluoroalkylchlorosulphites with the salts of acrylic and methacrylic acids results in obtaining of corresponding esters with the yield of 80 % [107]. On the basis of these monomers the co-polymer for contact eye-lenses is obtained.

to be continued