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Synthesis and Application of Fluorine-Containing Ethers Based on Perfluoroolefins

G. G. FURIN

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademika Lavrentyeva 9, Novosibirsk 630090 (Russia)

E-mail: furin@nioch.nsc.ru

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Abstract

Methods of synthesis of fluorine-containing dialkyl and fatty-aromatic ethers involving the reactions of aliphatic alcohols and phenols, including aromatic ones, with perfluoroolefins are considered. To obtain various fluorine-containing polyethers, polyhydric alcohols were used in reactions with perfluorinated tri-, tetrafluoroethylene and hexafluoropropylene. Some properties of fluorine-containing ethers are discussed; examples are their application are presented.

INTRODUCTION

Due to thermal and electrophysical properties of perfluorinated dialkyl ethers, these compounds are used as new dielectrics in electric devices and machinery. Complete substitution of hydrogen atoms with fluorine in the carbon chain promotes improved thermal stability and resistance to the action of oxidizers, a decrease in freezing point, improvement of electrophysical and thermal characteristics of molecules in general, an increase in lubricating property [1–5]. The high strength of C–O, C–C, C–F bonds in perfluorinated polyethers, flexibility of chains and small value of interaction between the chains provide a set of properties essential from the viewpoint of application of these compounds in machinery, namely, a combination of high thermal and chemical stability with good low-temperature properties. Due to this, perfluroinated ethers are widely used in machinery as thermally and chemically stable oil, lubricants and liquids. Stabilized perfluoropolyethers are stable to the action of strong acids and bases even at elevated temperature (above 100 °C) and do not change their physicochemical properties under radiation with the dose rates up to 10^8–10^9 rad [6], which allows one to use them as liquid dielectrics, heat carriers, lubricants, inert solvents in electronic industry, and during the recent years as the components of freons not dangerous for ozone. Not only improved characteristics of electric strength and low electric conductivity are important in this situation but also high thermal properties which are characteristic of the liquid state of substance. Modern requirements to electronics and electric machines are very high; a trend to more severe requirements can be observed: first of all, it is microminiaturization and therefore an increase in the local electric field strength, thermal fluxes and the power of high-frequency fields. These problems to be solved are closely connected with the development of dielectric heat carriers based on perfluorinated organic compounds used both in liquid and in vapour phase.

3M Company (USA) developed HFE 7110 Freon ($CH_3OCF_2CF_2CF_2CF_3$), however, it has several disadvantages, too, while tetrafluoroethyldifluoromethyl ether ($CHF_2CF_2OCHF_2$) can replace Freon 11 as a frothing agent in the production of foam plastics and can be used instead of perfluorinated hydrocarbons for dry etching in microelectronics [7]. Ethers like $C_4F_9OCH_3$ (m.p. 61 °C), $(CF_3)_2CFCF_2OC_2H_5$ and so on are used to extract lavender essential oils (good results with respect both to the quality of extracted substance and to the purity of formed oil were obtained [8]), and also as cleaners to clean silicone substrates (mixture composition, %: HF 1.3, *i*-PrOH 6.7, 40 % $C_4F_9OCH_3$ + 60 % $(CF_3)_2CFCF_2OCH_3$ 92) [9]. In addition, they are used as solvents to carry out chemical reactions, in particular to synthesize the amides of fluoropolyalkyl ethers for magnetic reproducing media [10], oxidation of tetrafluoroethylene [11] and as solvents transporting organic compounds [12]. These fluorinated solvents destroy the ozone layer to a smaller extent. The addition of $C_4F_9OCH_3$ to nitrogen increases the flame-extinquishing capacity of the system by 31.5 %, which allows one to increase the efficiency of nitrogen (and other inert gases) in fire put out due to a decrease in the necessary volume of flame-extinquisher [13].

The main methods of synthesis of this class of compounds are based on fluorination of hydrocarbon analogues [14, 15]. However, the yield of target products obtained using this method is rather low. For example, fluorination of monoglyme and diglyme with elemental fluorine results in perfluorinated products with the yield of 21 and 16 %, respectively [16]; similar values were also obtained for electrochemical fluorination. However, using an apparatus of special design, Lagov and coworkers [17–19] succeeded in obtaining perfluorinated dialkyl ethers with branched radicals and a good yield. The majority of perfluorinated crown ethers and perfluorocryptands were obtained using this procedure [20]. Another method of obtaining perfluorinated products is fluorination of polyethers involving destructive decomposition of the polymer chain along with fluorination itself [1].

At present, the most efficient method to synthesize perfluorinated dialkyl ethers is fluorination of partially fluorinated ethers obtained by means of the action of aliphatic alcohols on available perfluoroolefins [5]. We suppose that this method has substantial advantages and allows cost-effective synthesis of various perfluorinated dialkyl ethers. The goal of the present review is to analyse this approach and to determine the range of the practical application of perfluorinated dialkyl ethers.

A number of basic problems, which cannot be solved without the development of the chemistry of partially and fully fluorinated ethers will be considered below.

REACTIONS OF PERFLUOROOLEFINS WITH ALIPHATIC ALCOHOLS AS A WAY TO SYNTHESIZE PARTIALLY FLUORINATED DIALKYL ETHERS FOR VARIOUS APPLICATIONS

The problem of the development of new ozone-safe solvents is to a great extent determined by the possibility to replace Freon 113, which is widely used as a solvent but prohibited for production. Analysis of the properties of this freon shows that its main disadvantages are: limited and low solubility of hydrocarbon oils in it, and insolubility of fluorinated organic and organosilicon liquids. Up to now, no ideal alternative has been found for Freon 113 that would correspond in all the parameters to the compound to be replaced. Because of this, it is still urgent to obtain such a substitute.

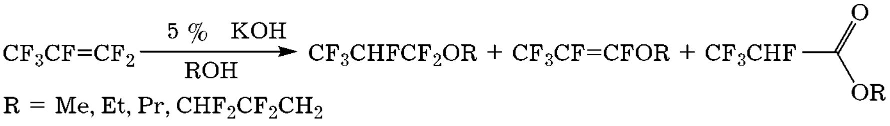
The authors of [21] proposed hexafluorocyclobutane as one of the alternatives. Its synthesis method starting from dichlorohexafluorocyclobutane (the latter being synthesized by dimerization of trifluorochloroethylene) makes it commercially available and effective solvent.

It was assumed [22] that partially fluorinated dialkyl ethers can be an alternative for Freon 113. Their synthesis is carried out according to a known reaction of tetrafluoroethylene, octafluoroisobutylene and hexafluoropropylene with alcohols in the presence of bases. For instance, the reaction of tetrafluoroethylene with aliphatic alcohols proceeds in the presence of KOH at temperatures 50–100 °C and pressure 9–16 kgf/cm^2 [22]:

$$CF_3CF{=}CF_2 \xrightarrow[KOH]{ROH} CF_3CHFCF_2OR$$

$R = Me, Et, Pr^i, HCF_2CF_2CH_2$

The reactions of tetrafluoroethylene with partially fluorinated alcohols become important. For example, 1,1,2,2-tetrafluoroethylmethyl ether was obtained by the interaction of tetrafluoroethylene with methyl alcohol in the presence of NaOH in a-pinene at a tempera-



Scheme 1.

ture of 40 °C and a pressure up to 15 kgf/cm^2 [22]. The reaction of tetrafluoroethylene with 2,2,2-trifluoroethyl alcohol proceeding in the presence of KOH in tetraglyme [23, 24] or in *tert*-butyl alcohol [25] results in the formation of $CF_3CH_2OCF_2CHF_2$ ether with a high yield (up to 99.99 %). It was established that the interaction of hexafluoropropylene with alcohols in the presence of an alkali [26, 27], alcoholates in toluene [28], dioxane [29] and methanol [30] at a temperature of 20–40 °C performed by passing gaseous hexafluoropropylene through the solution or in an autoclave results in the formation of the products of alcohol addition to the double bond. The direction of the reaction is only slightly dependent on its conditions. Hexafluoropropylene with polyoxyalkyleneglycoles in the presence of the trace amount of water form the products of addition to the olefin double bond [31] (Scheme 1).

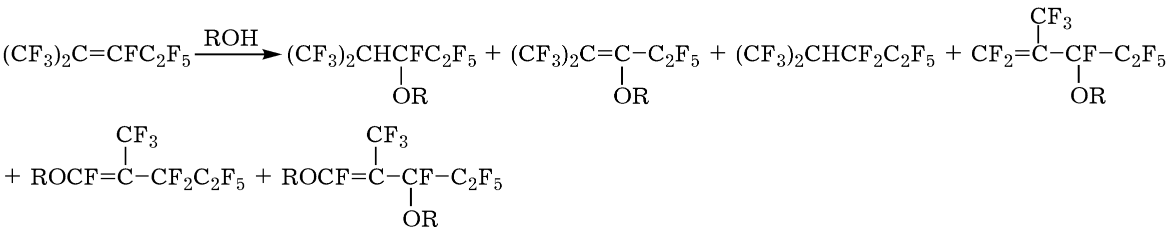
It was shown [32] that the action of methyl alcohol on hexafluoropropylene dimer in the presence of KOH or triethylamine in tetrahydrofuran (acetone, acetonitrile, dimethylformamide) results in the formation of the products of substitution of the fluorine atom at the unsaturated bonds and the products of addition to these bonds. Depending on the ratio of reacting molecules, the formation of methyl ethers of unsaturated perfluorinated acids and substituted ketones is observed [33]. At the same time, the introduction of two methoxy groups into perfluoro-2-methylpent-2-en occurs: isomeric 1,3-dimethoxyperfluoro-2-methylpent-1-enes are formed (yield: 51 %). Perfluoro-4-methylpent-2-ene reacts only with sodium methylate forming isomeric 1,3,4-trimethoxyperfluoro-2-methylpent-1-enes at a ratio of 3 : 1 (yield: 57 %) [33].

The interaction of a mixture of isomeric trimers of hexafluoropropylene with alcohols in the presence of trialkyl amines (preferably triethylamine) in a solvent (dimethylformamide, dioxane, acetonitrile) at a temperature of 20–150 °C results in the formation of the ether with the yield of 82 %. In this case, it is not necessary to separate isomeric trimers (using the products obtained industrially) because these isomers are transformed into each other under the action of triethylamine; the most reactive one enters the reaction [33].

Fully fluorinated dialkyl ethers are synthesized in two stages. At first, the interaction of octafluoroisobutylene with aliphatic alcohols results in the formation of addition products, then their electrochemical defluorination is carried out in anhydrous hydrogen fluoride. This method was used to synthesize $(CF_3)_2CFCF_2OC_nF_{2n+1}$ ether (n = 1–4); it can be used as a solvent [34–36].

The interaction of internal perfluoroolefins with alcohols proceeds only in the presence of bases giving the products of addition and substitution of fluorine atoms, as well as the products of more complicated transformations [37]. The reaction of polyfluorinated alcohols with perfluoroolefins is usually carried out without preliminary isolation of alkaline metal alcoholates but in the presence of bases [38–40], for example sodium hydroxide [41, 42], triethylamine, mercury acetate [43], *etc.* Polyfluorinated alcohols interact with perfluoroolefins in the presence of sodium hydride [43] giving rise to the products of substitution of the fluorine atom at the unsaturated bond. In this situation, cesium fluoride turned out to be an efficient catalyst also in the reactions of perfluoroolefins with a,a,w-trihydroperfluorinated alcohols [44]. In the case when a base is taken in a microquantity, the major products are those formed by substitution; an increase in the amount of the base causes an increase in the amount of unsaturated products (vinyl ethers) in the products. The use of Et_3N gives the product of substitution of the fluorine atom at the internal unsaturated bond, while the product of insertion of two alkoxy groups dominates in the presence of NaOH (Scheme 2).

Relatively easy addition and substitution under the action of a nucleophilic reagent on a

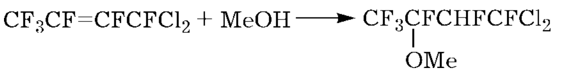


$$(CF_3)_2C{=}CFC_2F_5 \xrightarrow{ROH} (CF_3)_2CH\underset{OR}{C}FC_2F_5 + (CF_3)_2C{=}\underset{OR}{C}{-}C_2F_5 + (CF_3)_2CHCF_2C_2F_5 + CF_2{=}\overset{CF_3}{C}{-}\underset{OR}{C}F{-}C_2F_5$$

$$+ ROCF{=}\overset{CF_3}{C}{-}CF_2C_2F_5 + ROCF{=}\overset{CF_3}{C}{-}\underset{OR}{C}F{-}C_2F_5$$

Scheme 2.

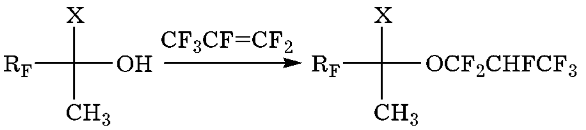
perfluoroolefin is due to spatial and electron effects in the carbanion formed as an intermediate product. The site of the primary attack of the alkoxy anion is also determined by electron and spatial factors. For instance, the action of methyl alcohol and phenol on *trans*-1,1-dichlorohexafluorobut-2-ene results in the formation of addition products affecting the carbon atom of unsaturated bond in position 3 [45]:



$$CF_3CF{=}CFCFCl_2 + MeOH \longrightarrow CF_3\underset{OMe}{C}FCHFCFCl_2$$

Perfluorinated ethers with the number of carbon atoms equal to 3–6 were obtained by the interaction of the initial fluoroolefin with low-molecular alcohols (methyl, ethyl, propyl) followed by fluorinated of the intermediate products with elemental fluorine. These compounds are characterized by boiling points 40–150 °C and can be used as new ozone-safe multipurpose freons.

We suppose that such an approach has substantial advantages and allows one to obtain various polyfluorinated dialkyl ethers in a cost-effective manner. Indeed, the method of synthesis of partially fluorinated ethers turned out to be rather general; along with primary alcohols, also secondary and tertiary ones were used in it. For example, a secondary and a tertiary alcohols react with hexafluoropropylene forming ethers (**1a, b**) according to the scheme



$$R_F{-}\overset{X}{\underset{CH_3}{C}}{-}OH \xrightarrow{CF_3CF=CF_2} R_F{-}\overset{X}{\underset{CH_3}{C}}{-}OCF_2CHFCF_3$$

1a, b

$R_F = CF_3CHFCF_2, X = H$ (**a**);

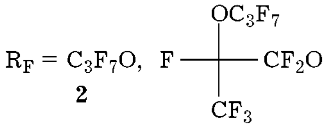
$R_F = CF_3CHFCF_2, X = CH_3$ (**b**).

The interaction of equimolar amounts of perfluoro(2-propoxy-2-propoxy)-ethylene **3** and an alcohol (methyl, ethyl, b,b,b-trifluoroethyl, 2-methoxyethyl, 2-ethoxyethyl, isopropyl, butyl, 1-pentafluorophenylethyl) or phenol derivatives (pentafluorophenol, 4(2-methoxyethyl)-phenol) in the presence of an equimolar amount of KOH in tetrahydrofuran (tetramethyloene sulphon, DMSO, acetonitrile) results in the formation of the products of addition to the unsaturated bond – perfluoro-2-propoxy-3-(1′H)-ethoxy-2′′-alkoxypropanes [46–49]:

$$R_F{-}CF{=}F_2 \xrightarrow[THF]{AlkOH,KOH} R_F{-}CHFCF_2OAlk$$

$Alk = Me, Et, Pr^i, Bu^n, CF_3CH_2,$

$CH_3OCH_2CH_2,\ C_2H_5OCH_2CH_2$



$$R_F = C_3F_7O,\ F{-}\overset{OC_3F_7}{\underset{CF_3}{C}}{-}CF_2O$$

2 **3**

The reactions of olefin **2** with $CF_3(CF_2)_7CH_2CH_2OH$ in the presence of NaH at 80 °C leads to the formation of the product of addition to the double bond (yield: 79.2 %), which is then fluorinated with elemental fluorine at 20 °C under ultraviolet irradiation to form $C_3F_7OCF_2CF_2O(CF_2)_9CF_3$ (yield: 69.9 %) [50].

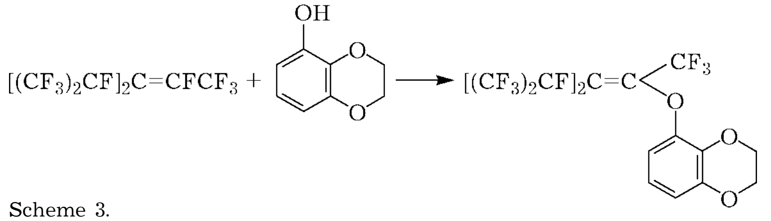
SYNTHESIS OF FLUORINATED ALIPHATIC-AROMATIC ETHERS

Among widely used herbicides, a substantial place is occupied by fluorinated diphenyl ethers and the compounds containing phenoxy group. One of the approaches to the synthesis of this class of compounds is based on nucleophilic substitution of fluorine atoms with O-nucleophilic reagents in internal perfluoroolefins. The majority of aromatic compounds containing OH group act as efficient O-nucleophilic reagents under the catalytic conditions. Thus, it was shown [51] that the reaction of phenol with tetrafluoroethylene at

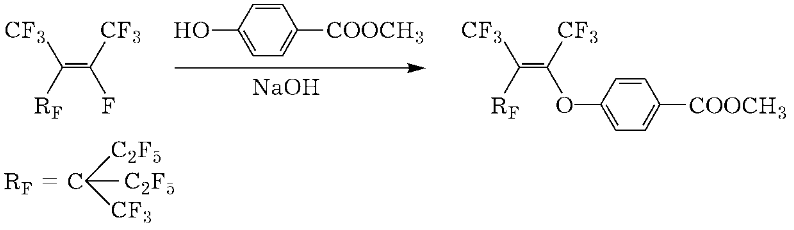
150 °C in acetonitrile–water in the presence of KOH for 14 h results in the formation of 68 % $PhOCF_2CHF_2$. Similarly, hexafluoropropylene dimer and trimer react with phenol in the presence of triethylamine [52, 53] or sodium phenolate, *para*-cresol [54], hexafluoropropylene dimer and N-(4-hydroxyphenyl)acetamine [55], hexafluoropropylene trimer and 3-oxybenzdioxan [56], tetrafluoroethylene pentamer and the methyl ester of 4-oxybenzoic acid [57] forming the products of substitution of the fluorine atom at the internal double bond (Scheme 3). The latter may be used as high-temperature heat carriers, dielectrics and lubricants, and also for the synthesis of various surfactants (Scheme 4).

Similar results were obtained for the reactions of phenol with the dimers and trimers of hexafluoropropylene in the presence of Et_3N [52, 53, 58] (Scheme 5).

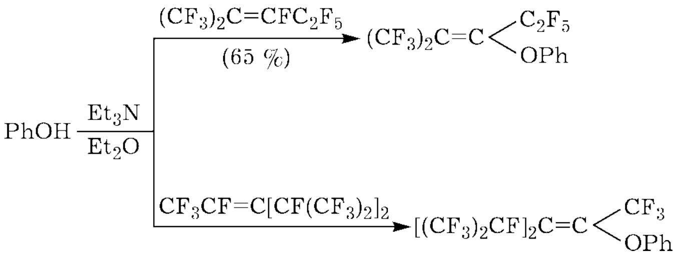
It should be kept in mind that, as a result of mutual transformations of isomeric hexafluoropropylene trimers under the action of bases, the reaction of *e.g.* perfluoro-2,4-dimethylhept-3-ene with sodium phenolates can result in the formation of a mixture of monosubstituted derivatives [52] (Scheme 6).



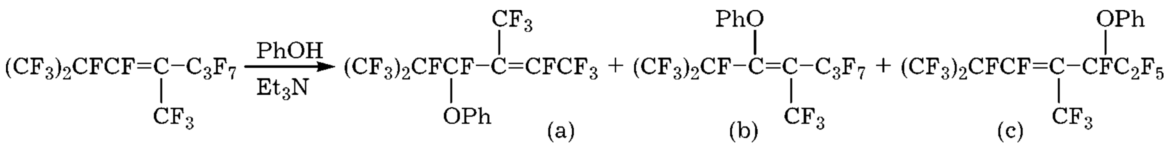
Scheme 3.



Scheme 4.



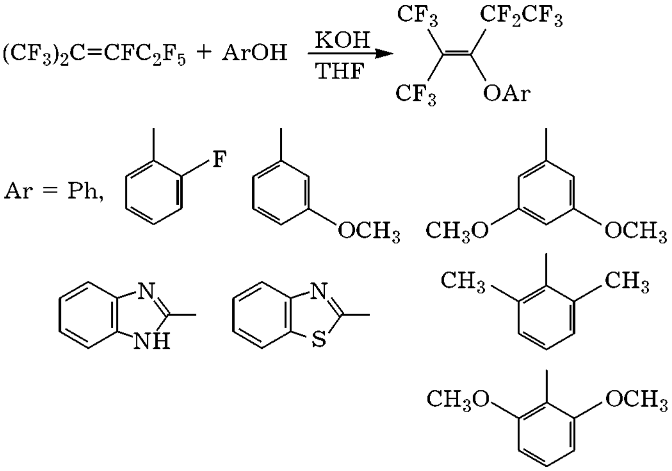
Scheme 5.



$$(CF_3)_2CFCF{=}\underset{CF_3}{C}{-}C_3F_7 \xrightarrow[Et_3N]{PhOH} \underset{(a)}{(CF_3)_2CF\underset{OPh}{C}F{-}\overset{CF_3}{C}{=}CFCF_3} + \underset{(b)}{(CF_3)_2CF{-}\overset{PhO}{C}{=}\underset{CF_3}{C}{-}C_3F_7} + \underset{(c)}{(CF_3)_2CFCF{=}\underset{CF_3}{C}{-}\overset{OPh}{C}FC_2F_5}$$

Reagent	Solvent	Yield, %		
		(a)	(b)	(c)
PhONa	Et_2O	46	12	2
$PhOH/Et_3N$	Et_2O	–	2	56
$PhOH/Et_3N$	DMF	–	7	87
$4\text{-}MeCOC_6H_4OH/Et_3N$	DMF	–	10	35

Scheme 6.

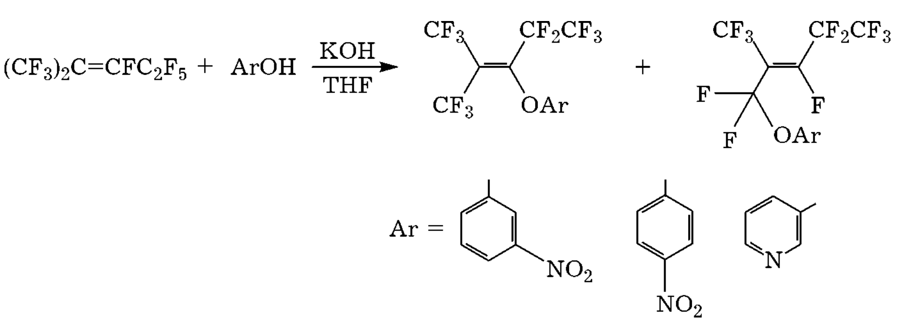


Scheme 7.

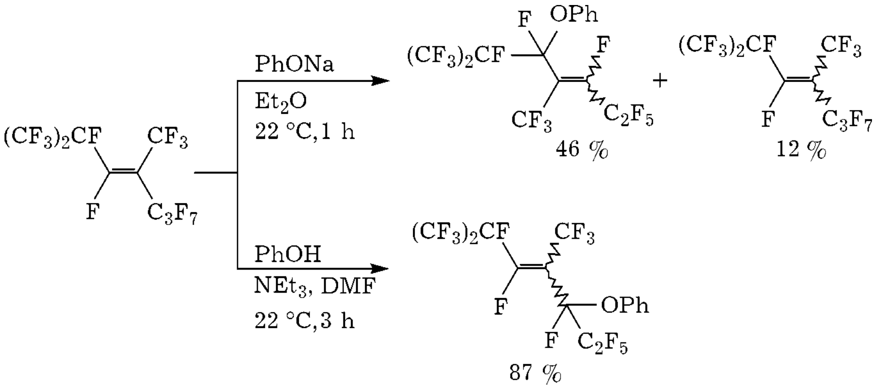
It was shown previously that the interaction of phenol with perfluoro-2-methylpent-2-ene in the presence of KOH in tetrahydrofuran leads to the formation of [3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-oxypropenyl]benzene [59], a product of the formal substitution of fluorine atom at the double bond (Scheme 7).

It was established [59, 60] that the interaction of perfluoro-2-methylpent-2-ene with phenol compounds containing electron-donor substituents (2-fluorophenol, 3-methoxyphenol, 3,5-dimethoxyphenol) does not change the character of formation of the products and leads to the formation of the corresponding alkyl phenyl ethers. At the same time, the products of the reaction of perfluoro-2-methylpent-2-ene with 2,6-dichlorophenol and pentafluorophenol under the same condtiions are (1,1,3,4,4,5,5,5-octafluoro-2-trifluoromethylpent-2-enyloxy)-2′,6′-dichlorobenzene and (1,1,3,3,4,4,5,5,5-nonafluoro-2-trifluoromethylphenoxy)-pentafluorobenzene, respectively. This may be due to the substitution of the fluorine atom of terminal olefin – an intermediate product formed as a result of isomerization of perfluoro-2-methylpent-2-ene under the action of a base.

Such behaviour of phenols is likely to be due to the presence of chlorine and fluorine atoms in positions 2 and 6 of the benzene ring, and due to the low reactivity of the corresponding phenolate anions. However, the reaction of perfluoro-2-methylpent-2-ene with 2,6-dimethylphenol and 2,6-dimethoxyphenol leads to the formation of fluorinated allyl and alkyl phenyl ethers, in spite of substantial spatial requirements [60]. At the same time, the results obtained cannot be explained only by electron donor properties of these substituents because in the case of the interaction of perfluoro-2-methylpent-2-ene with 3-nitrophenol, 4-nitrophenol and 3-oxypyridine, a mixture of the products of substitution of fluorine at the internal double bond and at the terminal bond of the intermediate perfluoro-2-methylpent-1-ene is formed [60] (Scheme 8).



Scheme 8.



Scheme 9.

The interaction of perfluoro-2,4-dimethylhept-3-ene with sodium phenolate in diethyl ether gives a mixture of isomers of (E/Z)-3-phenoxysubstituted perfluoro-2,4-dimethylhept-4-ene and perfluoro-2,4-dimethylhept-3-ene, while with phenol in the presence of triethylamine in dimethylformamide the main product is (E/Z)-4-phenoxyperfluoro-2,4-dimethylhept-3-ene [52] (Scheme 9).

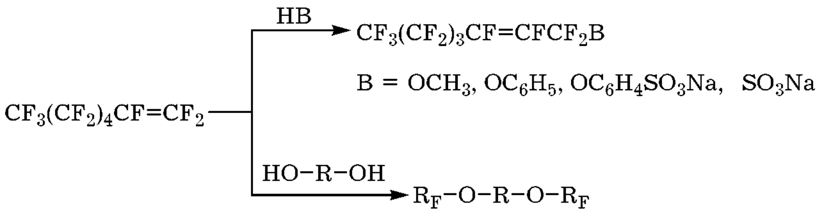
Perfluorinated vinyl ethers interact with phenols in the presence of bases forming the corresponding ethers with a high yield according to the addition reaction [61]

$$CF_2{=}CFOR_F \xrightarrow[\text{base}]{ArOH} ArOCF_2CHFOR_F$$

$R_F = C_3F_7$, $CF_2CF(CF_3)OC_3F_7$, $CF_2CF(CF_3)OCF_2CF_2COOCH_3$

The area of the reactions of nucleophilic addition was successfully broadened due to the use of metal phenolates and tetrafluoroethylene, as well as such solvents as dimethylformamide, dimethoxyethane, tetrahydrofuran. Due to this, difficultly proceeding nucleophilic addition of sodium phenolate to tetrafluoroethylene is easily performed at temperatures above 80 °C [62]. A simple, technologically safe and more economical method of obtaining a,a,b,b-tetrafluoroethyl ethers of phenol and its derivatives, described by the general formula $ROCF_2CF_2H$ (where R is phenyl or *p*-, *o*-, *m*-cresyl) was developed. This method is based on the interaction of the corresponding phenol with tetrafluoroethylene in the presence of a hydroxide of an alkaline metal at elevated temperature and pressure (with methyl alcohol as a solvent). A mixture of phenol and cresol with methyl alcohol is brought to the interaction with tetrafluoroethylene. The yield of the target product is 80–87 %.

1,1,2,2,-Tetrafluoroethylphenyl ethers ($ROCF_2CF_2H$) are applied as intermediate products for the synthesis of amines, dyes and plant



R = $-C_6H_4C_6H_4-$, 10 % NaOH, 80 °C, 6 h;

$R_F = -CF_2CHFC_5F_{11}$ (10 %), $-(CF_2)_4CF{=}CFCF_3$ (25 %),

$-(CF_2)_3CF{=}CFC_2F_5$ (27 %), $-(CF_2)_2CF{=}CFC_3F_7$ (38 %);

R = $-C_6H_4SO_2C_6H_4-$, sodium phenolate in diglyme, 70 °C, 2 h;

$R_F = -CF_2CHFC_5F_{11}$ (55 %), $-(CF_2)_4CF{=}CFCF_3$ (11 %),

$-(CF_2)_3CF{=}CFC_2F_5$ (19 %), $-(CF_2)_2CF{=}CFC_3F_7$ (15 %).

Scheme 10.

protecting chemicals, monomers for thermoplastic polymers and as inhalation anesthetic agent [62]. 1,2,2-Trifluorovinyl ether can be synthesized from 1,1,2,2-tetrafluoroethylphenyl ether by dehydrofluorination under the action of alkalis or with the help of organolithium compounds. Polymerisation of this monomer at high pressure and under g-radiation results in a polymer with the molecular mass of 4500.

In the case of terminal perfluoroolefins, as a rule, the action of alkaline metal phenolates results in the formation of the products of addition to the double bond, with the simultaneous migration of the double bond along the perfluoroalkyl chain [63, 64] (Scheme 10).

PARTIALLY FLUORINATED ETHERS WITH ALKENYL GROUPS

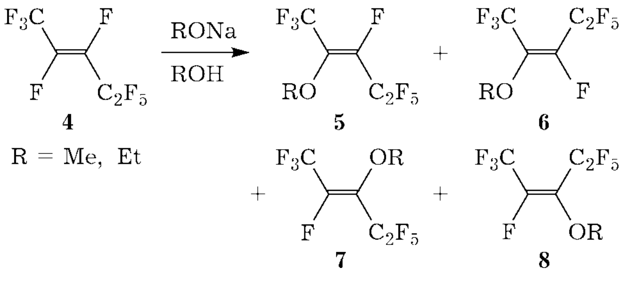
Perfluoro-2-methylpent-2-ene reactions with a,a,w-trihydroperfluorinated alcohols forming the products of substitution of the fluorine atom at the unsaturated bond [44]. Instead of CsF, triethylamine and pyridine can be used as catalysts.

Sodium methylate and ethylate reacting with *trans*-perfluoropent-2-ene **4** form a mixture of isomers **5–7** at a ratio of 9 : 1 : 4.5 (total yield: 60.2 %), while under the action of potassium phenolate in tetrahydrofuran suspension at 0–10 °C a mixture of isomers **5–7** and isomer **8** is formed [51] (Scheme 11).

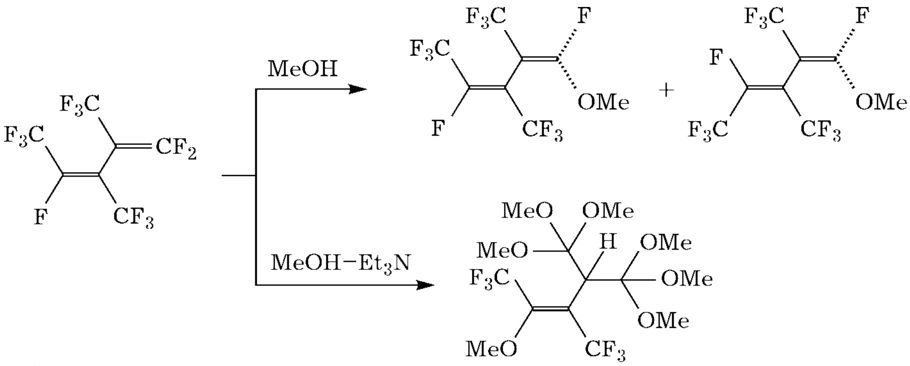
The action of methyl alcohol on a diene at 0 °C results in a mixture of monosubstituted products, which points to the isomerisation of unsaturated bonds [65] (Scheme 12).

Due to the presence of a base capable of generating MeO^- anion in the system, the formation of polysubstituted product (E)-5,5,5-trifluoro-1,1,1,4-tetramethoxy-3-trifluoromethyl-2(trimethoxymethyl)pent-3-ene occurs.

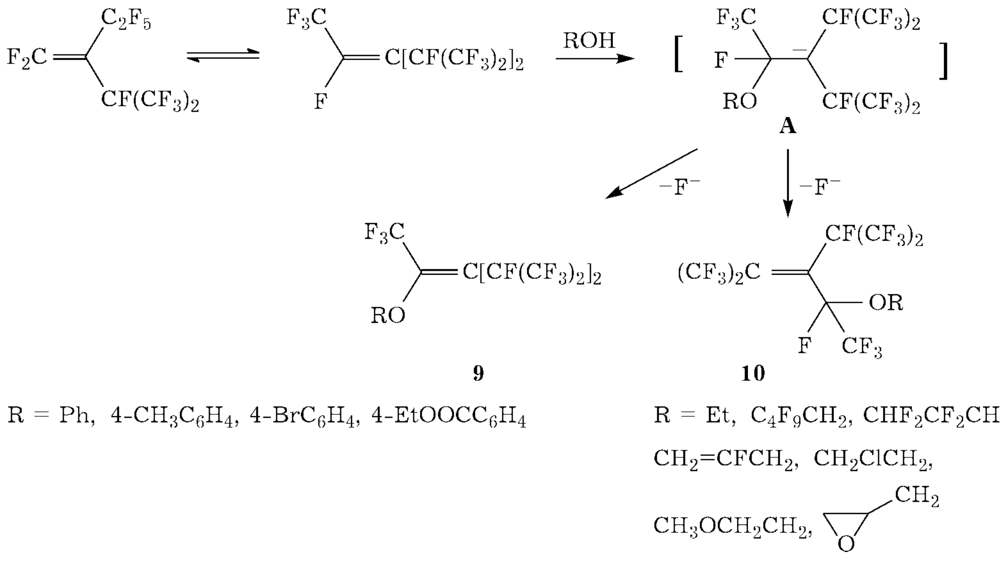
In the case of a mixture of hexafluoropropylene trimer isomers, the reaction with alcohols and substituted phenols results in the formation of two different products. The primary step of these reactions is the attack of the O-nucleophilic reagent at the carbon atom of the double bond containing fluorine atom. Further transformations of carbanion **A** depend on the nature of the O-nucleophilic agent: in the case of alcohols, fluoride ion is eliminated from b-position, which gives compound **10**, while in the case of phenols it gets eliminated from a-position with the formation of product **9** (Scheme 13).



Scheme 11.



Scheme 12.



Scheme 13.

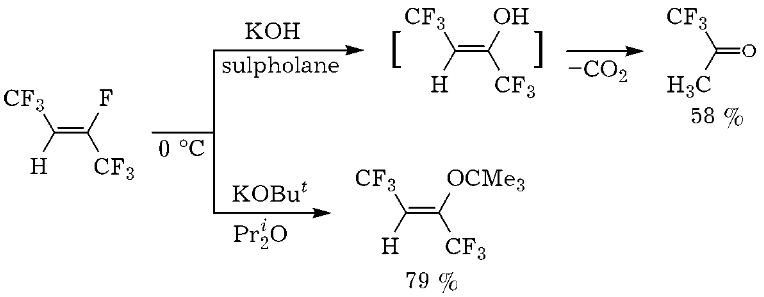
Under the action of potassium *tert*-butylate in triglyme at 0 °C on a mixture of E- and Z-perfluorobut-2-enes, the isomers of (E)- and (Z)-2-*tert*-butoxyperfluorobut-2-enes is formed [62].

2H-Heptafluorobut-2-ene does not eliminate hydrogen fluoride forming acetylene group under the action of bases. In this case, the fluorine atom at the double bond gets substituted. For example, under the action of KOH in sulpholane, 1,1,1-trifluoroacetone is formed, while the action of potassium *tert*-butylate in diisopropyl ether results in the product of substitution of the fluorine atom at the double bond [66] (Scheme 14).

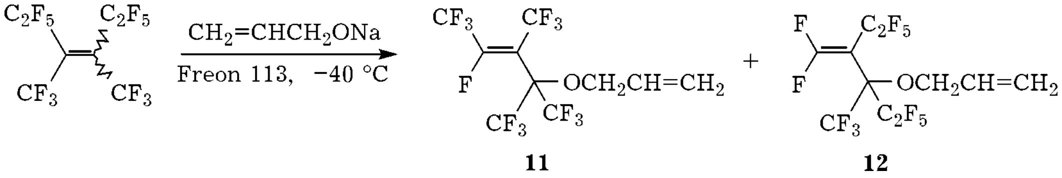
Fluorinated alkenes containing cyclopentenyl and cyclohexenyl substituents were synthesized stereoselectively by the interaction of hexafluoropropylene with cyclohexanol and cyclopentanol [61]. They react with C- and O-nucleophils forming the products of substitution of F atoms at the double bond [67].

The reaction of tetrafluoroethylene tetramer with sodium alcoholate of allyl alcohol in Freon 113 at −40 °C results in the formation of two products – compounds **11** and **12** [68] (Scheme 15).

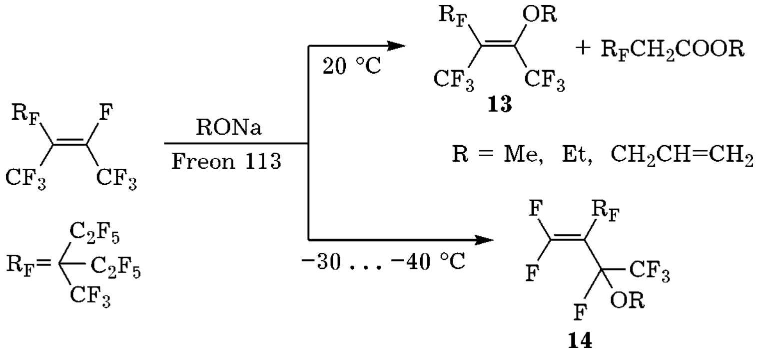
Tetrafluoroethylene pentamer contains a mobile fluorine atom at the internal double



Scheme 14.



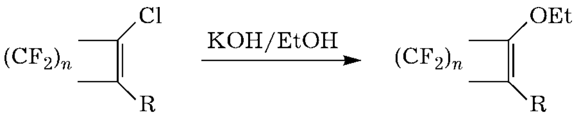
Scheme 15.



Scheme 16.

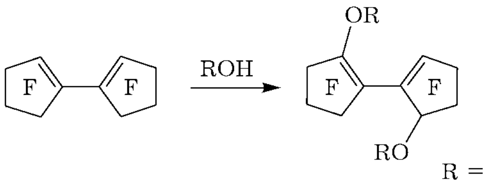
bond; under the action of alcohols in the presence of Et_3N or sodium alcoholates, the products are formed the structure of which depends on the process temperature [69]. At room temperature, the product **13** is formed by the substitution of the fluorine atom at the internal double bond, while at temperatures −30...−40 °C compound **14** is formed (Scheme 16).

A similar phenomenon is observed for the reaction of perfluorinated cyclic olefins with alcohols [37, 51]. The reaction of substituted 2-chloroperfluorocycloalkenes with potassium hydroxide in ethyl alcohol leads to the formation of the products of chlorine substitution with ethyoxy group [70, 71]:

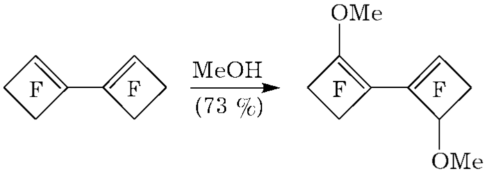


$n = 2, 3$
R = $COCH_3$, COPh, $4\text{-}NO_2C_6H_4$

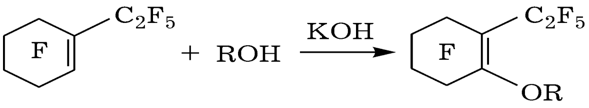
Perfluorobicyclopentene and perfluorobicyclobutene react with methyl alcohol and phenol forming the products of substitution of fluorine atoms at the double bond – disubstituted methoxy or phenoxy derivatives [72]:



R = Me, Ph



Under the action of alcohols, perfluorocyclohexene gives the product **15** of fluorine substitution at the double bond with a high yield [70, 71].



15

R = $CH_2CF_2CHF_2$, $CH_2(CF_2CF_2)_2H$

The action of alcoholates on octafluoroisobutylene results in the formation of partially fluorinated dialkyl ethers [34].

The reactivity of internal perfluoroolefins is affected both by the electron factors and by spatial ones. This can be demonstrated for the reactions of three compounds with methyl alcohol. Decafluorobicyclobutyl-1,1′-diene reacts efficiently with neutral methyl alcohol, tetradecafluorobicyclopentyl-1,1′-diene reacts with it within several days, while the presence of a base is necessary for the reaction of octafluoro-3,4-bis(trifluoromethyl)-hexa-2,4-diene with methyl alcohol. Since the electron factors for these compounds are identical, such a difference is due to the effect of the spatial factors.

POLYHYDRIC ALCOHOLS IN REACTIONS WITH PERFLUOROOLEFINS

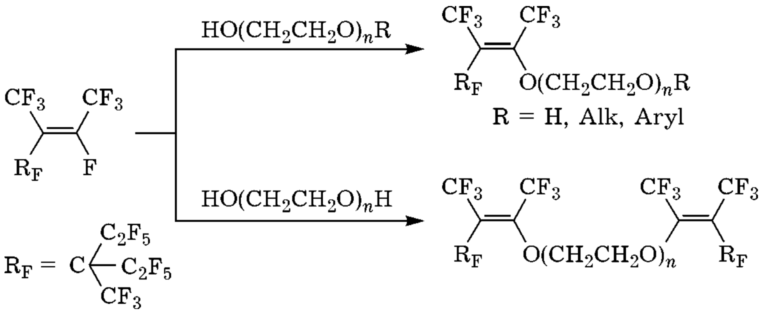
Tetrafluoroethylene reacts with ethylene glycol through both hydroxyl groups [73, 74]. Photochemical fluorination of the formed ether in the solution of Freon 113 leads to the formation of perfluorinated ether which finds application as an efficient dielectric (Scheme 17).

Tetrafluoroethylene tetramer, pentamer and hexamer react with ethylene glycols to form

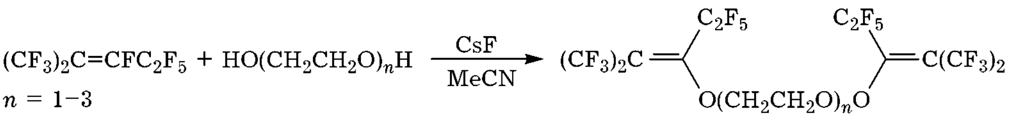
$$CF_2{=}CF_2 + HOCH_2CH_2OH \text{ ® } \underset{39\ \%}{HCF_2CF_2OCH_2CH_2OCF_2CHF_2}$$

$$\xrightarrow[\text{UV, Freon 113}]{F_2} \underset{85\ \%}{CF_3CF_2OCF_2CF_2OCF_2CF_3}$$

Scheme 17.

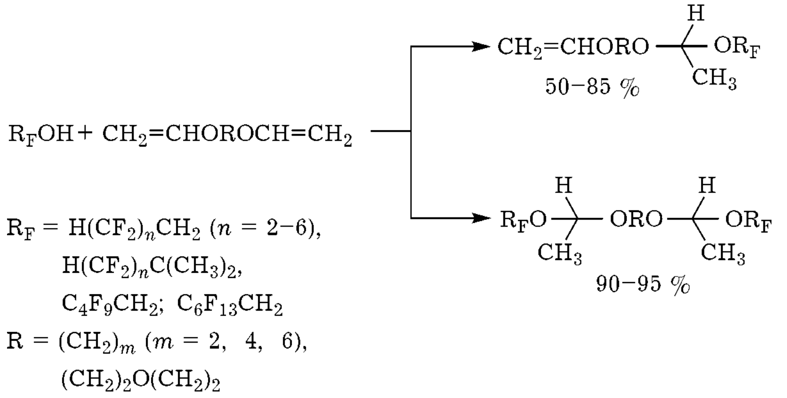


Scheme 18.



16

Scheme 19.



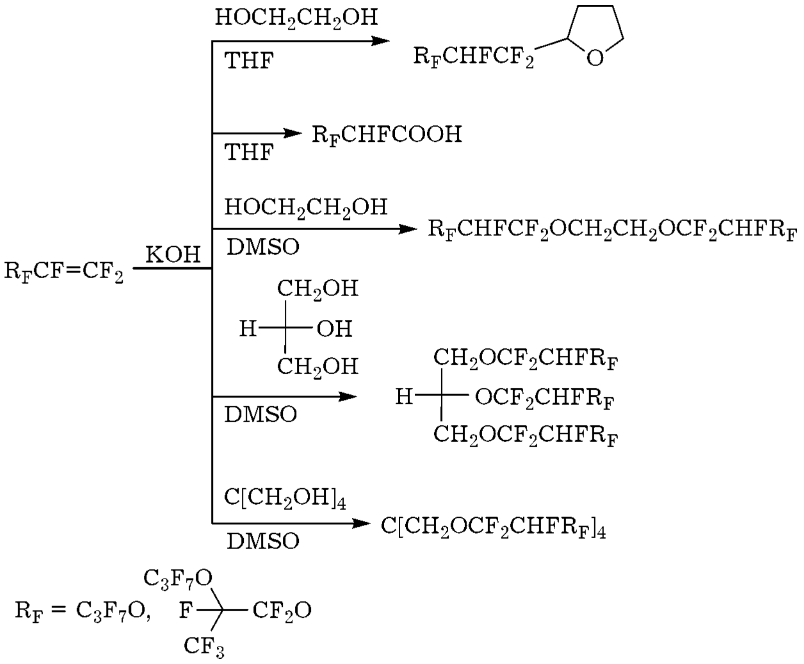
Scheme 20.

the products of substitution of the fluorine atoms at the double bond. These compounds are successfully used as efficient surfactants [70, 71] (Scheme 18).

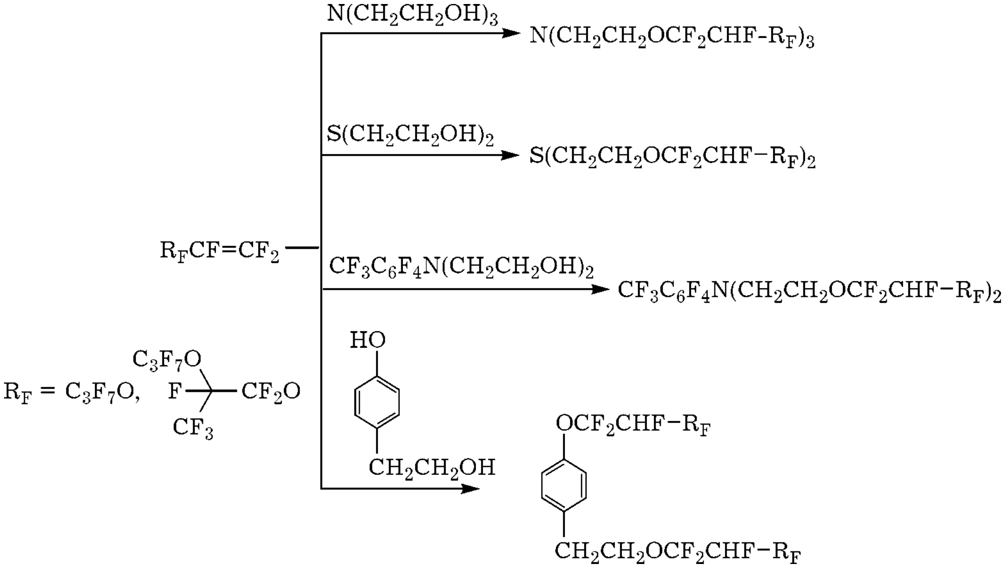
It was shown [59] that the reaction of perfluoro-2-methylpent-2-ene with mono-, di- and triethylene glycols at the reagents ratio of 3 : 1 in MeCN (or THF, DMF, acetone) in the presence of Et_3N (or KOH) leads to the formation of the corresponding partially fluorinated vinyl ethers **16**. Subsequent fluorination with elemental fluorine in $(C_4F_9)_2O$ results in the formation of fully fluorinated products (Scheme 19).

It is interesting that butane-1,4-diol reacts with hexafluoropropylene and perfluoropropylvinyl ether at atmospheric pressure under UV irradiation to form mono- and difluoroalkylated products, while 1,3-diols are inactive under these conditions [73].

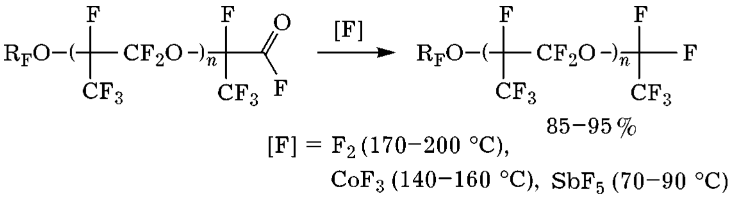
Due to the possibility of selective addition of polyfluoroalkanols to divinyl ethers and to 2-vinyloxyethoxymethyloxirane [74], 2-vinyloxyethyl ether of glycidol [75], 2-vinyloxyethylisothiocyanate [76, 77], methods of synthesis of new highly active ethers containing polyfluoroalkyl substituents were developed (Scheme 20).



Scheme 21.



Scheme 22.



Scheme 23.

Polyfluorinated vinyl ethers become important because they can be used as a raw material for the production of materials for many purposes. For example, polycondensation of hexafluoropropylene oxide results in the formation of a substantial amount of fluoroanhydrides of perfluoropolyether acids; the action of K_2CO_3 in diglyme on these acids [46, 47, 59, 78] leads to the formation of perfluoro(2-propoxy-2-propoxy)-ethylene **3** [32]. It was shown that the action of polyhydric alcohols (triethylene glycol, glycerol, pentaerythrite, triethanolamine, *etc.*) on this compound leads to the formation of ethers due to the addition to the double bond. These compounds are liquids with boiling points within 400–450 °C, medium viscosity; they are thermally stable and fireproof.

Compounds **2** and **3** reacting with alcohols interact through all the OH groups of these alcohols forming the products of addition to the double bond. The reaction is carried out in DMSO, sulpholane or MeCN (Scheme 21).

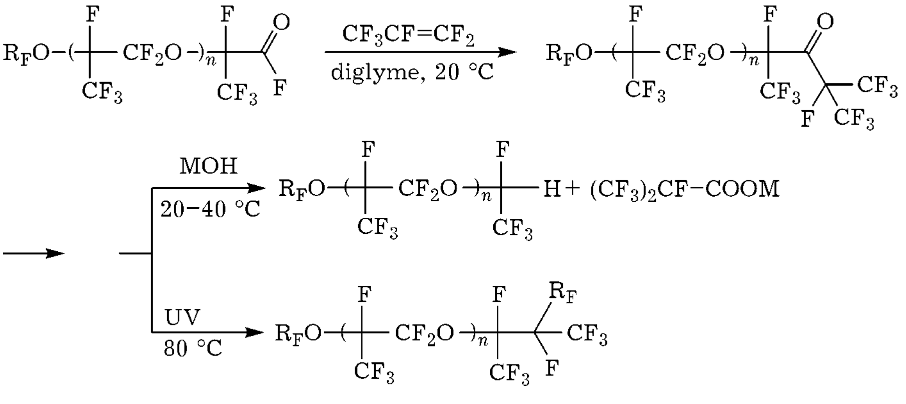
A similar situation also occurs when compounds **2** and **3** react with triethanolamine, 2(2-hydroxyethyl)-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-amino)-ethanol, 2(2-hydroxyethyl)phenol. In these cases, due to the interaction of alcohol and phenol groups with compounds **2** and **3**, polyethers are formed [49, 48] (Scheme 22).

The authors of [6] carried out a detailed investigation of the properties and application area of fluoroanhydrides of perfluoropolyether acids obtained by the interaction of hexafluoropropylene oxide participated by fluoride ion. It was established that the fluoroanhydride group of perfluoropolyether acid is eliminated during the interaction of elemental fluorine or with higher fluorides of elements, which results in the formation of perfluoropolyethers; reaction temperature depends on the nature of fluorinating reagents (Scheme 23).

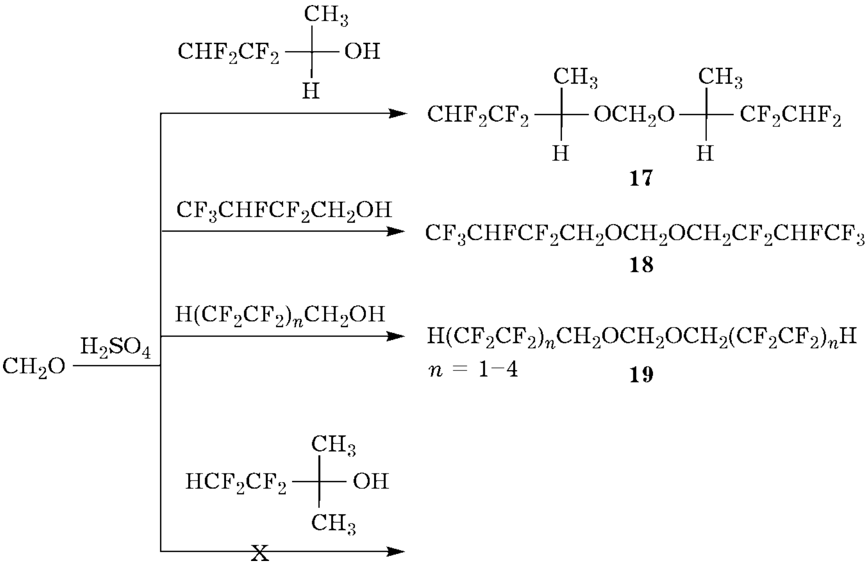
The authors of [6] showed that fluoroanhydrides of perfluoropolyether acids that form alcoholates with alkaline metal fluorides at a temperature of 40 °C (without the use of aprotic solvents) react with hexafluoropropylene in the presence of HF; with an aprotic solvent at 20 °C they form perfluoropolyether ketones with a quantitative yield. Subsequent action of alkalis at 20–40 °C leads to the formation of monohydropolyether and a salt of perfluoroisobutyric acid; perfluoroethers are formed under the action of UV irradiation. The latter products are mixtures of compounds with the viscosity up to 2000 cSt at 20 °C, vapour pressure 10^{-3}–0^{-14} torr, congelation point within the range from −80...−110 to −20 °C (Scheme 24).

SOME APPROACHES TO THE SYNTHESIS OF FLUORINATED POLYETHERS

Methods of obtaining fluorinated polyethers are numerous. We will consider only one approach based on the interaction of flyuorinated alcohols and formaldehyde in concentrated sulphuric acid, which results in the formation of acetales **17–19**, respectively (Scheme 25). In the case of an alcohol with steric hindrance, the reaction does not proceed under these conditions [79, 80].



Scheme 24.



Scheme 25.

Reactions of alcohols $HCF_2CF_2CH_2OH$ and CF_3CH_2OH with CH_2O in the presence of concentrated sulphuric acid at room temperature for 0.5 h results in the formation of acetales which can be used as the components of explosives and mix solid propellants [81].

Instead of formaldehyde, aliphatic aldehydes can also be used in this reaction. For example, fluorinated 1,1-dialkoxyalkanes with the general formula $[H(CF_2)_nCH_2O]_2CHR$ ($n = 2$, R = H, Me, Pr^i) were synthesized through the interaction of $H(CF_2)_nCH_2OH$ alcohol with RCHO aldehydes [82].

Perfluoroalkyl *ortho*-ethers with the general formula $[X(CF_2)_nCH_2O]_3CH$ (X = H, F; $n = 1–20$) were synthesized by the interaction of alcoholates of polyfluorinated alcohols with chloroform at a temperature of 108–140 °C [83].

Such an approach to the synthesis of high-temperature dielectrics is rather widespread. It should be kept in mind that perfluorination of organic compounds, dissolved, emulsified or suspended, for example polyethers, under the action of elemental fluorine in nitrogen flow at a temperature of −40...−90 °C proceeds in such solvents as Freon 113 and perfluorinated simple polyethers [84].

CONCLUSIONS

The information presented above suggests that researchers still keep an eye on fluorinated dialkyl and alkyl phenyl ethers, which is to a great extent due to the wide area of application of these compounds. New application areas of the materials based on these compounds have appeared, in particular, they are used as high-temperature dielectrics, heat carriers, hydraulic liquids with high parameters for electric machines, working liquids for high-pressure compressors, hydraulic systems of aircrafts.

Decarboxylation of perfluorinated ether acids like $R_FO(CF_2)_nCOOH$ (R_F is perfluoroalkyl $C_1–C_{18}$, $n > 3$) under the action of KOH in ethylene glycol under heating results in the formation of w-hydrofluoroalkyl ethers $R_FO(CF_2)_nH$ which are used for cleaning and dehydration of parts in microelectronics, as foam-forming agents, *etc.* [85]. w-Carboxy and w-hydro derivatives of perfluorinated di- and polyethers of aliphatic series are obtained and applied in a similar way.

Since these compounds are incompressible under pressure, they can be used as hydraulic liquids for robotics and as lubricating oil for the units of machinery. In spite of the wide assortment of lubricants and additives based on hydrocarbon materials, the need for high-temperature and specialized lubricants remains great. The parameters of fluorinated lubricants allow one to use them for rolling mills, stamping machines, as well as for oil equipment and oil pipelines because, in comparison with mineral oil, they are not washed out with the lightweight components of the hydrocarbon raw material.

The synthesized partially fluorinated dialkyl ethers are of interest as intermediate products for the synthesis of perfluorinated dialkyl ethers by means of direct additional fluorination with elemental fluorine; they can be used as liquid dielectrics for many purposes. In addition, new solvents and medical preparations can be developed on their basis. The methods of obtaining these compounds are based on the transformations of available and commercial perfluorinated olefins.

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