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REVIEW

Internal Perfluoroolefins in the Synthesis of Organofluorine Compounds

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Abstract—The review discusses reactions of internal perfluoroolefins with nucleophilic reagents. Modes of generation of carbon-centered anions and radical species containing perfluoroalkyl groups are considered.

I. INTRODUCTION

In the recent time much attention is given to the development of methods for preparation of new organofluorine compounds having, as a rule, various functional groups. Syntheses of a number of fluoro derivatives utilize accessible perfluoroolefins and some their oligomers which are characterized by enhanced electrophilicity [1]. Just this property of perfluoroolefins underlies a branch of organofluorine chemistry which deals with reactions of fluorinated compounds with nucleophiles. This line turned out to be fruitful both from theoretical viewpoint (it becomes possible to get a deeper insight into the properties of olefinic systems) and from the practical point of view (numerous organofluorine compounds become accessible). Due to specific influence of fluorine atoms on unsaturated system, reactions of fluorinated compounds with nucleophilic reagents not only supplement the chemistry of olefins but also demonstrate their unique properties. Among these, compounds have been found which possess interesting electro- and thermophysical properties and strong physiological activity. Thus, a basis is created for the synthesis of drugs, lubricants, liquid dielectrics and heat carriers, highly efficient surface-active substances, and numerous materials for other applications [2–8].

Systematic studies of reactions of branched linear and cyclic perfluoroolefins include mainly three aspects which are most typical of the perfluoroolefin series due to specific influence of fluorine atoms on the olefinic system: (1) reactions with nucleophiles; (2) radical reactions and reactions with oxidants; and (3) reactions with electrophilic reagents, in particular processes occurring in superacids and in SbF_5.

Reactions of perfluoroolefins with nucleophiles are key reactions in the chemistry of organofluorine compounds; they are extensively studied and are widely used in the synthesis of various derivatives, including heterocyclic ones [9–11]. Systematic studies of reactions of internal perfluoroolefins with nucleophiles are of specific interest. Unlike terminal perfluoroolefins (mainly perfluoropropylene, perfluoroisobutylene, and tetrafluoroethylene), the effect of perfluoroalkyl groups and fluorine atoms on the double bond in internal perfluoroolefins gives rise to a series of unusual reactions which essentially extend the range of addition–elimination processes typical of reactions with nucleophiles and lead to formation of various products. Various nucleophilic reagents are capable of reacting with compounds having an electron-deficient double bond to give both addition products at that bond and heterocyclic compounds with perfluoroalkyl groups. Some reviews have covered in part reactions of perfluoroolefins with nucleophilic reagents [12–15]. However, these are mainly reactions with C-nucleophiles and difunctional reagents, leading to formation of heterocyclic compounds. Such reactions are not discussed in the present review. Nevertheless, one of the most important problems is not only development of approaches to partially fluorinated compounds on the basis of internal perfluoroolefins but also formation of reactive intermediate species (such as anions, radicals, and carbocations) and their participation in reactions with organic substrates [12, 16]. Keeping the above in mind, the present review analyzes mainly available experimental data on (1) reactions of internal perfluoroolefins with nucleophilic reagents; (2) methods of generation of anionic and radical species having perfluorinated fragments, which may be used as synthons; and (3) specific features of olefinic systems with perfluoroalkyl substituents.

Taking into account that alcohols and amines could form the basis for preparation of perfluorinated organic compounds with various practically useful properties, the corresponding reactions have also been considered with the goal of formulating general relations holding therein and attracting attention to specific problems of the chemistry of internal perfluoroolefins and possible ways of solving them.

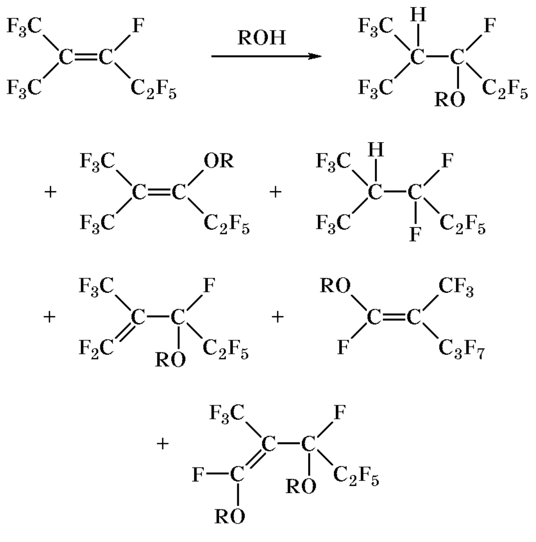
II. REACTIONS OF INTERNAL PERFLUOROOLEFINS WITH NUCLEOPHILIC REAGENTS AS A ROUTE TO VARIOUS DERIVATIVES CONTAINING PERFLUOROALKYL FRAGMENTS

Reactions of perfluoroolefins with nucleophiles have been studied in sufficient detail. They play an important role in the synthesis of key intermediate products of organic synthesis. However, reactions of internal perfluoroolefines with nucleophilic reagents have been studied insufficiently. Moreover, internal perfluoroolefins attract interest as a particular class of compounds; their derivatives can be regarded as raw materials for synthesis of new organofluorine compounds [1–8].

According to the data of photoelectron spectroscopy, the presence of perfluoroalkyl groups at the double bond reduces the energy of its π orbital, which favors nucleophilic attack at a carbon atom of that bond. Reduction potentials are important parameters characterizing the reactivity of olefinic systems [14]. Their values depend on the substituent nature: the reduction potential decreases in going from fluorine atom to polyfluoroalkyl group. Increase in the number of perfluoroalkyl groups at a double bond also reduces the reduction potential, thus enhancing the reactivity of perfluoroolefin: $(R_F)_2C{=}C(R_F)_2 > (R_F)_2C{=}CFR_F > (R_F)_2C{=}CF_2 \approx R_FCF{=}CFR_F > R_RCF{=}CF_2 > CF_2{=}CF_2$. Unlike fluorine atom, polyfluoroalkyl group essentially stabilizes intermediate carbanion [17–19]. All these factors favor reactions of internal perfluoroolefins with nucleophiles. Nevertheless, the structure of perfluoroolefin itself should also be taken into account.

Internal perfluoroolefins react with alcohols only in the presence of bases, yielding addition and fluorine replacement products; sometimes, more complex transformations occur [20]. Polyfluorinated alcohols react with metallic sodium (in excess alcohol) to give the corresponding sodium alkoxides [21–23]. However, reactions of polyfluorinated alcohols with perfluoroolefins and polyfluoroaromatic compounds are carried out without preliminary isolation of alkali metal alkoxides but in the presence of bases, such as sodium hydroxide [24, 25], triethylamine, mercury acetate [26], etc. Polyfluorinated alcohols react with perfluoroolefins in the presence of sodium hydride

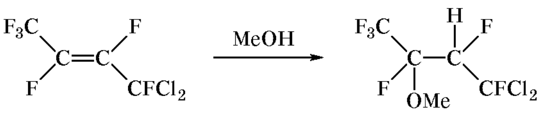
Scheme 1.



[26] to form products of fluorine replacement at the double bond. Cesium fluoride turned out to be an efficient catalyst in reactions of perfluoroolefines with α*H*,α*H*,ω*H*-polyfluorinated alcohols [27]. Addition products are the major ones when a catalytic amount of base is used; increase of the amount of the catalyst leads to increased fraction of unsaturated products, vinyl ethers. In the presence of triethylamine, products of fluorine replacement at the double bond are formed, whereas sodium hydroxide as a base catalyst gives rise mainly to products of addition of two alkoxy groups (Scheme 1).

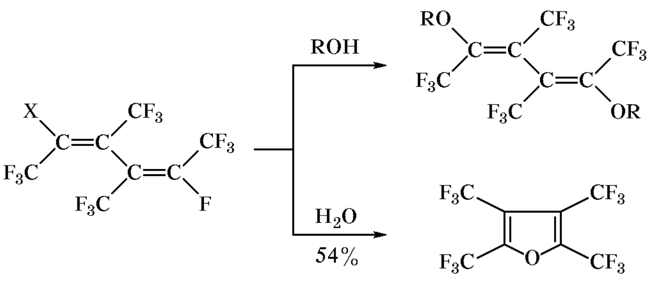
The addition and replacement reactions between perfluoroolefins and nucleophilic reagents occur relatively easily due to steric and electronic effects in the intermediate carbanion. The direction of primary attack by alkoxide ion is also determined by steric and electronic factors. For example, methanol and phenol react with *trans*-1,1-dichlorohexafluoro-2-butene to give addition products, involving the C^3 carbon atom at the double bond [28] (Scheme 2).

Scheme 2.



As shown in [29], the reaction of methanol with hexafluoropropylene dimers in the presence of KOH or triethylamine in tetrahydrofuran, acetone, acetonitrile, or dimethylformamide gives products of fluorine replacement at the double bonds and also addition products. Depending on the reactant ratio, unsaturated perfluorinated carboxylic acid methyl esters and substituted ketones are also formed [20]. Simultaneously, addition of two methoxy groups to perfluoro(2-methyl-2-pentene) occurs to give 1,3-dimethoxyperfluoro(2-methyl-1-pentene) in 51% yield. Perfluoro(4-methyl-2-pentene) reacts only with sodium methoxide, yielding 57% of isomeric 1,3,4-trimethoxyperfluoro(2-methyl-1-pentenes) (ratio 3:1) [30]. Perfluoro(2-methyl-2-pentene) reacts with α*H*,α*H*,ω*H*-polyfluorinated alcohols, affording products of fluorine replacement at the double bond [27]. Triethylamine or pyridine can be used as catalyst instead of CsF. Perfluoro-2-butene reacts with MeOH and PhOH with formation of the corresponding disubstituted products; its reaction with water yields perfluoro(tetramethylfuran) [31] (Scheme 3).

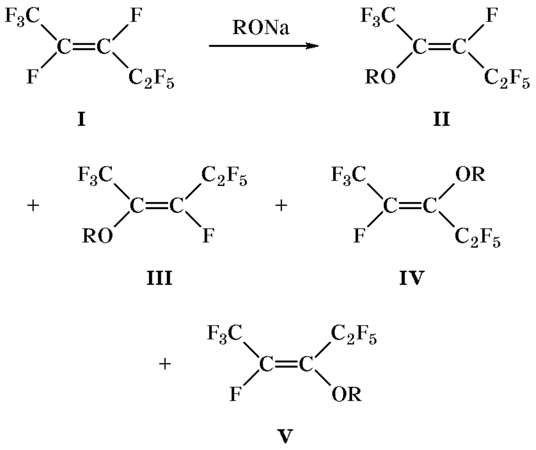
Scheme 3.



R = Me, Ph.

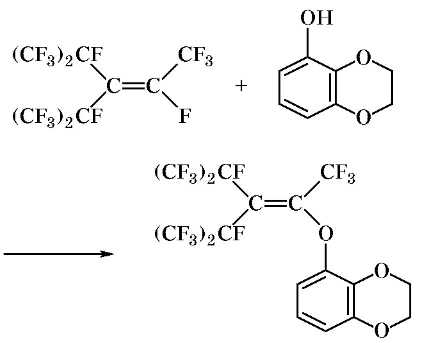
Sodium methoxide and ethoxide with *trans*-perfluoro-2-pentene (**I**) give rise to isomeric mixture (**II**, **III**, and **IV**) at a ratio of 9:1:4.5 (overall yield 60.2%); the action on the same substrate of potassium phenoxide dispersed in tetrahydrofuran at 0–10°C gives a mixture of isomers **II**–**V** [32] (Scheme 4).

Scheme 4.



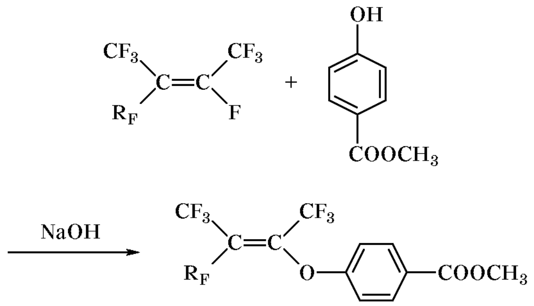
Reactions of phenols with a number of internal perfluoroolefins in the presence of triethylamine lead to formation of only products of fluorine replacement at the double bond. Examples are the reactions of *p*-cresol with perfluoro(2-methyl-2-pentene) [33], of 5-hydroxy-1,4-benzodioxane with hexafluoropro-

Scheme 5.



pylene trimer in the presence of Et_3N [34], and of methyl 4-hydroxybenzoate with tetrafluoroethylene pentamer in the presence of NaOH [35] (Scheme 5). Such reactions are used in the synthesis of surfactants (Scheme 6).

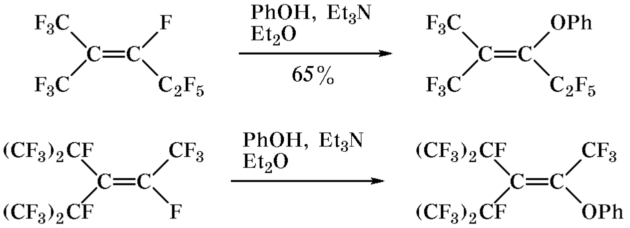
Scheme 6.



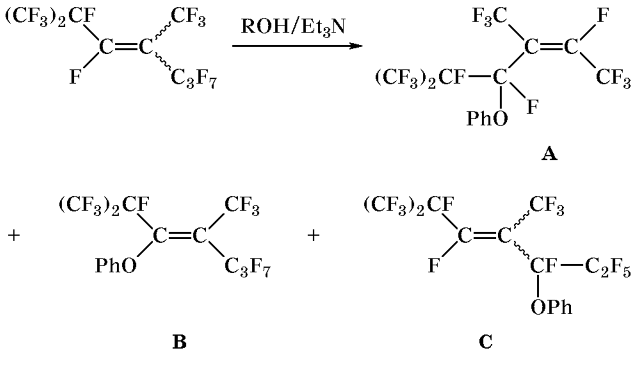
R_F = $C(CF_3)(C_2F_5)_2$.

Analogous results were obtained in the reactions of phenol with hexafluoropropylene dimers and trimers in the presence of triethylamine [36–39] (Scheme 7). It should be kept in mind that isomeric hexafluoropropylene trimers can undergo mutual transformations under the action of bases. For example, the reaction of perfluoro(2,4-dimethyl-3-heptene) with sodium phenoxide leads to formation of a mixture of monosubstituted derivatives [38, 40] (Scheme 8). Isomeric hexafluoropropylene trimers react with alcohols and substituted phenols, yielding two different products [40]. These reactions begin with attack by O-nucleophile on the fluorine-substituted carbon atom at the double bond. Further transformations of the carbanion thus formed depend on the nucleophile nature: In the reactions with alcohols elimination of fluoride ion from the β-position occurs to give compound **VI**; in the reactions with phenols elimination of fluoride ion from the α-position gives product **VII** (Scheme 9).

Scheme 7.

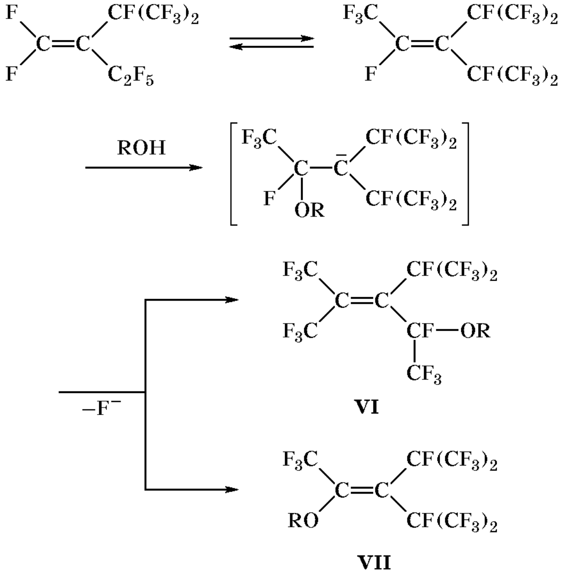


Scheme 8.



Reagent	Solvent	A	B	C
PhONa	Et_2O	46%	12%	2%
PhOH/Et_3N	Et_2O	–	2%	56%
	DMF	–	7%	87%
4-$MeCOC_6H_4OH$/Et_3N	DMF	–	10%	35%

Scheme 9.

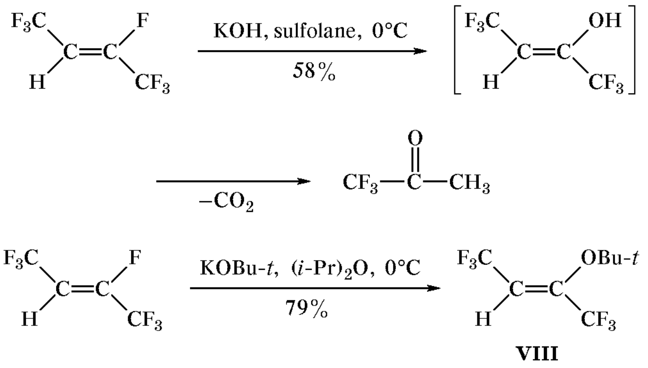


R = Ph, 4-$CH_3C_6H_4$, 4-BrC_6H_4, 4-$EtOCOC_6H_4$; R = Et, $C_4F_9CH_2$, $CHF_2CF_2CH_2$, $CH_2{=}CHCH_2$, CH_2ClCH_2, $CH_3OCH_2CH_2$, 2,3-epoxypropyl.

Makarov *et al.* [40] showed that allyl ethers could undergo isomerization into vinyl ethers by the action of cesium fluoride, so that nucleophilic reagent could react with two substrates. Therefore, the required conditions should be met rigorously in order to obtain the desired results. Treatment of a 4:1 mixture of (*E*)- and (*Z*)-perfluoro-2-butene with potassium *tert*-butoxide in triethylene glycol dimethyl ether at 0°C leads to formation of (*E*)- and (*Z*)-2-*tert*-butoxyperfluoro(2-butenes) [41]. When treated with bases, 2*H*-heptafluoro-2-butene does not lose hydrogen fluoride to give an acetylene derivative, but fluorine atom at the double bond is replaced. Its reaction with

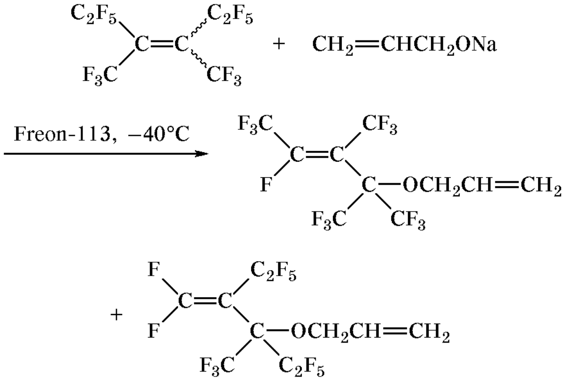
KOH in sulfolane yields 1,1,1-trifluoroacetone, and with potassium *tert*-butoxide in diisopropyl ether, fluorine replacement product **VIII** is obtained [42] (Scheme 10).

Scheme 10.

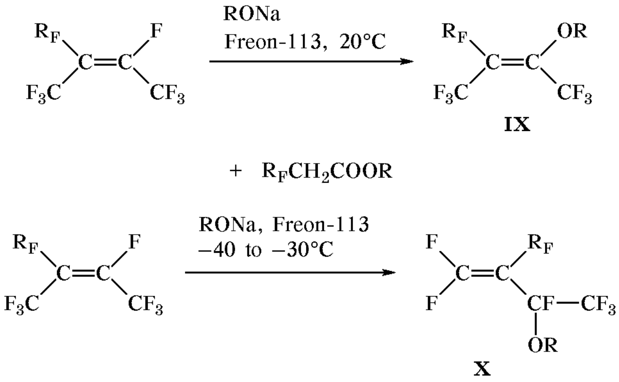


The reaction of tetrafluoroethylene tetramer with sodium 2-propenolate in Freon-113 at –40°C gives rise to two products [43] (Scheme 11).

Scheme 11.



Scheme 12.

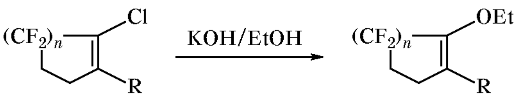


R = Me, Et, $CH_2CH{=}CH_2$; R_F = $C(CF_3)(C_2F_5)_2$.

Tetrafluoroethylene pentamer possesses a fairly labile fluorine atom at the internal double bond; it reacts with alcohols in the presence of triethylamine or sodium alkoxides to give products whose structure depends on the temperature [44]. At room temperature fluorine replacement product **IX** is formed, while at –30 to –40°C compound **X** is obtained (Scheme 12).

A similar pattern was observed in reactions of perfluorinated cycloalkenes with alcohols [20, 32]. Substituted 2-chloroperfluorocycloalkenes react with potassium hydroxide in ethanol, affording products of chlorine replacement by ethoxy group [45] (Scheme 13).

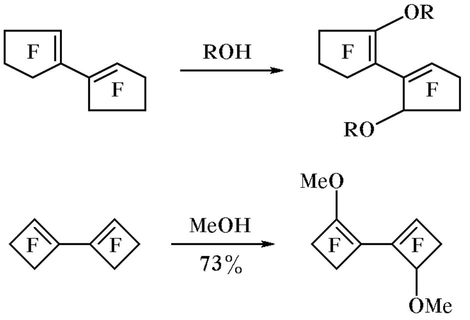
Scheme 13.



n = 1, 2; R = COMe, COPh, 4-$NO_2C_6H_4$.

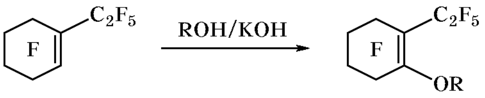
Perfluorobi(cyclopentene) and perfluorobi(cyclobutene) react with methanol and phenol to give products of fluorine replacement at the double bond, disubstituted methoxy or phenoxy derivatives [31] (Scheme 14).

Scheme 14.



The reaction of perfluorocyclobutene with potassium phenylmethoxide gives product of fluorine replacement at the double bond in high yield [46]. Alkali metal alkoxides derived from polyfluorinated alcohols react in a similar way [27] (Scheme 15).

Scheme 15.

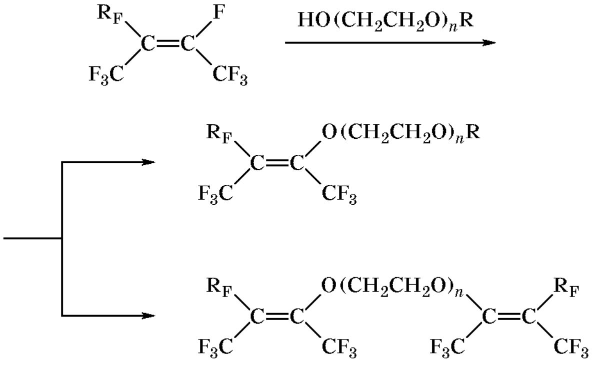


R = $CH_2CF_2CHF_2$, $CH_2(CF_2CF_2)_2H$.

The reactivity of internal perfluoroolefins is determined by both electronic and structural factors [47]. This is clearly seen by comparing reactions with methanol of the following three compounds. Decafluoro-1,1′-bi(cyclobutene) readily reacts with neutral methanol, tetradecafluoro-1,1′-bi(cyclopentene) react with methanol in several days, and the reaction of octafluoro-3,4-bis(trifluoromethyl)-2,4-hexadiene with the same alcohol requires the presence of a base [47]. These data could not be explained by electronic factors (which are similar for the above compounds), so that they illustrate the effect of structural factors.

Tetrafluoroethylene tetramer, pentamer, and hexamer with ethylene glycols form products of fluorine replacement at the double bond; these products were successfully used as efficient detergents [48, 49] (Scheme 16).

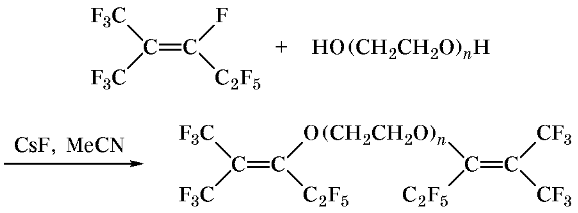
Scheme 16.



R = H, Alk, Ar; R_F = $C(CF_3)(C_2F_5)_2$.

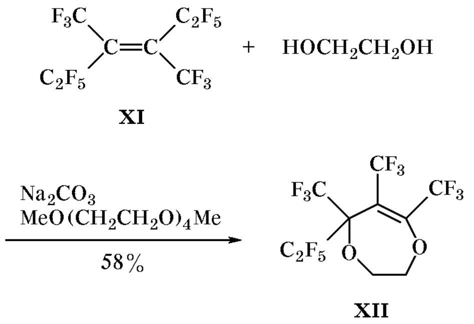
Reactions of perfluoro(2-methyl-2-pentene) with mono-, di-, and triethylene glycols (reactant ratio 3 : 1) in acetonitrile, tetrahydrofuran, dimethylformamide, or acetone in the presence of triethylamine or potassium hydroxide were shown [50] to give the corresponding partially fluorinated diethers (Scheme 17). However, the main direction of the reaction of internal perfluoroolefins with ethylene glycols is that leading to formation of cyclic products, namely 1,3-dioxolane derivatives. Such reactions of ethylene glycol with perfluoro-2-butene [51], perfluoro(2-methyl-2-pentene) [52, 53], tetrafluoroethylene pentamer [44, 54, 55], and perfluoro(3,4-dimethyl-2-hexene) [56] have been reported. For example, the reaction of equimolar amounts of ethylene glycol and perfluoro(4-methyl-2-pentene) in dipolar aprotic solvents in the presence of triethylamine gives rise to a mixture of products containing 2-pentafluoroethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-1,3-dioxolane (72–81%), 5,7-difluoro-5-pentafluoroethyl)-6-trifluoromethyl-3,5-dihydro-2*H*-1,3-dioxepine (3–5%), and 5,5-difluoro-7-pentafluoroethyl-6-trifluoromethyl-3,5-dihydro-2*H*-1,3-dioxepine (19–28%) [53, 54]. 5-Pentafluoroethyl-5,6,7-tris(trifluoromethyl)-1,4-dioxepine (**XII**) was obtained by reaction of perfluoro(3,4-dimethyl-3-hexene) (**XI**) with ethylene glycol [56] (Scheme 18).

Scheme 17.



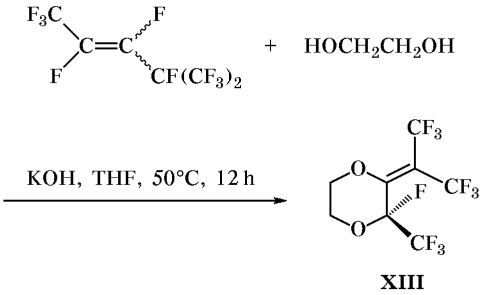
n = 1–3.

Scheme 18.



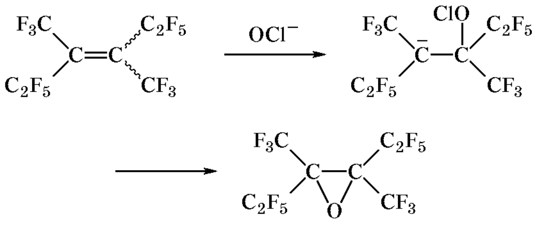
The reaction of perfluoro(4-methyl-2-pentene) with ethylene glycol in tetrahydrofuran in the presence of KOH is not accompanied by isomerization, and 1,4-dioxane derivative **XIII** is formed in a low yield [50] (Scheme 19).

Scheme 19.



Reactions of internal perfluoroolefins with sodium hypochlorite in alkaline medium containing acetonitrile provide an example of epoxidation via nucleophilic addition of OCl^- ion and subsequent replacement of the chlorine atom by the action of intermediate carbanion [57–62] (Scheme 20).

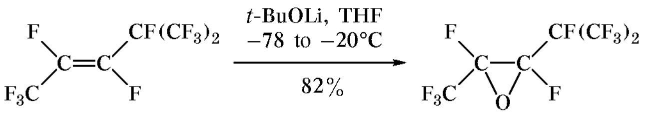
Scheme 20.



$Z:E = 1:1$ (74%)

Lithium *tert*-butoxide can also be used in such reactions. For example, epoxidation of electron-deficient olefins has been reported [63, 64] (Scheme 21).

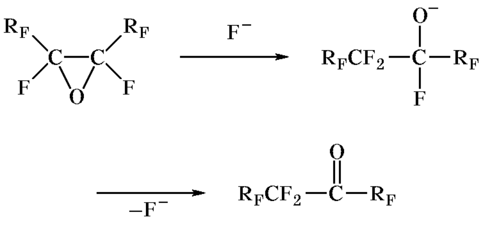
Scheme 21.



The application of the above technique to fluorine-containing systems essentially extends our knowledge on the properties of olefinic systems. The role of the reagent itself is also important. In some cases calcium hypochlorite turned out to be inefficient in epoxidation of fluorinated olefins, whereas lithium *tert*-butoxide is very efficient [65, 66].

The reactivity of perfluoroolefins in epoxidation corresponds to their reactivity with respect to nucleophilic reagents. Epoxy derivatives of perfluoroolefins readily react with fluoride ion, and this reaction underlies a convenient procedure for synthesizing perfluorinated ketones (Scheme 22).

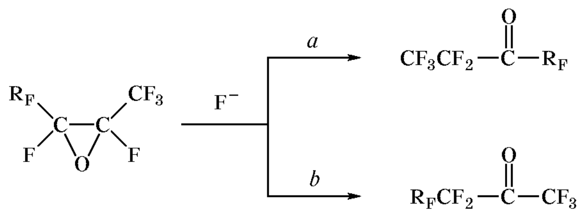
Scheme 22.



R_F = CF_3, C_2F_5; R_FR_F = $(CF_2)_3$, $(CF_2)_4$.

The site of attack by fluoride ion is determined by the nature of substituents at the oxirane ring. Increase in steric hindrance created by perfluorinated substituent favors formation of such a ketone in which the carbonyl group is neighboring to that substituent (Scheme 23).

Scheme 23.

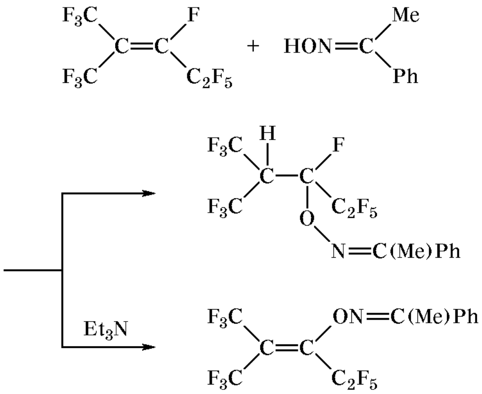


R_F	Path *a*	Path *b*	Yield, %
CF_3	–	–	92.5
C_2F_5	55	45	91.6
C_3F_7	74	26	89.4
C_5F_{11}	77	23	93.4
iso-C_3F_7	100	0	92.0

Aldehyde and ketone oximes are widely used in organic synthesis as effective O-nucleophiles. Perfluoro(2-methyl-2-pentene) reacts with acetone oxime [67] and cyclic ketone oximes [68] in the presence of triethylamine, resulting in formation of fluorine replacement and addition products at the double bond. On the other hand, reactions of perfluoro(2-methyl-2-pentene) with aliphatic aldehyde oximes were reported to give new fluorinated dihydroisoxazoles. Snegirev *et al.* [67–70] revealed thermal rearrangement of oxime *O*-fluoroalkenyl ethers into dihydropyrrole derivatives. Interest in heterocyclic compounds having perfluoroalkyl groups must be noted; such compounds usually exhibit enhanced biological activity, and they can be regarded as a basis for the development of new drugs and products for agriculture.

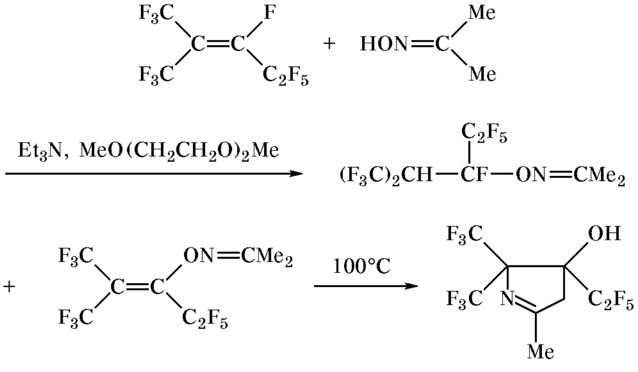
Unlike acetone oxime which reacts with perfluoro-(2-methyl-2-pentene) in the presence of a base (triethylamine), the reaction of perfluoro(2-methyl-2-pentene) with (*E*)-acetophenone oxime was shown [71] to occur in the absebce of triethylamine in diethylene glycol dimethyl ether or acetonitrile. It leads to formation of acetophenone oxime *O*-1,3,3,3-tetrafluoro-1-pentafluoroethyl-2-trifluoromethylpropyl ether via addition at the double C=C bond. In the presence of triethylamine, fluorine atom at the internal double bond is replaced to afford acetophenone oxime *O*-perfluoro(1-ethyl-2-methyl-1-propenyl) ether (Scheme 24). Terminal perfluoroolefins are known to react with acetone oxime, yielding only addition products at the double bond. By contrast, internal perfluoroolefins, e.g., perfluoro(2-methyl-2-pentene), give rise to mixtures of addition and fluorine replace-

Scheme 24.



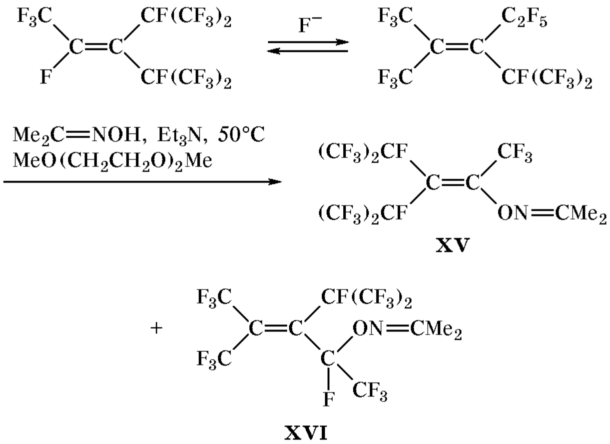
ment products. The yield of the latter increases as the amount of base rises. The product is stable on storage below 30°C; on heating to 100°C, it is converted in 1 h into 4-hydroxy-2-methyl-4-pentafluoroethyl-5,5-bis(trifluoromethyl)-4,5-dihydro-3*H*-pyrrole (**XIV**) [67] (Scheme 25).

Scheme 25.



XIV

Scheme 26.

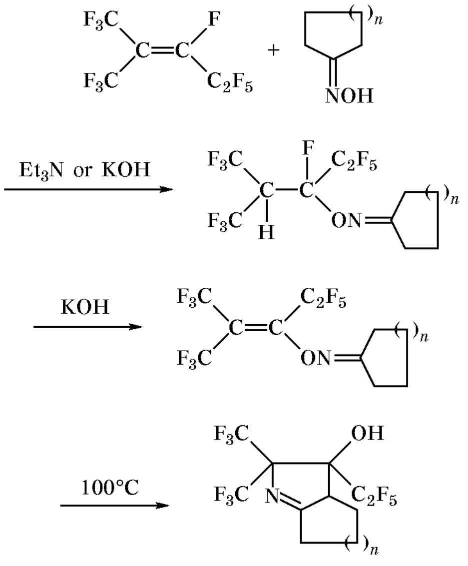


XV

XVI

Hexafluoropropylene trimers react with acetone oxime to give two isomeric products **XV** and **XVI** via nucleophilic replacement of fluorine at the double bond (Scheme 26). Other oximes react with internal perfluoroolefins in a similar way. The reactions of cyclopentanone oxime and cyclohexanone oxime with perfluoro(2-methyl-2-pentene) in the presence of a catalytic amount of a base result in formation of addition products and products of their dehydrofluorination, but the yield of the latter does not exceed 10% [68]. Vinyl ethers are thermally unstable, and they are completely converted into pyrrolidines **XVII** on heating to 100°C (Scheme 27).

Scheme 27.



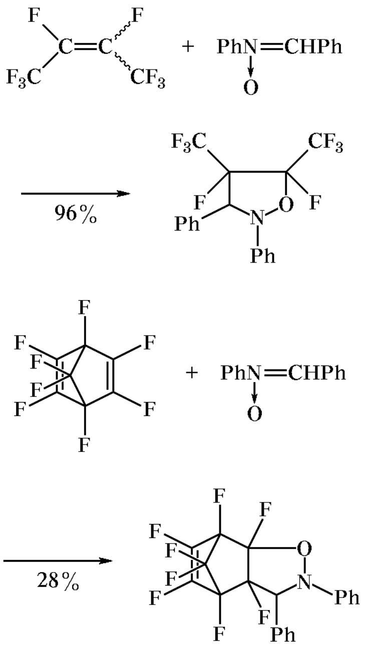
XVII

n = 1, 2.

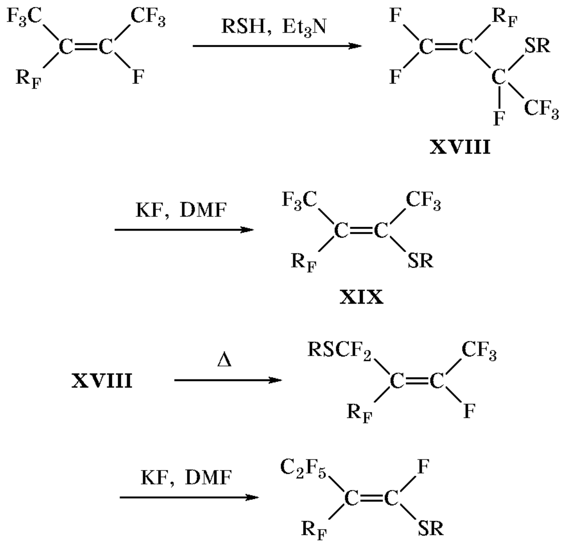
Cyclization products (the corresponding isoxazolidines) are directly obtained by reactions of *N*-benzylideneaniline *N*-oxide with octafluoro-2-butene and octafluoronorbornadiene at room temperature [72] (Scheme 28).

Reactions of sulfur-containing nucleophiles with internal perfluoroolefins are very sensitive to temperature conditions. Treatment of tetrafluoroethylene pentamer with thiols in the presence of triethylamine leads to formation of a mixture of products [73, 74] (Scheme 29). Kinetically controlled product **XVIII** is formed at –65 to –30°C, whereas at room temperature thermodynamically controlled product **XIX** is obtained (Table 1). Hexafluoropropylene dimers react with phenylmethanethiol and benzenethiol in the presence of triethylamine, yielding products of fluorine replacement at the double bond and also products of more profound transformations under the action of thiolate ion [37]. The results depend primarily on the nucleophile nature. Products having an RS group at the double bond are formed by reactions of hexafluoropropylene trimers with thiols in the presence of triethylamine [40, 75] (Scheme 31). Sodium dialkyldithiocarbamates were also used as S-nucleophiles [76] (Scheme 32).

Scheme 28.



Scheme 29.



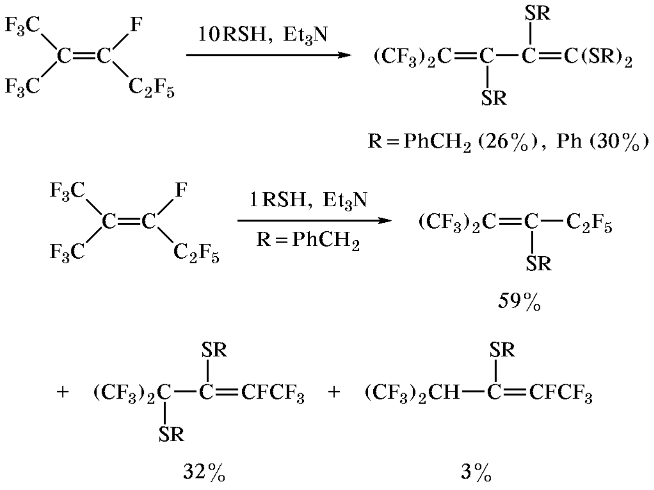
R = PhCH$_2$, Ph, CH$_2$CH=CH$_2$; R$_F$ = C(CF$_3$)(C$_2$F$_5$)$_2$.

Table 1. Temperature effect on the **XVIII** : **XIX** product ratio [73]

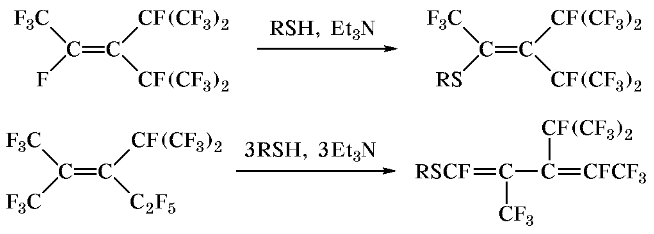
Product no.	Yield, %				
	–60 to –50°C	–35 to –30°C	–20 to –10°C	13°C	34°C
XVIII	100	95.2	71.9	37.5	13.3
XIX	0	4.8	28.1	62.5	86.7

Terminal perfluoroolefins readily react with trialkyl phosphites to afford dialkyl perfluoroalkenylphosphonates [77–79]. Specific feature of the Arbuzov reaction with perfluorinated unsaturated compounds is that it takes two pathways. One of these leads to formation of ethyl fluoride and perfluoroalkenylphosphonic acid ester, and the other, to diethyl ether and ethyl perfluoroalkenylphosphonofluoridate [80]. It is generally accepted that reactions of trialkyl phosphites with alkyl halides involve intermediate formation of thermally unstable fluorophosphoranes which decompose following the Arbuzov rearrangement mechanism

Scheme 30.

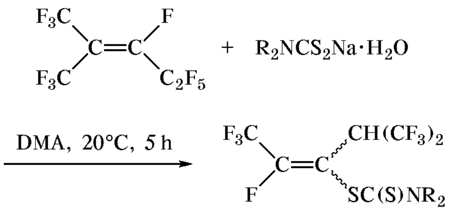


Scheme 31.



R = Et, *n*-Bu, *t*-Bu, Ph.

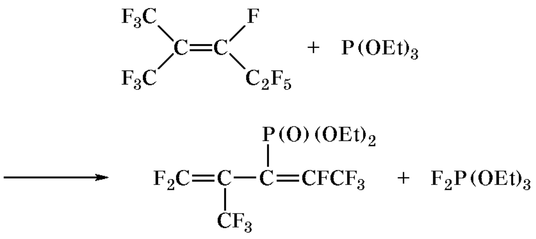
Scheme 32.



R = Me (yield 42%), Et (35%).

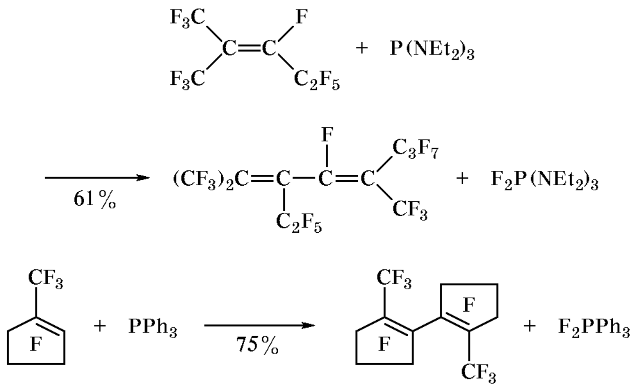
to give alkylphosphonates. In some cases such phosphoranes turned out to be stable compounds which can be isolated, e.g., those derived from perfluoro(2-methylpropene) [80], pentafluoroazapropene [81], and hexafluorocyclobutene [82, 83]. A different pattern is observed with internal perfluoroolefins. The reaction of triethyl phosphite with perfluoro(2-methyl-2-pentene) gives not the expected Arbuzov rearrangement product but diethyl 3,3-difluoro-1-(1,2,2,2-tetrafluoroethylidene)-2-trifluoromethyl-2-propenylphosphonate as a ~1 : 1 mixture of two stereoisomers [86] (Scheme 33). With equimolar amounts of triethyl phosphite and perfluoro(2-ethylcyclohexene), the major reaction product is 1-ethyloctafluoro-2-(pentafluoroethyl)cyclohexene, while the Arbuzov rearrangement product, diethyl octafluoro-2-(pentafluoroethyl)-1-cyclohexenylphosphonate is formed in a poor yield (cf. [84]).

Scheme 33.



Reactions with internal perfluoroolefins of the other P-nucleophile, hexaethylphosphorous triamide, lead to reductive dimerization of the olefins [85]. For example, from perfluoro(2-methyl-2-pentene), perfluoro(3-ethyl-2,5-dimethyl-2,4-octadiene) was obtained, and perfluoro(1-methylcyclopentene) gave rise to perfluoro[1-methyl-2-(2-methyl-1-cyclopentenyl)cyclopentene]. These reactions involve intermediate formation of phosphorus ylides which are converted into thermally unstable fluorophosphoranes. Decomposition of the latter gives carbanions [86, 87] which react with the initial olefin to afford the final products (Scheme 34).

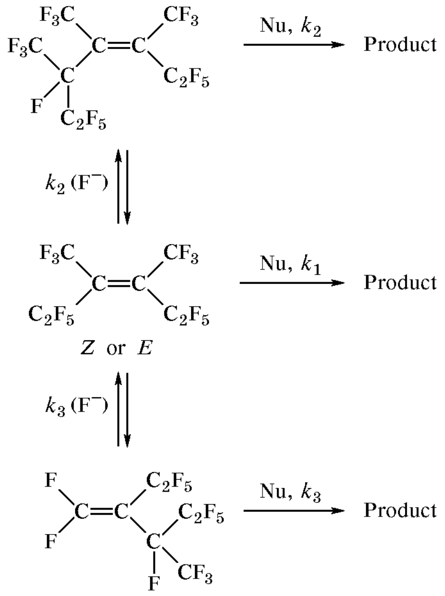
Scheme 34.



III. SYNTHESIS OF NITROGEN-CONTAINING PARTIALLY FLUORINATED COMPOUNDS BY REACTIONS OF INTERNAL PERFLUOROOLEFINS WITH AMINES

Reactions of perfluoroolefins with nitrogen-containing mono- and difunctional nucleophiles are of specific importance in the chemistry of organofluorine compounds [88]. These reactions ensure preparation of various intermediate products for the synthesis of materials for numerous applications, including a diversity of heterocyclic compounds. Terminal perfluoroolefins react with nucleophiles solely at the carbon atoms of the terminal C=C bond, leading to formation of derivatives having the corresponding functional group at the double bond. Analogous reactions with internal perfluoroolefins can take several pathways. Primary amines react with internal perfluoroolefins possessing a fluorine atom at the double bond to afford the corresponding Schiff bases rather than enamines. This result is explained by tautomerization intrinsic to systems in which NH group is attached to double-bonded carbon atom. This process is essentially determined by the structure of perfluorinated group at the double bond and by thermodynamic factor. Moreover, possible isomerization of internal perfluoroolefin by the action of liberated fluoride ion must be taken into account. Such isomerization could generate a different perfluoroolefin structure with a labile fluorine atom at the double bond. In addition, alkylamine is capable of acting as catalyst of the isomerization of internal perfluoroolefin into terminal. Here, the crucial factor is the ratio of reaction rates of these isomers with nucleophile. An example is the reaction of isomeric tetrafluoroethylene tetramers with methanol [89]. The corresponding rate constants form the following series (Scheme 35): $k_3 \gg k_2 \gg k_1$ [90].

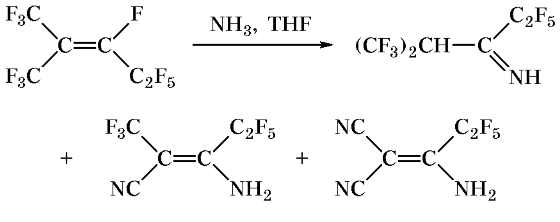
Scheme 35.



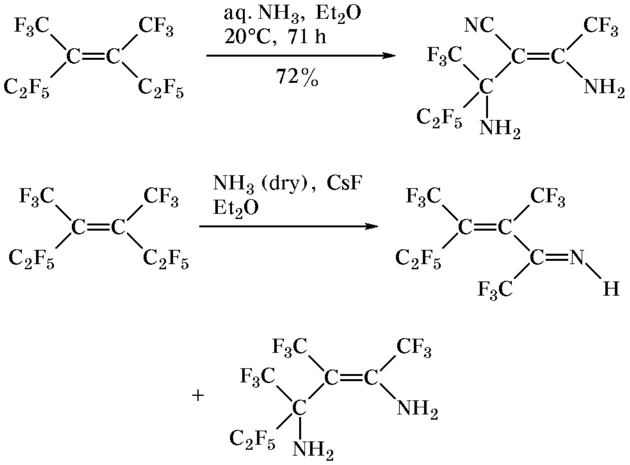
Reactions of internal perfluoroolefins with ammonia usually involve vinyl substitution, enamine–imine isomerization, and dehydrofluorination. As a result, iminoenamines or products of their further transformations are obtained. For instance, treatment of *trans*-perfluoro-2-pentene with ammonia leads to a nitrogen analog of β-diketone [88], and from perfluoro-2-butene 3-amino-2,4,4,4-tetrafluoro-2-butenenitrile is formed [91]. Similar transformations are typical of nucleophilic reagents having an amino group. Such reactions are widely used to explain the results of syntheses of heterocyclic compounds from perfluoroolefins. Some of these are the following: reaction of perfluoro-2-pentene with ethylenediamine [92, 93], reactions of perfluoro(2-methyl-2-pentene) with benzamides [93] and hydrazones [94], and reaction of perfluoro(2-methyl-2-pentene) with acetamidine [95].

As shown in [75, 96], the reaction of perfluoro(2-methyl-2-pentene) with dry ammonia in tetrahydrofuran gives rise to a mixture of products, including the corresponding ketene imine (formed by fluorine replacement at the double bond) and two internal unsaturated compounds having a cyano group. These data may be explained by comparable rates of replacement of the vinylic fluorine atom and subsequent dehydrofluorination which eventually yields polyamination products (Scheme 36). Perfluoro(3,4-dimethyl-3-hexene) reacts with aqueous ammonia to afford a product having NH_2 and CN groups at the internal double bond, whereas with dry ammonia a mixture of products is formed via replacement of fluorine by NH_2 group [89] (Scheme 37).

Scheme 36.

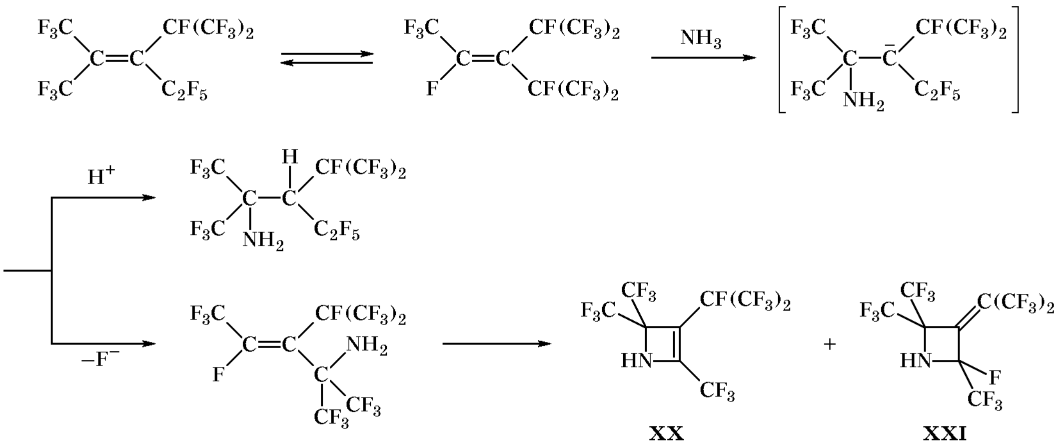


Scheme 37.

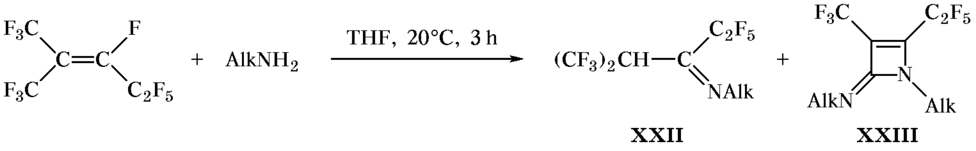


A mixture of 2-amino-3*H*-perfluoro(3-ethyl-2,4-dimethylpentane) and 4-aminoperfluoro(3-isopropyl-4-methyl-2-pentene) was obtained by reaction of hexafluoropropylene trimer with ammonia; heating of the latter product resulted in formation of two azetines **XX** and **XXI** [97] (Scheme 38). An analogous pattern was observed in the reaction of aqueous ammonia with perfluoro(2-ethyl-2-methyl-2-pentene) [98]. Reactions of perfluoro(2-methyl-2-pentene) with 2 equiv of primary alkylamines (such as propylamine, butylamine, isobutylamine, *tert*-butylamine, ethylamine, and cyclohexylamine) yield 1,4-addition products, N-substituted ketone imines **XXII** as ~1 : 1 mixtures of *syn* and *anti* isomers [99] (Scheme 39). When these reactions are carried out in the presence of triethylamine, *N*-alkylamino derivatives of perfluoro(2-ethyl-3-methylazete) (**XXIII**) are formed together with compounds **XXII**. The yield of product **XXIII** increases from 5 to 25%, when perfluoro(2-methyl-2-pentene) salt with triethylamine is used instead of the olefin itself (the preparation of such salts was described in [100]). Weakly basic primary amines exhibit a lower catalytic activity in the isomerization of internal perfluoroolefins into terminal ones; in these cases, the major product is that formed via

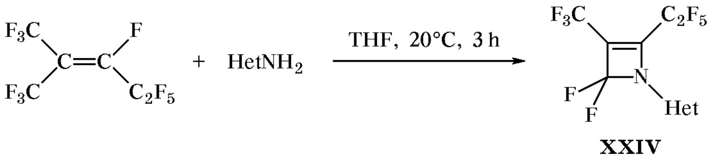
Scheme 38.



Scheme 39.

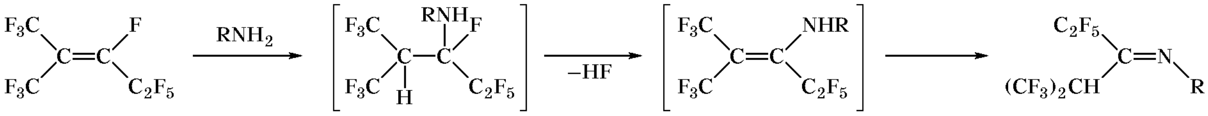


Alk = *i*-Pr, *n*-Bu, *i*-Bu.



Het = 1-methyl-2-benzimidazolyl; 6-bromo-2-benzothiazolyl; 1-methyl-2-nitro-5-imidazolyl.

Scheme 40.

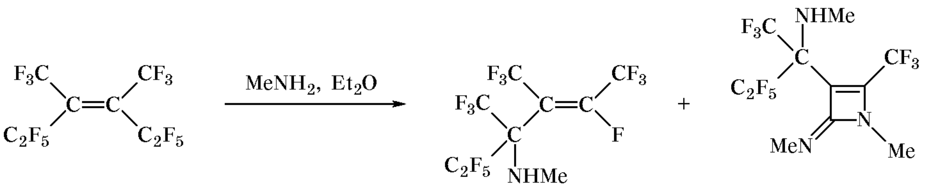


R = Ph, C_6F_5, SO_2Ph.

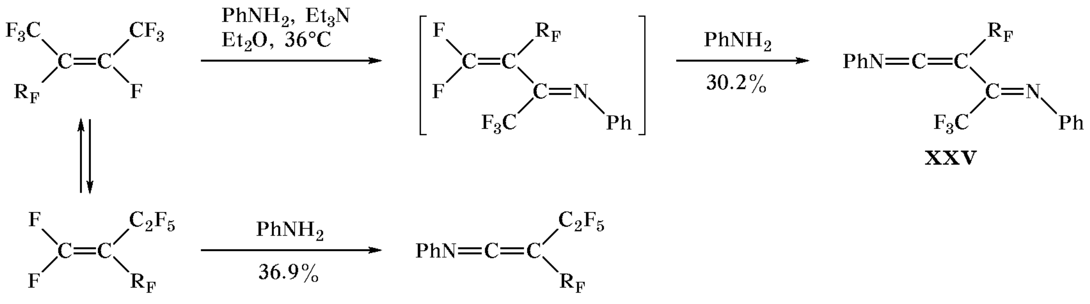
addition at the double bond and the subsequent enamine–imine rearrangement [101] (Scheme 40). On the other hand, perfluoro(2-methyl-2-pentene) reacts with 2-amino-1-methylbenzimidazole and 2-amino-6-bromobenzothiazole to give exclusively addition products **XXIII** (at the internal double bond); the subsequent treatment of **XXIII** with potassium carbonate leads to formation of azetine derivatives **XXIV** (Scheme 39). These findings indicate a considerable effect of the substituent at the amino group on the reaction direction.

2-Alkylaminoazetes were also obtained by the action of alkylamines RNH_2 (R = Me, Et, Bu) on perfluoro(3-ethyl-2,5-dimethyl-2-pentene (R = Bu) and perfluoro(3,4-dimethyl-3-hexene [102] and of hexamethyldisilazane on perfluoro(2-methyl-2-pentene) [96] (Scheme 41). Tetrafluoroethylene pentamer does not react with aromatic amines under standard conditions, but in the presence of triethylamine a complex mixture of products is formed, the major of which is disubstituted derivative **XXV** [103, 104] (Scheme 42). Tetrafluoroethylene pentamer reacts with primary

Scheme 41.



Scheme 42.

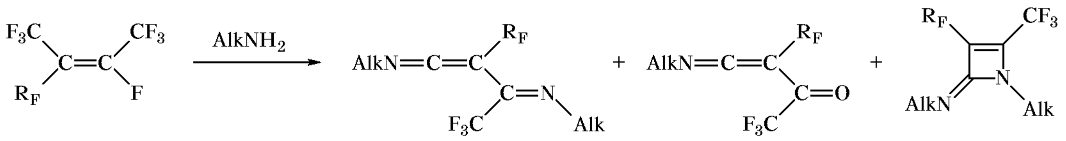


XXV

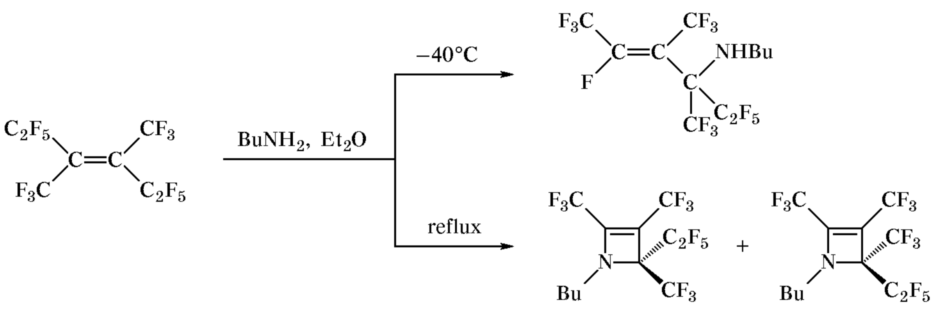
R_F = C(CF$_3$)(C$_{F5}$)$_2$.

aliphatic amines, e.g., butylamine or methylamine, to form three products: iminoketene imine, trifluoroacetylketene imine, and azetidine [105] (Scheme 43). Tetrafluoroethylene tetramer with *tert*-butylamine [43] and methylamine [106] at reduced temperature forms addition product at the double bond, whereas on heating stereoisomeric azetine derivatives **XXVI** are formed (Scheme 44). Ketene imines are obtained by reactions of tetrafluoroethylene hexamer with primary ($EtNH_2$ and $PhNH_2$) and secondary amines (Me_2NH) [107, 108] (Scheme 45). The reaction of perfluoro(2-methyl-2-pentene) with aniline results in formation of heterocyclic compound **XXVII** rather than product of fluorine replacement at the double bond [109] (Scheme 46). Hexafluoropropylene trimers react with primary amines to afford initially addition products at the double bond, compounds **XXVIII** and **XXIX**, which are converted into azetine derivatives **XXX** on heating or in the presence of triethylamine [97] (Scheme 47). Compounds **XXX** undergo isomerization into azetidines **XXXI** by the action of triethylamine or cesium fluoride in acetonitrile.

Scheme 43.

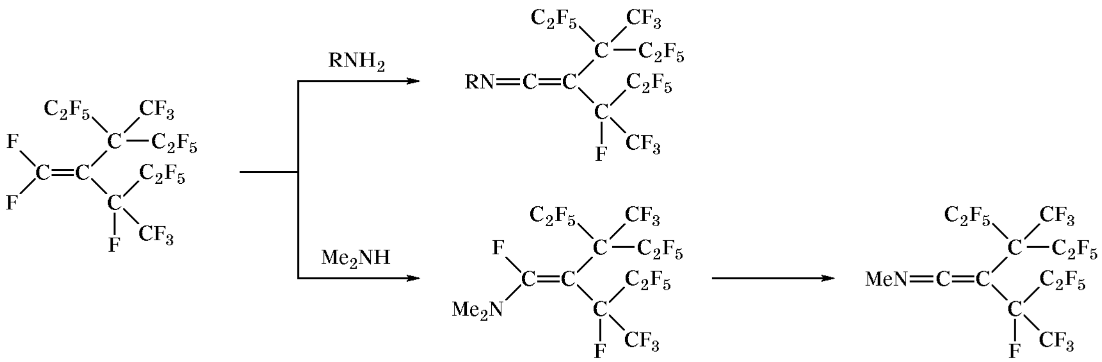


Scheme 44.



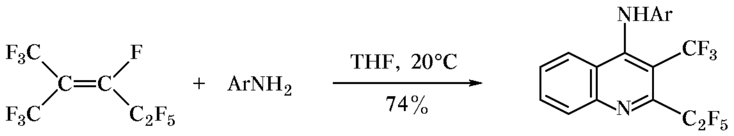
XXVI

Scheme 45.



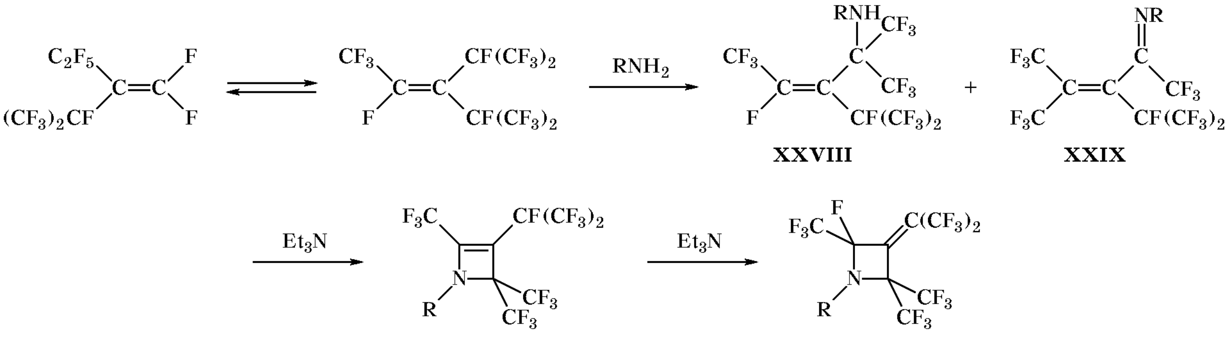
R = Et, Ph.

Scheme 46.



XXVII

Scheme 47.

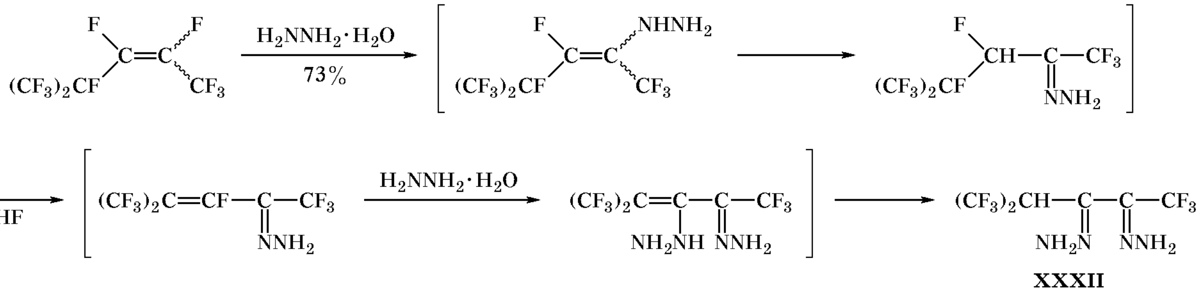


XXVIII **XXIX** **XXX** **XXXI**

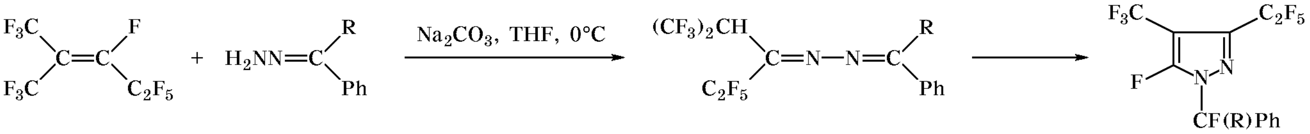
R = Me (89%), Et (82%), Bu (90%).

If a nucleophile possesses two reaction centers, intramolecular nucleophilic cyclization is possible through formation of intermediate with a terminal double bond. The reaction of perfluoro(2-methyl-2-pentene) with ethylenediamine in the presence of triethylamine in THF yields 7-fluoro-5-pentafluoroethyl-6-trifluoromethyl-2,3-dihydro-1*H*-1,4-diazepine [56]. In this case, intermediate imine with a terminal double bond is formed, and attack on the latter by the second nucleophilic nitrogen atom gives rise to further intramolecular cyclization. Treatment of perfluoro(4-methyl-2-pentene) with hydrazine hydrate results in replacement of fluorine atoms at the double bond to afford hexafluoro-4-trifluoromethyl-2,3-pentanedione bishydrazone (**XXXII**) [110, 111] (Scheme 48). The same perfluoroolefin reacts with hydrazones, initially yielding the corresponding ketene imine which undergoes intramolecular cyclization during the process [112] (Scheme 49). Reactions of perfluoro(2-methyl-2-pentene) with acetamidine and trifluoroacetamidine hydrochlorides in the presence of sodium hydroxide and benzyltriethylammonium chloride give initially fluorine replacement product (at the double bond), whose subsequent prototropic isomerization [109], dehydrogenation, and cyclization [113] lead to 4-fluoropyrimidine derivatives (Scheme 50).

Scheme 48.

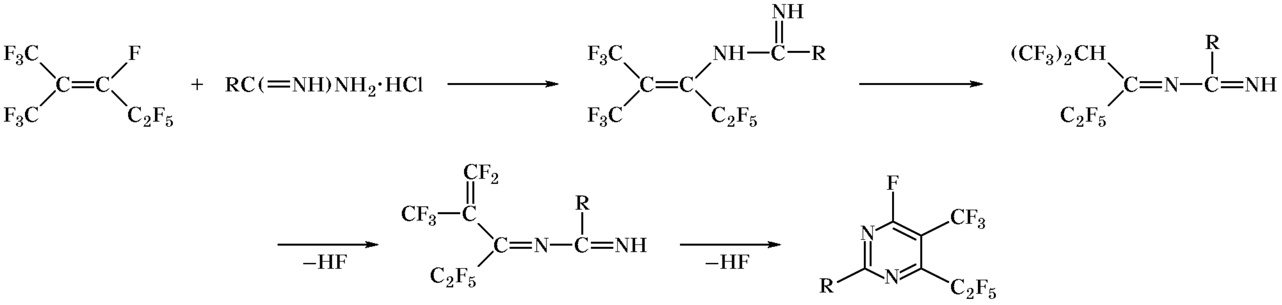


Scheme 49.



R = H (91%), CH_3 (90%).

Scheme 50.



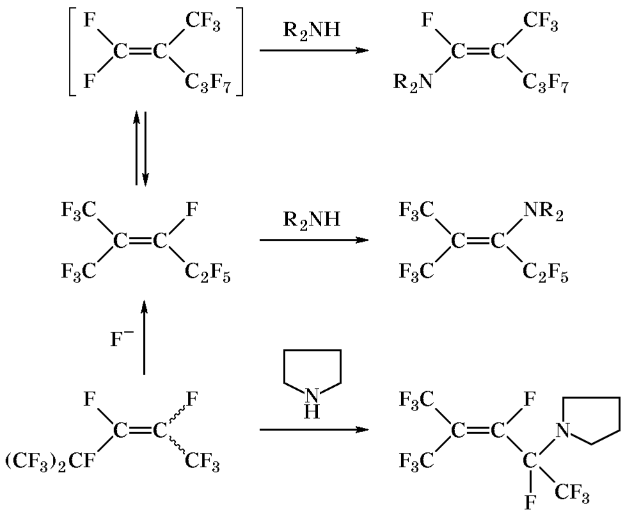
R = CH_3, CF_3.

Reactions of internal perfluoroolefins with secondary amines do not give products of fluorine replacement at the double bond, but enamines are obtained via fluorine replacement at terminal double bond [114]. Here, the site of fluorine replacement is determined by preliminary isomerization of internal perfluoroolefin into terminal [115, 116]. Also, internal perfluoroolefins give products of fluorine replacement in the correponding terminal olefin formed during the process by isomerization initiated by fluoride ion [115, 117–119]. However, the available data do not confirm the above stated, for either mixtures of two isomeric products or only one fluorine replacement product (either at the internal or terminal double bond) were obtained from some secondary amines [115, 117–119]. Analysis of the data on the orientation of fluorine substitution in internal perfluoroolefins with respect to secondary amine structure suggests a common reaction mechanism for internal and terminal perfluoroolefins, which does not include preliminary isomerization of internal perfluoroolefin into terminal [120]. Presumably, the key stage in these reactions is transformation of intermediate carbanion generated by attack of N-nucleophile having any structure on the carbon atom of the internal double bond. Thus, the transformation pathway of initial olefin is determined by relative contributions of the energy and steric factors supplemented by the possibility for formation of intermediate species with multiple bonds.

Hexafluoropropylene dimers react with secondary amines along several pathways. With diethylamine, enamino derivative of the corresponding terminal perfluoroolefin is exclusively formed [89, 117], whereas from piperidine, analogous derivative of internal perfluoroolefin is obtained [109, 116]. Other secondary amines also react in a nonselective fashion [115].

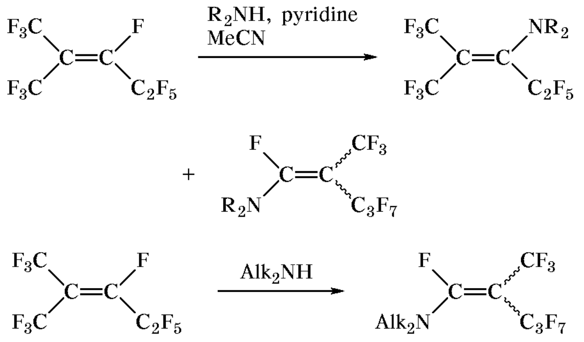
England and Piecara [116] performed a detailed study of this reaction and found that in fact two isomeric enamines are formed: 1-[3,3,3-trifluoro-1-(pentafluoroethyl)-2-(trifluoromethyl)-1-propenyl]piperidine and 1-[1,3,3,4,4,5,5,5-octafluoro-2-(trifluoromethyl)-1-pentenyl]piperidine at a ratio of 1:2.07 (1:6.69, according to [115]). As the size of cyclic amine increases (e.g., in the series pyrrolidine, piperidine, cycloheptylamine) the yield of the enamine derived from terminal perfluoroolefin rises: the corresponding enamine ratios are 1:0.82, 1:6.69, and 1:8.09, respectively [115]. The results were explained [115, 116] in terms of preliminary isomerization of internal perfluoroolefins into terminal ones by the action of trialkylamines and fluoride ion and subsequent replacement of fluorine at the terminal double bond. Analogous relations were revealed for reactions of cyclic amines with perfluoro(4-methyl-2-pentene) [115] and of dialkylamines with perfluoro-2-pentene [121]. These reactions afforded enamines via nucleophilic replacement of fluorine at the terminal double bond. On the other hand, study of the reaction of perfluoro(2-methyl-2-pentene) with piperidine [121] showed that fluorine atom can be replaced exclusively at the double bond of internal perfluoroolefin to give the corresponding enamine (Scheme 51). The same pathways are typical for the reactions of hexafluoropropylene trimer [118].

Scheme 51.



The reaction of perfluoro(2-methyl-2-pentene) with morpholine in anhydrous acetonitrile in the presence of an equimolar amount of pyridine or triethylamine (to bind the liberated hydrogen fluoride) was shown [120] to give 1-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-1-propenyl)morpholine and 1-(octafluoro-2-trifluoromethyl-1-pentenyl)morpholine at a ratio of 1:3.49 (Scheme 52).

Scheme 52.

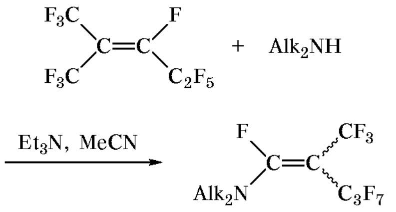


NR$_2$ = morpholino, (4-CF$_3$C$_6$F$_4$)$_2$N, 2,5-dioxo-1-pyrrolidinyl, 2-oxo-1-pyrrolidinyl, 1,3-dioxo-2,3-dihydro-1*H*-isoindol-1-yl; Alk = Et, Bu.

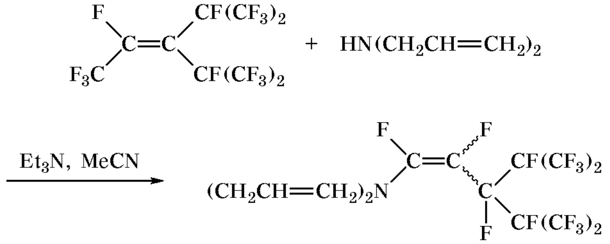
Two enamines, *N*,*N*-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)-3-aminoperfluoro(2-methyl-2-pentene) and *N*,*N*-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)-1-aminoperfluoro(2-methyl-1-pentene) at a ratio of 1:3, were also obtained by the reaction of perfluoro(2-methyl-2-pentene) with bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)amine in the presence of triethylamine. However, the reactions of perfluoro(2-methyl-2-pentene) with pyrrolidin-2-one, succinimide, and phthalimide in the presence of triethylamine gave exclusively products of fluorine replacement at the internal double bond: *N*-perfluoro(2-methyl-3-pentenyl)succinimide, *N*-perfluoro(2-methyl-3-pentenyl)phthalimide, and 1-[3,3,3-trifluoro-1-pentafluoroethyl)-2-trifluoromethyl-1-propenyl]pyrrolidin-2-one [122] (Scheme 52). Thus, reduction of the amine basicity is accompanied by reduction of its catalytic activity in the isomerization of internal perfluoroolefin into terminal; as a result, products of fluorine replacement at the internal double bond are formed.

As shown in [115, 119], the reaction of perfluoro(2-methyl-2-pentene) with an equimolar amount of diethylamine or dibutylamine in acetonitrile in the presence of acetonitrile leads to formation of *N*,*N*-diethyl-1-aminoperfluoro(2-methyl-1-pentene) and *N*,*N*-dibutyl-1-aminoperfluoro(2-methyl-1-pentene), respectively, whereas with dipropylamine and diallylamine in the presence of Et$_3$N an enamine derived from terminal perfluoroolefin is formed [119]. A mixture of hexafluoropropylene trimers reacts with diallylamine to give only product **XXXIII** (Scheme 53). The reaction of perfluoro(1-ethylcyclohexene) with dialkylamines results in fluorine replacement at the double bond [119] (Scheme 54).

Scheme 53.

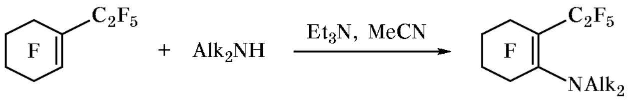


Alk = Bu (yield 51%), Pr (64%), $CH_2CH{=}CH_2$ (53%).



XXXIII

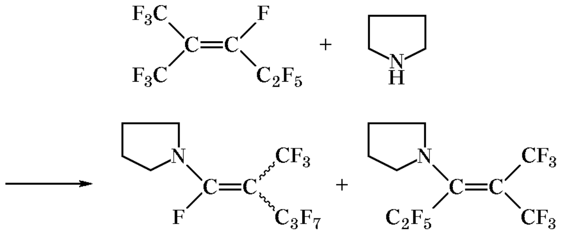
Scheme 54.



Alk = Pr (yield 56%), Bu (67%), $CH_2CH{=}CH_2$ (53%).

Bis(dimethylamino)methane and diethylaminotrimethylsilane react with perfluoro(2-methyl-2-pentene) to afford exclusively fluorine replacement products [123], but those derived from the terminal perfluoroolefin which is formed by isomerization of the initial internal olefin by the action of bases [123]. It is known [124–126] that such isomerization is promoted by fluoride ion. On the other hand, the reaction of pyrrolidine with the same substrate yields a mixture of enamines **XXIV** and **XXXV** (Scheme 55).

Scheme 55.

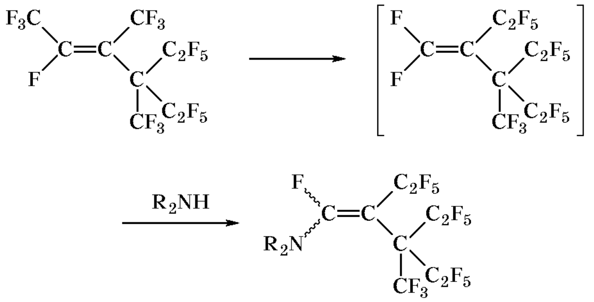


XXXIV **XXXV**

Solvent	Ratio **XXXIV**:**XXXV**
Dioxane	80:20
Diethyl ether	70:30
DMF	70:30

Tetrafluoroethylene pentamer was reported [105] to react with dimethylamine, diethylamine, morpholine, and piperidine to afford the corresponding fluorine replacement products at the terminal rather than internal double bond (Scheme 56).

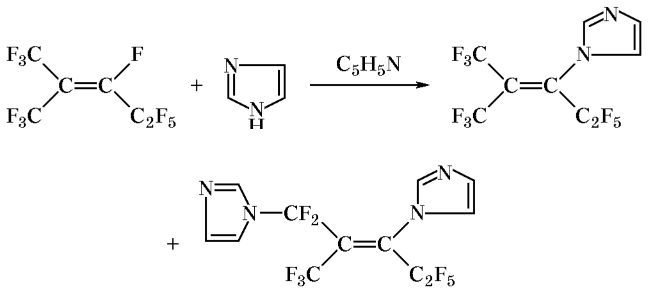
Scheme 56.



R_2N = Me_2N, Et_2N, piperidino, morpholino.

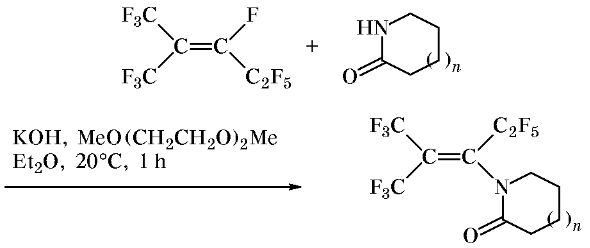
On the other hand, azoles react with perfluoro(2-methyl-2-pentene) in the presence of bases (such as pyridine or triethylamine), yielding exclusively products of fluorine replacement at the internal double bond, e.g., 3-(1-imidazolyl)perfluoro(2-methyl-2-pentene) and 1,3-bis(1-imidazolyl)perfluoro(2-methyl-2-pentene) [127] (Scheme 57).

Scheme 57.



In the presence of bases, lactams act as fairly effective N-nucleophiles; their reactions with perfluoro(2-methyl-2-pentene) give the corresponding *N*-perfluoroalkenyl derivatives **XXXVI** (yield 49% from piperidin-2-one and 51% from caprolactam) [68] (Scheme 58). Compounds **XXXVI** are unstable in acid medium. They readily undergo hydrolysis on heating in ether solution with a 5% solution of hydro-

Scheme 58.

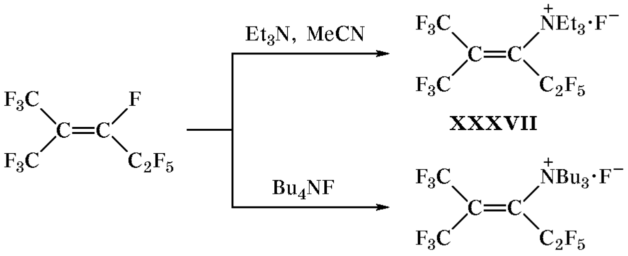


XXXVI

chloric acid; as a result, the corresponding ketone, $(CF_3)_2CHC(O)C_2F_5$ is formed.

It should be noted that some internal perfluoroolefins are capable of reacting with tertiary amines to form trialkylammonium salts. Perfluoro(2-methyl-2-pentene) gives such salts with triethylamine (**XXXVII**) [100] and tetrabutylammonium fluoride (**XXXVIII**) [128] (Scheme 59). These salts turned out to be much more reactive than the corresponding neutral perfluoroolefins, and they can be involved in reactions with weak nucleophiles so that only the Alk_3N group is replaced by N-nucleophile moiety, the other reaction centers remaining intact.

Scheme 59.

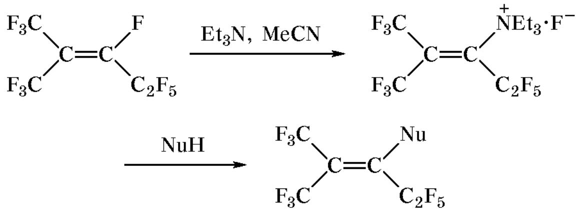


XXXVII

XXXVIII

Such salts react with dialkylamines at the double-bonded carbon atom with subsequent replacement of the Alk_3N group by dialkylamino group [129, 130]. In the reactions of perfluoro(2-methyl-2-pentene) with pyrazole, benzotriazole, and 1,2,4-triazole, temporary replacement of the fluorine atom at the double bond by a readily departing group (e.g., Et_3N; salt **XXXVII** was synthesized by the procedure described in [100]) ensures selective preparation of products of fluorine replacement at the internal double bond [127] (Scheme 60). Presumably, in this case N-nucleophile initially attacks the C=C bond at the carbon atom attached to positively charged nitrogen atom (due to powerful electron-acceptor effect of the $Et_3\overset{+}{N}$ group). Salt **XXXVII** is much more electrophilic than the initial perfluoroolefin.

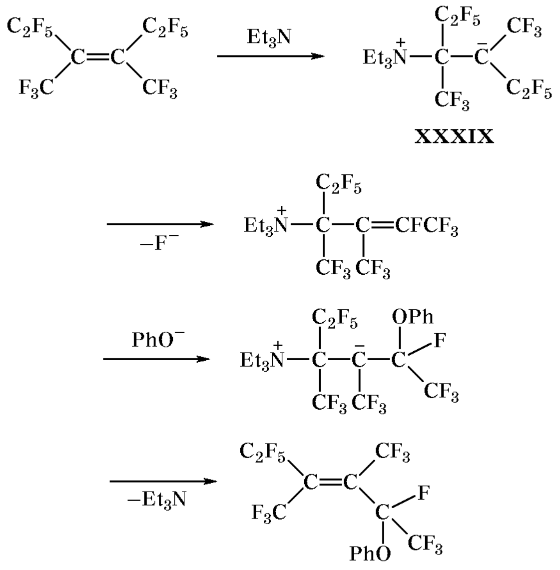
Scheme 60.



NuH = imidazole, pyrazole, 2*H*-1,2,3-triazole, benzotriazole.

This approach is also applicable to olefins having only perfluoroalkyl substituents. Initially, an inner salt is formed. For example, salt **XXXIX** is formed from triethylamine and perfluoro(3,4-dimethyl-3-hexene). Elimination of fluoride ion from the CF_2 group of **XXXIX** generates a double bond. The subsequent reaction of phenol at that bond yields either product **XL** (yield of the *trans* isomer 28%, and of the *cis* isomer, 37%) [116], or compound **XLI** (yield 35%) (Scheme 61).

Scheme 61.

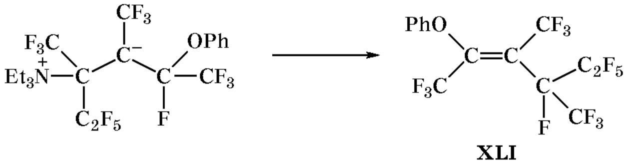


XXXIX

XL

In the first case, a new double bond is generated by elimination of triethylamine, and in the second,

Scheme 62.



XLI

via intramolecular attack by fluorine from the CF group on the carbon atom attached to the NEt_3 group (Scheme 62). The above example demonstrates a diversity of reaction paths for internal perfluoroolefins and nucleophilic reagents.

IV. GENERATION OF CARBANIONS BY THE ACTION OF FLUORIDE ION ON INTERNAL PERFLUOROOLEFINS AND THEIR REACTIVITY

A considerable group of reactions of internal perfluoroolefins includes processes with intermediate generation of carbanions. Perfluorinated carbanions are highly reactive species which are very important for the chemistry of organofluorine compounds. There are several methods for generation of perfluorinated carbanions. The first of these is based on reactions of internal perfluoroolefins with fluoride ion. In this case, the resulting carbanion may have either the same structure as the initial olefin or a different one, depending on the possibility for isomerization into a more thermodynamically stable olefin. The second procedure involves carbanion generation by decomposition of intermediate compounds formed by the action of some nucleophiles, e.g., phosphines, on internal perfluoroolefins.

IV.1. Generation of Carbanions from Internal Perfluoroolefins by the Action of Fluoride Ion

Fluoride ion in dipolar aprotic solvents is known to exhibit a high nucleophilicity, so that it is capable of attacking the double bond in internal perfluoroolefins to give primary carbanion [131, 132]. Alkali metal fluorides [133], their complexes with crown ethers [134, 135], $(Me_2N)_3S^+ \cdot Me_3SiF_2^-$ (TAS) [136, 137] (Table 2), perfluorocyclobutene salts with triethylamine [138, 139] (Scheme 63), etc., can be used as fluoride ion source. The carbanion is stabilized by perfluoroalkyl groups, and it may be involved in the following reactions: (1) isomerization with double bond transfer; (2) reactions with electrophiles; and (3) reaction with initial perfluoroolefin provided that fluorine atom at the double bond possesses a sufficient nucleophilic mobility. There is no need of obtaining a stable tertiary perfluorinated carbanion (via reaction of perfluoroolefin with metal fluoride); It is sufficient to generate an intermediate carbanion *in situ*. The latter can react with various electrophiles. Scheme 64 illustrates some reactions of the carbanion

Scheme 63.

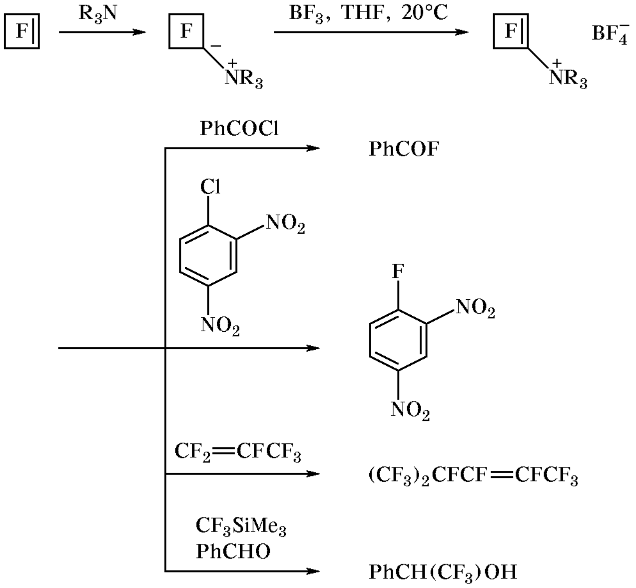
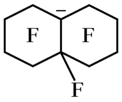
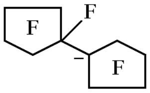
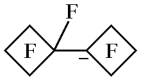
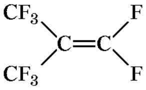
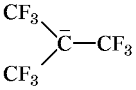
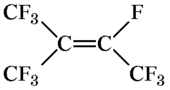
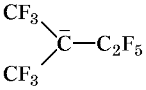
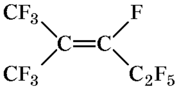
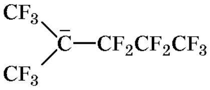
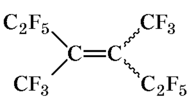
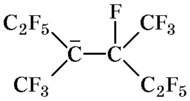
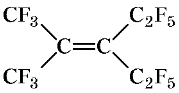
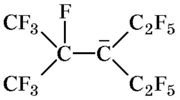
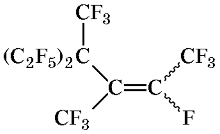
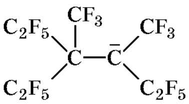
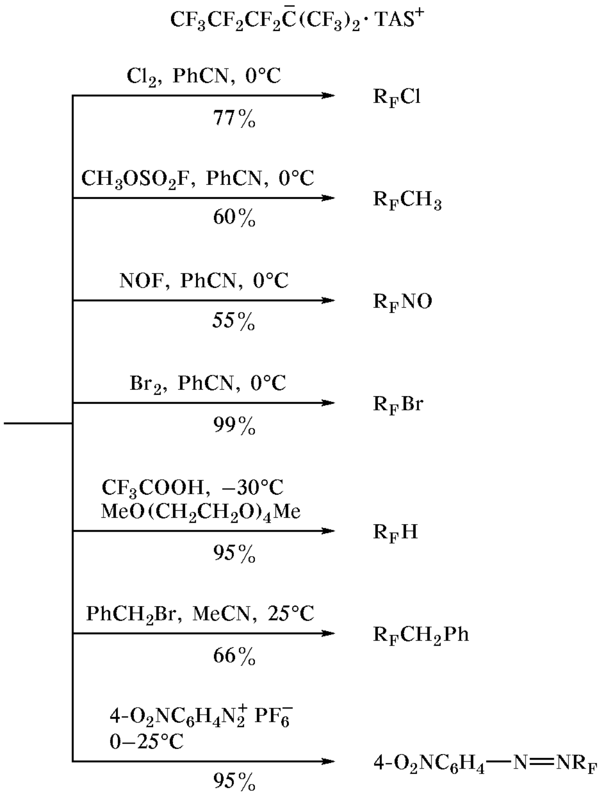


Table 2. Salts generated from perfluoroolefins by the action of $(Me_2N)_3S^+ \cdot Me_3SiF_2^-$ or CsF

Initial olefin	Salt	Reference
		[140]
		[140]
		[140]
		[140]
		[140]
		[141]
		[141]
		[140]
		[141]

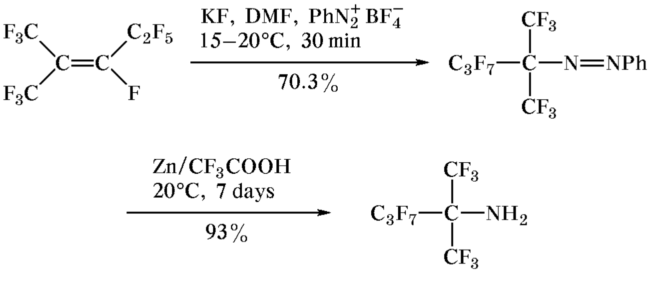
Scheme 64.



TAS = $(Me_2N)_3S^+ \cdot Me_3SiF_2^-$.

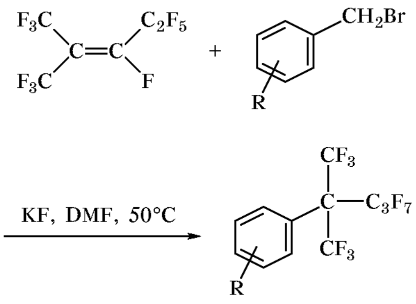
derived from perfluoro(2-methyl-2-pentene) [128, 140, 142, 143]. Its reaction with benzenediazonium tetrafluoroborate gave diazo compound which was reduced with zinc in trifluoroacetic acid to obtain primary amine with sterically hindered perfluoroalkyl group [123] (Scheme 65).

Scheme 65.



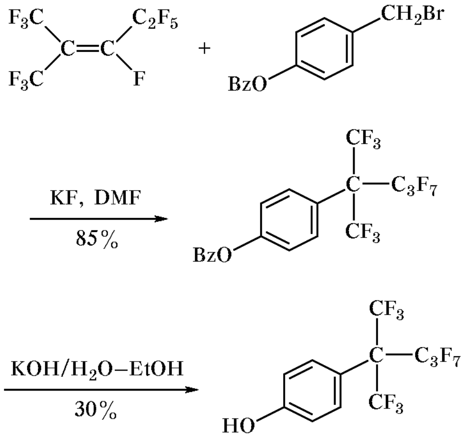
Perfluorinated carbanions are effective nucleophiles and strong alkylating agents. Various benzyl bromides $R'C_6H_4CH_2Br$ (R = H, *p*-, *m*-, *o*-CN, *p*-, *m*-, *o*-NO_2, *p*-, *m*-CH_2Br) readily react with perfluoro(2-methyl-2-pentene) in dipolar aprotic solvents in the presence of KF or alkali metal iodides, yielding more than 70% of bromine replacement products which are used in electronics as industrial oils for hydraulic fluids and surfactants [144–148] (Scheme 66).

Scheme 66.



p-(Bromomethyl)phenyl benzoate reacts with perfluoro(2-methyl-2-pentene) in DMF at 50–60°C; 85% of the substitution product is formed in 20 h, and its hydrolysis with KOH in aqueous ethanol gives 30% of hydroxy derivative **XLII** [149] (Scheme 67).

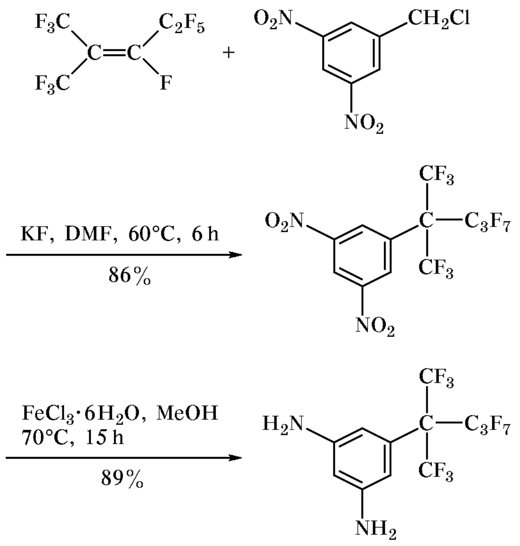
Scheme 67.



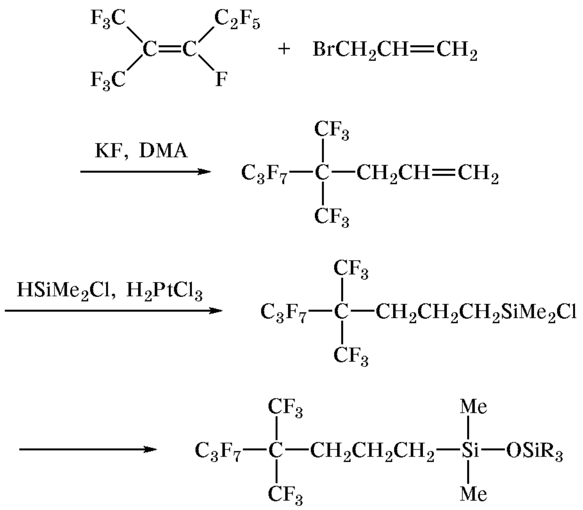
XLII

Analogous reactions with benzyl chlorides were also reported. 3,5-Dinitrobenzyl chloride reacts with hexafluoropropylene dimer in DMF at 60°C, yielding chlorine replacement product **XLIII** [150]. The latter is an intermediate product in the synthesis of aromatic diamines (Scheme 68). The reaction with benzyl bromide leads to formation of bromine replacement product which takes up chlorodimethylsilane to afford an adduct having a reactive Si–Cl bond (Scheme 69). The adduct has found application for the preparation of chromatographic stationary phases, e.g., 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-tridecafluoro(4,4-dimethylheptyl)dimethylsiloxane [Fluotix 120 N(A)] [151]. Alkyl halides can also be involved in such processes; as a result, partially fluorinated aliphatic compounds are obtained [142] (Scheme 70).

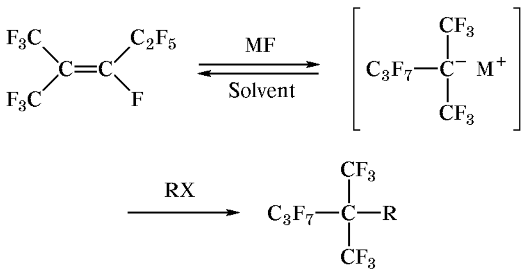
Scheme 68.



Scheme 69.



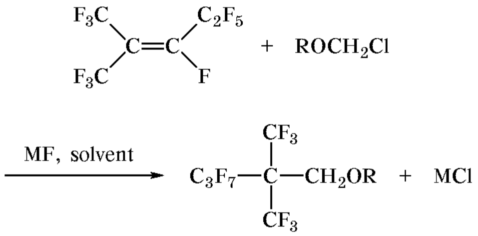
Scheme 70.



R = Me, Et, Pr, Bu, $CH_2CH{=}CH_2$; X = I, Br.

Partially fluorinated ethers were obtained by reaction of hexafluoropropylene dimers with chloromethyl ethers [152] (Scheme 71).

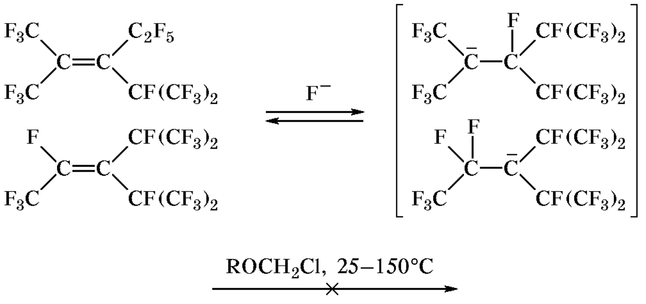
Scheme 71.



M = Cs, K; R = C_8H_{17} (yield 90%), Ph (81%), $PhCH_2$ (82%), $CH_2CH{=}CH_2$ (50%), $CH_2{=}CH(CH_2)_8$ (86%), $CH_2{=}CH$-$CH_2OCH_2CH_2$ (85%).

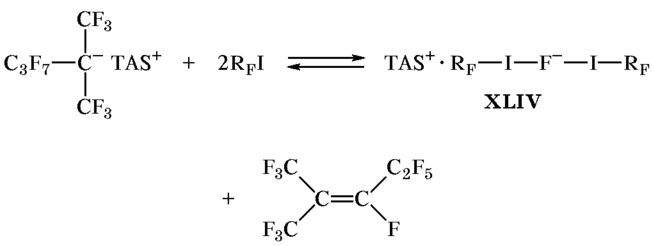
However, hexafluoropropylene trimer failed to react with chloromethyl ethers even on heating to 150°C. These data indicate a considerable effect of shielding of the anionic center by bulky substituents (Scheme 72).

Scheme 72.



On the other hand, the same carbanion reacts with perfluoroalkyl iodides, yielding salt **XLIV** via coordination of fluoride ion to two iodine atoms and initial perfluoroolefin [153] (Scheme 73).

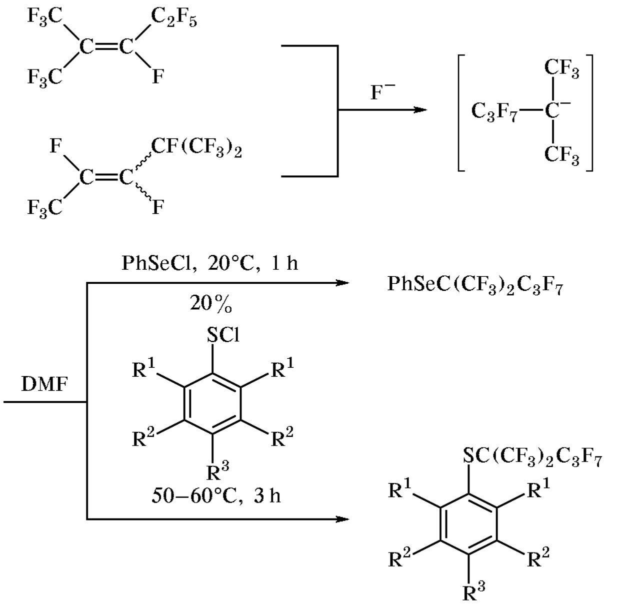
Scheme 73.



R_F = C_6F_5 (yield 86%), $(CF_2)_4$ (86%), C_6F_{13} (76%), $(CF_2)_2$, $(CF_2)_8$, $(CF_2)_{10}$.

High mobility of the chlorine atom in arenesulfenyl chlorides and areneselenyl chlorides made it possible to develop a procedure for preparation of partially fluorinated aryl perfluoroalkyl sulfides and selenides [152–155] (Scheme 74). Such products exhibit fungicide, insecticide, and detergent properties. In some cases, this procedure turned out to be more efficient than those known previously.

Scheme 74.

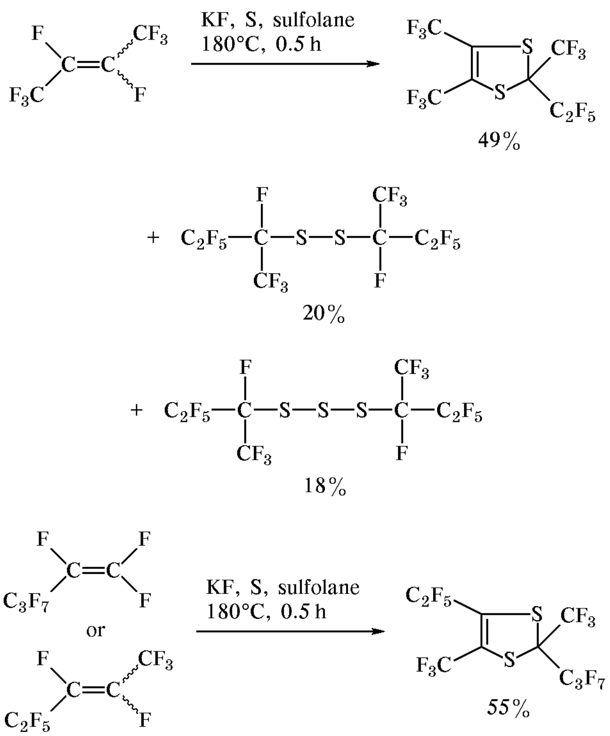


R^1	R^2	R^3	Yield, %
H	H	H	75
H	H	Me	60
Me	H	Me	86
Me	Me	H	80
Me	Me	Me	59
H	H	Cl	58

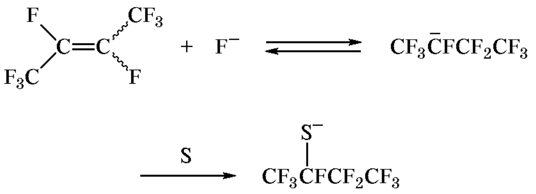
Perfluorinated carbanions are very reactive; they are capable of reacting even with neutral substances. For example, carbanions generated from perfluoro-2-butene, perfluoro-1-pentene, and perfluoro-2-pentene by the action of KF in sulfolane react with sulfur to afford 1,3-dithiole derivatives [156] (Scheme 75). Their formation may be explained by generation of intermediate S-anion and its further transformations (Scheme 76).

Cesium perfluoro(2-methylpentan-2-ide) reacts with perfluorocyclopentene and tetrafluoropyridazine in dipolar aprotic solvents, resulting in substitution of fluorine atom at C^2; with acetyl chloride, halogen replacement product is formed [128] (Scheme 77). A procedure for preparation of branched perfluorinated compounds [157] is based on the reaction of perfluoro(2-methyl-2-pentene) potassium salt with methyl iodide and allyl bromide. The subsequent electro-

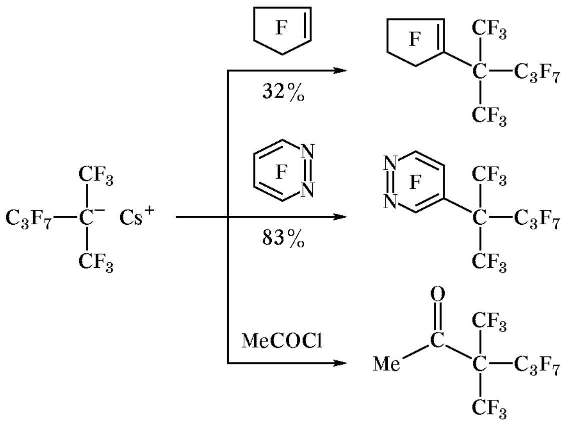
Scheme 75.



Scheme 76.

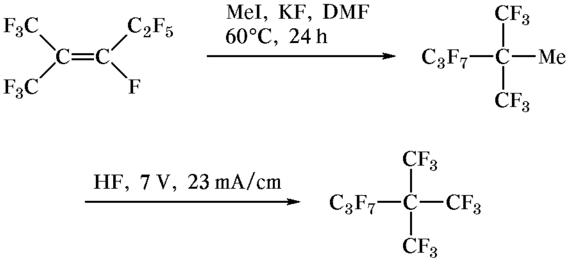


Scheme 77.



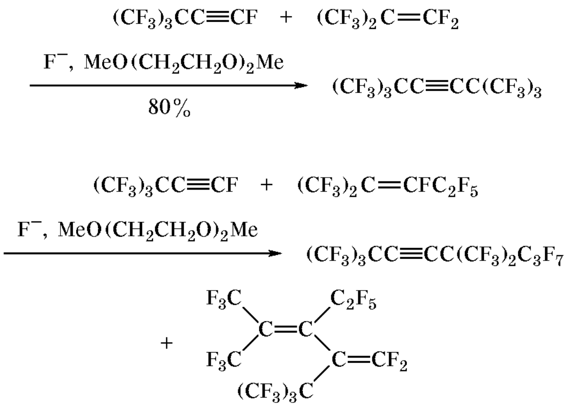
chemical fluorination yields exhaustively fluorinated branched alkane (Scheme 78).

Scheme 78.



Carbanions generated from perfluoroisobutylene and perfluoro(2-methyl-2-pentene) by the action of fluoride ion react with perfluoroalkyl-substituted acetylenes, yielding fluorine replacement products at the triple bond [158, 159]. With perfluoro(2-methyl-2-pentene), the reaction takes two pathways: replacement of fluorine atom in the ethyl group by tertiary carbanion and replacement of the vinyl fluorine atom by vinyl anion $[(CF_3)_3CC{=}CF_2]^-$ (Scheme 79).

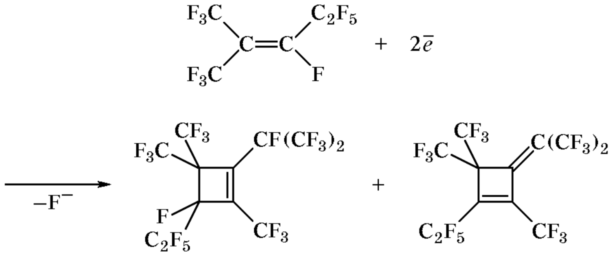
Scheme 79.



Anionic dimerization of perfluoroolefins by the action of fluoride ion (generated from different sources) is widely used in organic synthesis; also, this reaction underlies some large-scale processes for preparation of organofluorine compounds. For example, dimerization of perfluoropropylene is used for large-scale preparation of hexafluoropropylene dimers and trimers [160–162].

Perfluorinated carbanions can be generated not only by addition of fluoride ion at the carbon atom of perfluorinated olefin but also by electrolysis (e.g., at a platinum electrode using $MeCN{-}Et_4NF \cdot 2H_2O$ as supporting electrolyte). Electrochemical reduction of some higher perfluoroolefins is accompanied by dimerization, cyclization, and defluorination processes. Electrolysis of hexafluoropropylene dimers gives 60% of substituted perfluorocyclobutanes [153] (Scheme 80). In going to lead, zinc, titanium, or copper amalgam cathode, the yield of the dimers decreases to 30%.

Scheme 80.

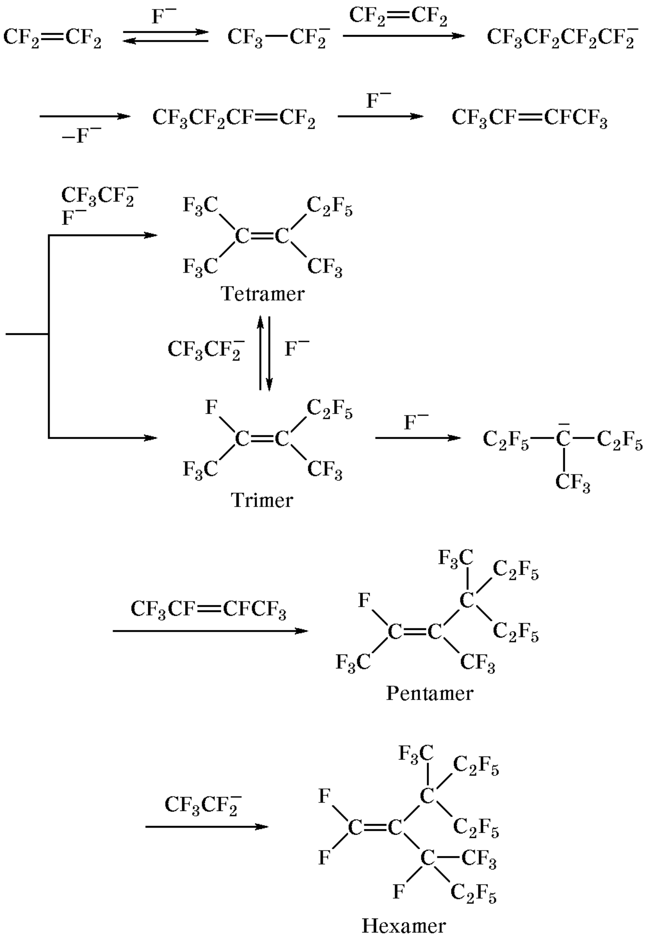


Et_4NF, mol	Product ratio
0.94	10 : 1
0.2	2 : 1

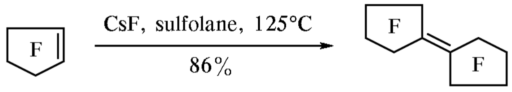
Obviously, cathodic dimerization may follow a radical mechanism involving recombination of radical anions or allyl radicals formed by elimination of fluoride ion. However, some data and structure of the products suggest that the dimerization mechanism is ionic. Presumably, the initial reaction stage is transfer of two electrons to perfluoroolefin, which is accompanied by elimination of fluoride ion with formation of allyl anion **XLV**. The subsequent cycloaddition reaction is typical of perfluoroolefins: attack by anion **XLV** on the substrate is followed by intramolecular substitution of the vinyl fluorine atom. The resulting dimeric product undergoes either isomerization by the action of fluoride ion to give perfluoro(4-ethyl-2-isopropyl-1,3,3-dimethylcyclobutene) or further reduction at a cathode to afford perfluoro-(2-ethyl-4-isopropylidene-1,3,3-trimethylcyclobutene). Raising the concentration of fluoride ion in the electrolyte favors isomerization of the dimer.

Oligomerization of perfluoroolefins and perfluorocycloolefins by the action of fluoride ion is well known [163, 164]. Oligomerization of tetrafluoroethylene gives rise to a mixture of its trimer, tetramer, pentamer, and hexamer via generation of fairly active carbanions and isomerization of intermediate perfluorolefins (Scheme 81). Oligomerization of perfluorocycloalkenes takes an analogous path. As a rule, mixtures of the corresponding dimers are formed. These reactions are very sensitive to the conditions. Perfluorobi(cyclopentylidene) is formed from per-

Scheme 81.



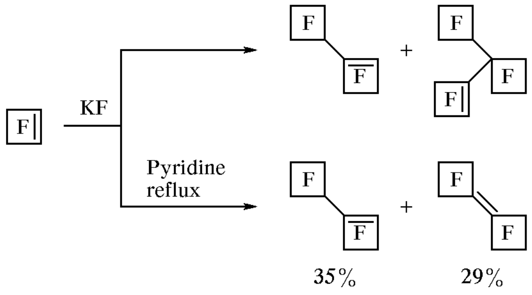
Scheme 82.



fluorocyclopentene by the action of CsF in sulfolane at 125°C [165] (Scheme 82).

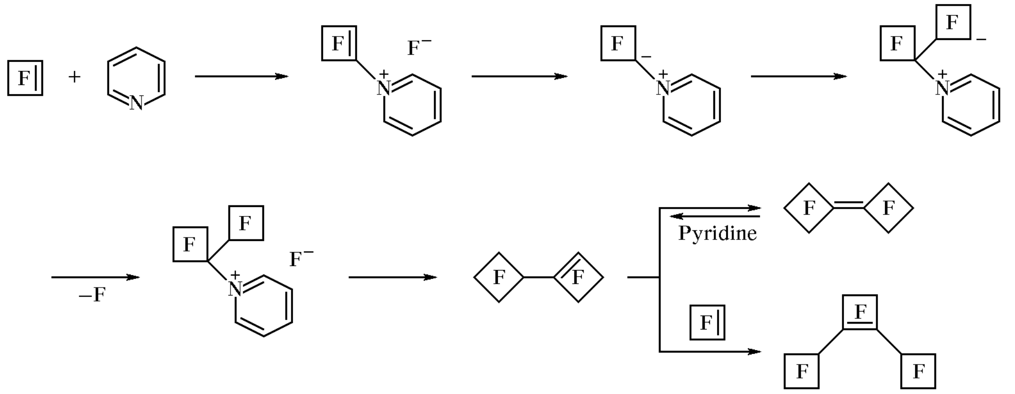
The yield of dimers from perfluorocyclobutene increases when pyridine is used as solvent [165–168] (Scheme 83).

Scheme 83.

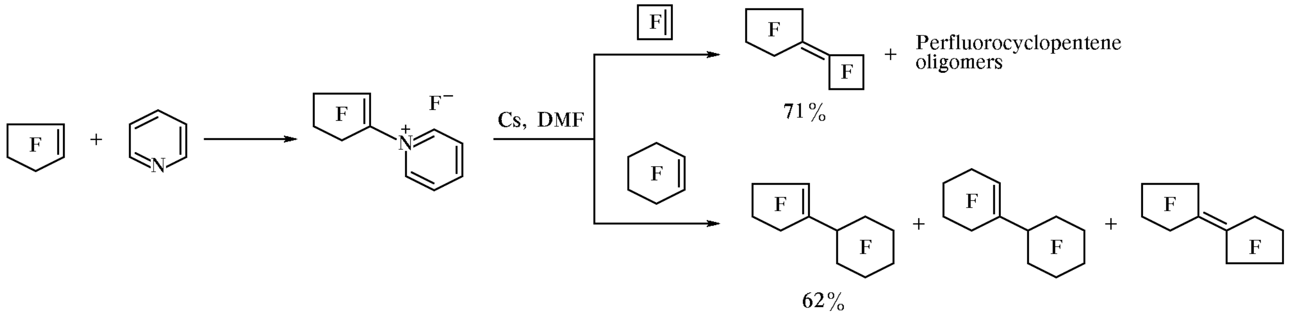


Initially, pyridine with perfluorocyclobutene gives pyridinium salt containing reactive cyclobutenyl anion [167, 169] (Scheme 84). With excess perfluorocyclobutene or on addition of another perfluoroolefin to the reaction mixture, fluorine replacement at the double bond occurs. The ratio of mono- and disubstituted products depends on the amount of pyridine. When the molar ratio olefin–pyridine is 15:1, the yield of monosubstituted products is 64%, whereas it decreases to 21% when the above ratio is 9:1. The other perfluorocycloolefins behave similarly [170, 171]. These processes formed the basis for the synthesis of new dienes from perfluorocyclobutene and perfluorocyclopentene [171] (Scheme 85). However, cesium fluoride was not always effective for the oligomerization to occur. For example, diene **XLVI** is converted into triene **XLVII** by the action of CsF [172, 173], while diene **XLVIII** gives only the corresponding salt **XLIX** [174] (Scheme 86).

Scheme 84.

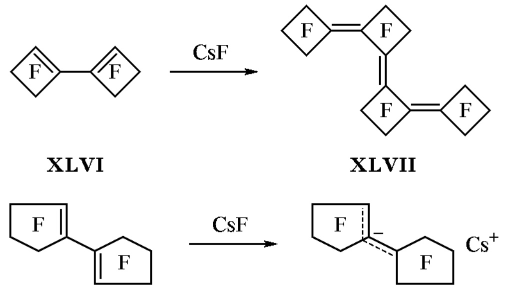


Scheme 85.



Perfluoro(*tert*-butylacetylene) reacts with fluoride ion to give trimer **L** due to ready generation and high reactivity of perfluorovinyl anion formed in a concurrent process [159] (Scheme 87).

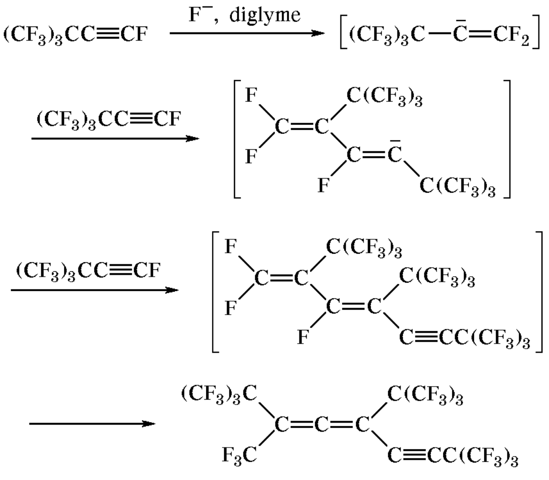
Scheme 86.



XLVI **XLVII**

XLVIII **XLIX**

Scheme 87.

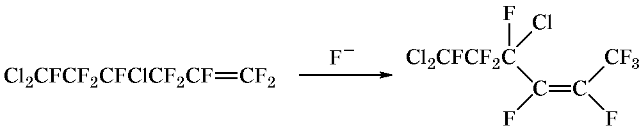


L

IV.2. Isomerization of Internal Perfluoroolefins

Terminal perfluoroolefins undergo isomerization into internal perfluoroolefins by the action of fluoride ion [175, 176] (Scheme 88).

Scheme 88.

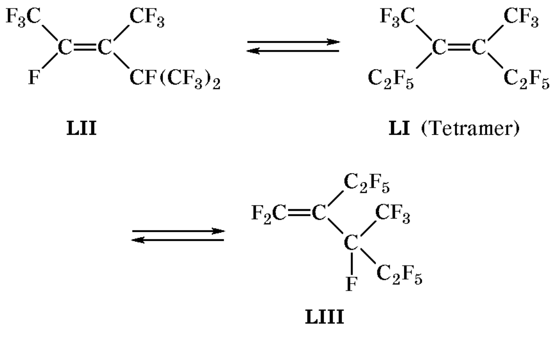


$$C_nF_{2n+1}CF{=}CF_2 \xrightarrow[93\text{–}96\%]{\text{CsF, diglyme}} C_{n-1}F_{2n+1}CF{=}CFCF_3$$

n = 3–6; n = 3, *cis*:*trans* = 19:81; n = 6, *cis*:*trans* = 6:94.

Internal perfluoroolefins also react with fluoride ion, yielding mixtures of isomeric internal olefins. For example, isomers **LII** and **LIII** are formed from tetrafluoroethylene tetramer [177] (Scheme 89). Therefore, nucleophilic reagents could induce isomerization of internal perfluoroolefins due to elimination of fluoride ion. If the rate of the nucleophile reaction with the isomerization products is higher than the rate of the reaction with initial olefin, the corresponding derivatives are obtained. This should be taken into account when carrying out such reactions.

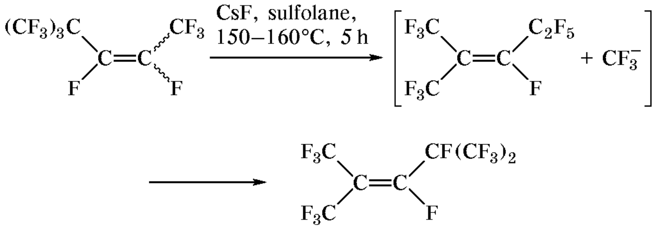
Scheme 89.



LII **LI** (Tetramer) **LIII**

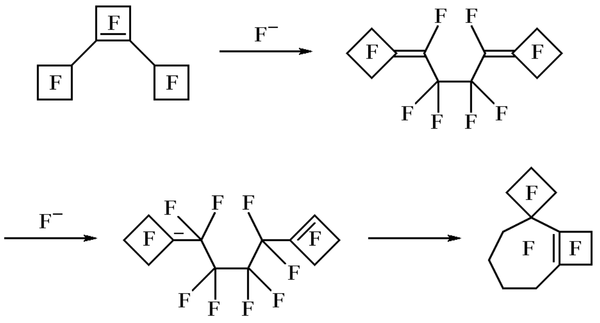
Fluoride ion is capable of promoting not only isomerization of internal perfluoroolefins with participation of the double bond but also rearrangements involving migration of CF_3^- anion. Intermediate trifluoromethyl anion was trapped via reaction with perfluoropyrimidine [17]. The result is that a new perfluoroolefin is formed, which can give rise to products having unexpected structure [12] (Scheme 90).

Scheme 90.



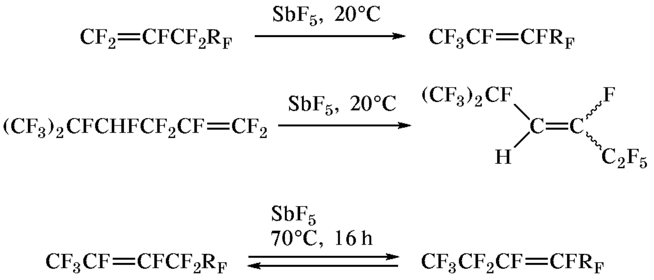
Generation of carbanions by the action of fluoride ion may result in transformation of the initial structure. Treatment of perfluorocyclobutene trimer with CsF yields a product with a seven-membered ring [18, 19] (Scheme 91).

Scheme 91.



Isomerization can also occur via transformation of a carbocation generated, e.g., by the action of SbF_5 on perfluoroolefin. Terminal perfluoroolefins, such as perfluoro-1-pentene, perfluoro-1-hexene, etc., in the presence of a catalytic amount of SbF_5 are smoothly converted into the corresponding *trans*-isomers in which the double bond is located at C^2 (yield 80–85%) [16, 178–180] (Scheme 92).

Scheme 92.



$$CF_2{=}CFCF_2R_F \xrightarrow{SbF_5,\ 20^\circ C} CF_3CF{=}CFR_F$$

$$(CF_3)_2CFCHFCF_2CF{=}CF_2 \xrightarrow{SbF_5,\ 20^\circ C} (CF_3)_2CF(H)C{=}C(F)C_2F_5$$

$$CF_3CF{=}CFCF_2R_F \overset{SbF_5,\ 70^\circ C,\ 16\ h}{\rightleftharpoons} CF_3CF_2CF{=}CFR_F$$

Other catalysts, e.g., $AlCl_xF_y$, are also effective in such processes [181] (Scheme 93).

Scheme 93.

$$(CF_3)_2CFCF{=}CFCF_3 \xrightarrow[25^\circ C,\ 24\ h]{AlCl_xF_y} (CF_3)_2C{=}CFCF_2CF_3$$

Perfluoroisopropylethylene rearranges into tris(trifluoromethyl)ethylene on heating to 30–40°C [178–180]. When an olefin possesses two terminal double bonds, isomerization at both of these occurs simultaneously to afford 80–90% of the corresponding *E,E* isomer and 10–20% of *E,Z* isomer [182, 183] (Scheme 94).

Scheme 94.

$$CF_2{=}CFCF_2(CF_2)_nCF_2CF{=}CF_2$$

$$\xrightarrow{SbF_5,\ 70^\circ C} CF_3CF{=}CF(CF_2)_nCF{=}CFCF_3$$

$n = 0, 2, 4, 6, 10.$

Heating of perfluoro-2-hexene or perfluoro-2-heptene with SbF_5 leads to formation of an equilibrium mixture containing 75–80% of olefin **LIV** and 20–25% of olefin **LV** [184]. These data indicate a reversible 1,3-migration of fluorine atom in fluoroolefins, catalyzed by SbF_5 (Scheme 95).

Scheme 95.

$$CF_3CF{=}CFCF_2(CF_2)_nCF_3$$

LV

$$\overset{SbF_5}{\rightleftharpoons} CF_3CF_2CF{=}CF(CF_2)_{n-1}CF_3$$

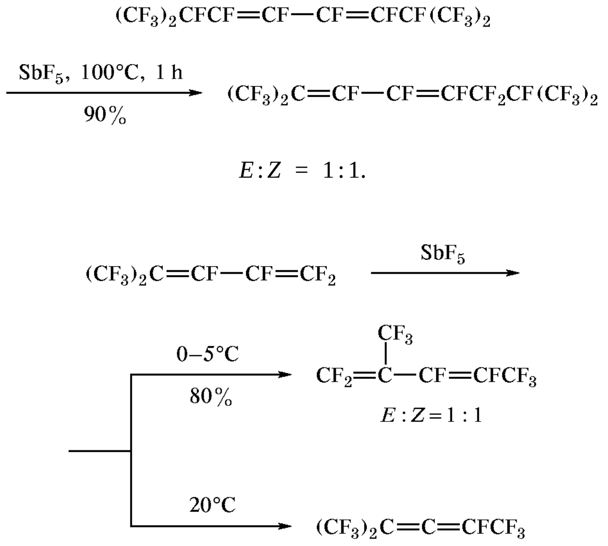
LIV

$n = 1,2.$

Migration of double bond under catalysis by SbF_5 is also observed in the series of perfluorinated dienes [185]. Perfluoro(2-methyl-2,4-pentadiene) in the presence of SbF_5 at 0–5°C gives rise to perfluoro(2-methyl-1,3-pentadiene). At 20–25°C, the latter is quantitatively converted into tris(trifluoromethyl)fluoroallene (Scheme 96).

As shown in [181–186], transformations of perfluorinated dienes in SbF_5 involve intramolecular cyclization leading to perfluoro(dialkylcyclopentenes). Conjugated perfluorinated dienes are converted into

Scheme 96.

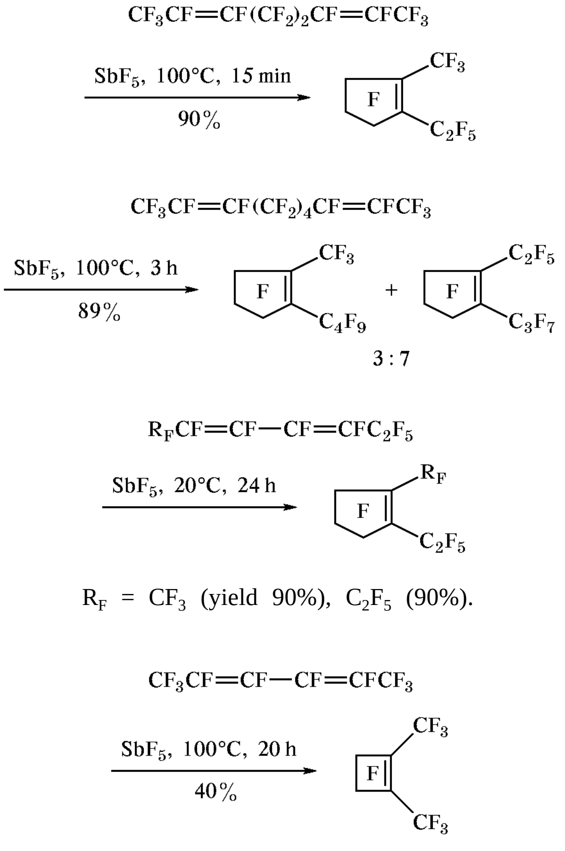


E:Z = 1:1.

E : Z = 1 : 1

cyclopentene derivatives by the action of SbF_5 under mild conditions (Scheme 97). However, if conjugated diene contains only one CF_3 group, no cyclic product is formed at room temperature, while at 100°C perfluoro(1,2-dimethylcyclobutene) is obtained [186].

Scheme 97.

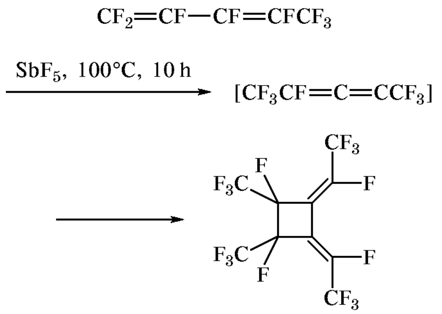


3 : 7

R_F = CF_3 (yield 90%), C_2F_5 (90%).

Cyclobutane system is formed when only one terminal CF_3 group is present [186]. Presumably, SbF_5 promotes isomerization of perfluoro-1,3-pentadiene to perfluoro(1,3-dimethylallene), and the latter undergoes dimerization and cyclization (Scheme 98).

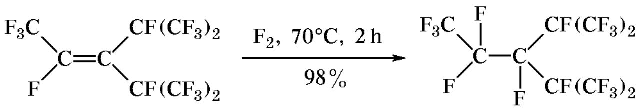
Scheme 98.



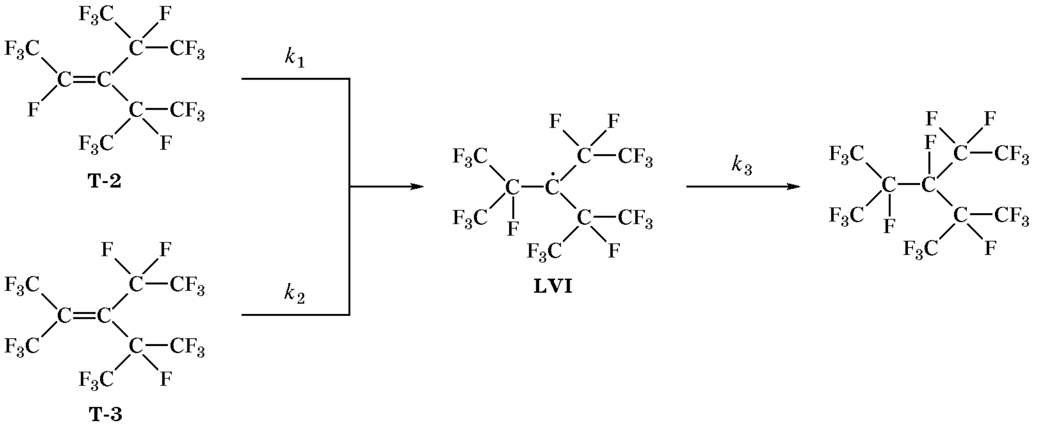
V. SUPERSTABLE RADICALS CONTAINING PERFLUOROALKYL GROUPS

A considerbale number of publications deal with fluorination of double bonds. This way turned out to be very important for the development of methods for preparation of perfluorinated paraffins and freons [187–192]. Treatment of tetrafluoroethylene with elemental fluorine, both in the gas phase and in solution in Freon 114 at 80°C, gives 87.8% of hexafluoroethane [193–195]. Taking into account that this compound is used as propellant and refrigerant and in dry etching of semiconductors, the above procedure can be utilized for its large-scale preparation [196]. Perfluorinated 2-methyl-2-pentene and 4-methyl-2-pentene behave similarly, but the best results were obtained without a solvent at –120 to 30°C [197]. Perfluoro(2-methylpentane) is used as low-temperature hydraulic fluid, dielectric, refrigerant, and heat carrier. The above approach is convenient for the preparation of other perfluorinated alkanes from various perfluoroolefin derivatives. Fluorination of hexafluoropropylene trimer with elemental fluorine gives 86% of perfluoro(3-isopropyl-4-methylpentane) [198]. High yields of the perfluorinated product were obtained at –40 to –120°C in inert solvents ($CFCl_3$, CF_2Cl_2) [199–202]. Perfluoro(3-isopropyl-2-methylpentane) was synthesized in almost quantitative yield at 70°C [203] (Scheme 99).

Scheme 99.



Scheme 100.



Other perfluoroolefins and their derivatives also give rise to perfluorinated products; some of these are as follows: perfluoro(3-isopropyl-4-methyl-2-pentene), perfluoro(3-ethyl-2,4-dimethyl-2-pentene), perfluoro(3,4,4-trimethyl-2-hexene), 4-(2,2,3,3,4,4,4-heptafluorobutoxy)perfluoro(3-isopropyl-2-methyl-2-pentene), perfluoro(3-ethyl-4-methyl-2-pentene), perfluoro(2,2-propanebicyclo[5.2.0.]non-1(7)-ene [197, 203], perfluoro(3-ethyl-2,4-dimethyl-1-pentene), and perfluoro(2-*tert*-butyl-3,3-dimethyl-1-butene) [200].

The fluorination process follows a radical mechanism. Some sterically hindered olefins give rise to radicals which are stable under conditions of gas-chromatographic separation at a temperature not exceeding 60°C. The average lifetime of fluorocarbon radicals, which are intermediates in various radical reactions, is considerably longer than that typical of their hydrocarbon analogs: 10^2–10^3 h in liquid phase at room temperature. Some perfluorinated radicals were found to be almost incapable of recombining in solution. Steric isolation is the main factor retarding recombination of such long-lived radicals.

Table 3. Composition of reaction mixtures obtained by direct fluorination of mixtures of olefins **T-2** and **T-3** (according to GLC data) [211]

Time, h	Composition, %				
	T-2	**T-3**	**LVI**	a	b
0	6.75	91.43	–	–	1.17
1	3.48	87.48	6.22	–	2.22
3.4	0.70	76.44	17.57	3.33	1.28
6	–	63.85	25.29	8.90	1.22
10	–	52.46	29.73	15.53	1.68
17	–	16.96	33.16	41.48	7.52
22	–	2.83	40.89	55.22	
26	–	–	25.91	71.77	1.41

[a] Perfluorinated paraffin.

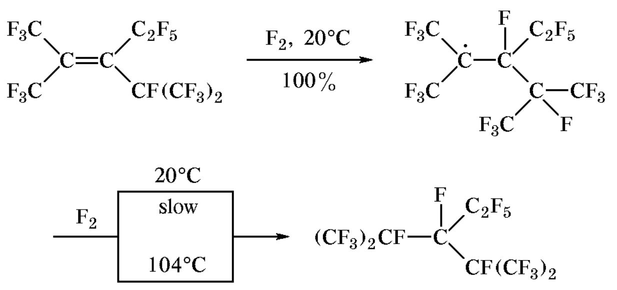
[b] Unidentified products.

Scherer *et al.* [204–206] studied reactions of perfluoro(3-ethyl-2,4-dimethyl-2-pentene) (**T-2**) and perfluoro(3-isopropyl-4-methyl-2-pentene) (**T-3**) with fluorine and were the first to obtain superstable perfluoro(3-ethyl-2,4-dimethylpentan-3-yl) radical (**LVI**) (Scheme 100). It had an anomalously long lifetime in solution at 20°C [205]. Olefin **T-2** having a fluorine atom at the double bond is more reactive than **T-3**. Olefin **T-2** reacts with fluorine in 3 h, whereas the reaction with **T-3** requires 22–24 h [211] (Table 3). Therefore, it was impossible to examine the kinetics of the reaction of **T-2** with fluorine [211]. Radical **LVI** is characterized by the following physical constants [204]: bp 37–37.5°C (35 mm), mp –28.2 to –28°C, d_4^{20} 1.845, n_D^{20} 1.2872. It is stable at room temperature (half-decomposition period 8 years), but at 100°C it rapidly decomposes with formation of trifluoromethyl radical [204–206]. Radical **LVI** does not react at room temperature with water, acids, alkalies, oxygen, chlorine and bromine (its concentration does not change within 15–20 h). It should be noted that analogous stable radicals were obtained from different sterically hindered olefins. Such radicals can exist in liquid at room temperature for long years. An important point is that such stable radicals are formed only from unsaturated compounds and that generation of radical center therein implies the presence of a tertiary or quaternary carbon atom. Stable radicals were obtained by the action of fluorine on the following sterically hindered perfluoroolefins: $(CF_3)_2C{=}C(C_2F_5)CF(CF_3)_2$, $(iso\text{-}C_3F_7)_2C{=}CFCF_3$, $(CF_3)_2CFC(C_2F_5){=}CFCF_3$, $CF_3CF{=}C(C_2F_5)CF(CF_3)_2$, perfluoro(2,2-propanebicyclo[5.2.0]non-1(7)-ene), and $(CF_3)_2CFC(C_2F_5){=}CFCF_3$ [206, 207]. Reactions of fluorine with $(CF_3)_2CFCF{=}CFCF_3$, $(CF_3)_2C{=}CF\text{-}C_2F_5$, $(CF_3)_2C{=}C(C_2F_5)_2$, perfluoro[4a(8)-octalin], and perfluoro[1-(1,1-dimethylbutyl)cycobutene] give only addition products at the double bond, and no formation of stable radicals is observed, presumably because of steric hindrances [208–212]. Up to now, the kinetics and mechanism of a number of radical processes have been studied, where the appearance of long-lived radical species is crucial. The mechanism of formation and structure of long-lived perfluorinated radicals were studied by the radiolysis and photolysis techniques and by fluorination of perfluorinated unsaturated compounds, fluoroaliphatic and fluoroaromatic compounds, linear perfluoroalkanes, and fluorinated polymers [209, 212–214]. Possible transformations of long-lived radicals into chemically active state were also examined.

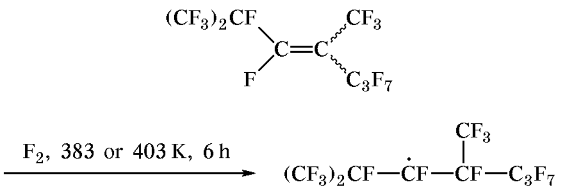
Ready elimination of the $CF_3^{\cdot}$ radical gives rise to new perfluoroolefins which (1) could produce radical species by the action of fluorine and (2) could yield perfluoroparaffins with a changed carbon skeleton. Studies in this field contributed much to the understanding of decomposition and isomerization processes accompanying fluorination of perfluoroolefins and made it possible to synthesize some important products.

The interest in superstable perfluorinated radicals has grown considerably, and many research teams have performed series of studies in this line. The reason is that unpaired electron is usually stabilized via delocalization over aromatic π-system or orbitals of heteroatoms (oxygen, nitrogen, etc.) [215, 216]. Steric shielding by bulky substituents favors such stabilization. The new radical is almost incapable of recombining in solution at room temperature [216–218]. Analysis of the structure of radical **LVI** showed that its stability is determined only by intramolecular conformational–steric isolation of the unpaired electron. Thus long-lived perfluorinated radicals constitute a new class of stable radicals whose stabilization does not require delocalization of the unpaired electron. In all cases, steric isolation of the radical center in intermediate perfluorinated radicals hampers their recombination and reduces their reactivity in the subsequent combination with fluorine atom [219–221] (Scheme 101).

Scheme 101.



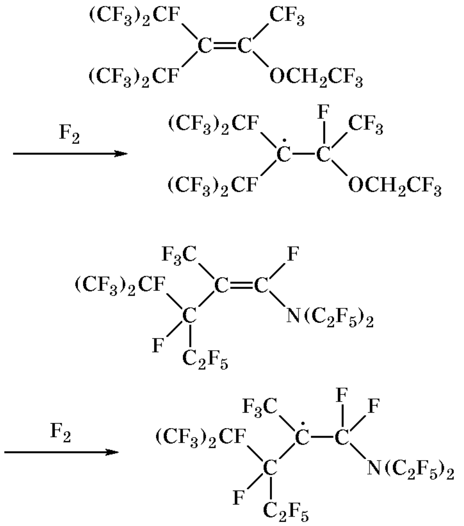
Scheme 102.



The radical generated according to Scheme 102 is thermally more stable than $[(CF_3)_2CF]_2\dot{C}C_2F_5$ formed by fluorination of $(CF_3)_2CFCF{=}C(CF_3)C_3F_7$ [221]. Its thermolysis yield $CF_3^{\cdot}$ radical whose reaction with hexafluoropropylene trimer leads to the radical $[(CF_3)_2C]_3C^{\cdot}$.

Fluorination of hexafluoropropylene trimer and its derivatives containing phenoxy [219], diethylamino, and β,β,β-trifluoroethoxy groups [220] also gives rise to long-lived radicals via fluorine addition at the double bond (Scheme 103).

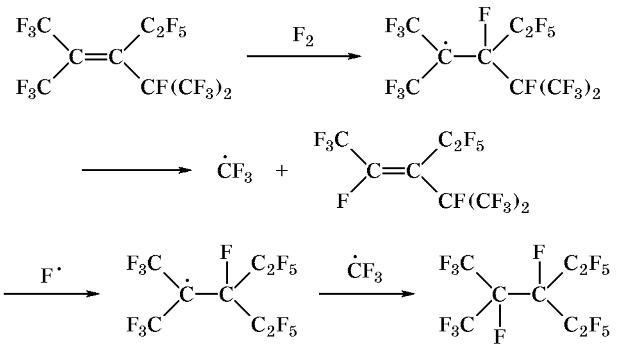
Scheme 103.



Stable fluorocarbon radicals may be used as spin labels and for creation of 2D-images in ESR tomography [220]. The rate of radical dimerization is determined mainly by steric shielding of the radical center and by the rate of their rotational diffusion [222].

Interesting prospects are opened by the reaction of fluorine with perfluoroolefins. Fluorine addition at double bond at –78°C in alcohol gives difficultly accessible vicinal products, whereas in aqueous acetonitrile at 0°C epoxy derivatives are formed (Scheme 104).

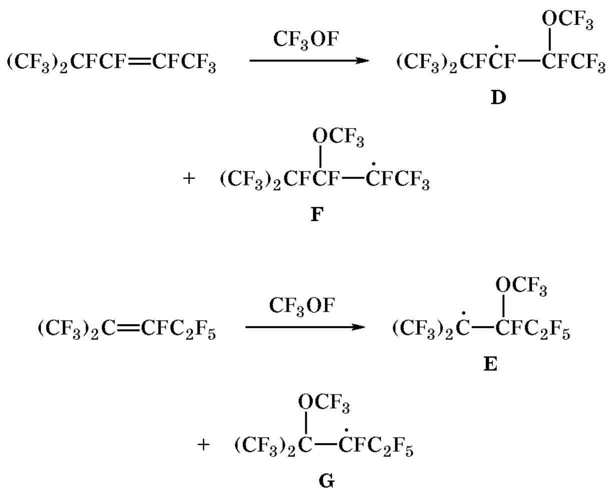
Scheme 104.



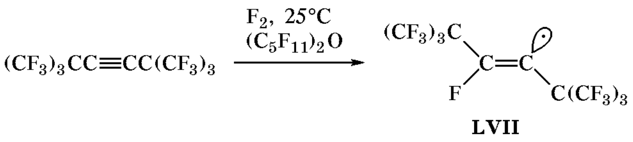
These reactions are strongly facilitated by UV irradiation. Other fluorinating agents can also be used to generate long-lived radicals. Treatment of perfluoro(2-methyl-2-pentene) and perfluoro(4-methyl-2-pentene) with CF_3OF leads to formation of stable radicals **D**–**G**. When the process was performed in an ESR cell at 330 and 320 K, sharp signals from radicals **D** and **E** were observed with hyperfine structure due to coupling with fluorine; radicals **F** and **G** were not identified, presumably because of their lower stability [223] (Scheme 105). This is the first example of detection of intermediate species in reactions of olefins with CF_3OF.

Analogous pattern is observed in the reactions of CF_3OF and $X(CF_2O)_n(CF_2CF_2O)_mCF_2OF$ with other perfluoroolefins [224]. Intermediate tertiary and secondary radicals were detected by ESR spectroscopy. Fluorine addition at double bond also leads to preparation of perfluoro(1,2-di-*tert*-butylvinyl) radical. Direct fluorination of perfluoro(di-*tert*-butylacetylene) with elemental fluorine gives stable radical **LVII** which was identified by the ESR spectrum [225, 226] (Scheme 106). Radical **LVII** is stable in the absence of oxygen.

Scheme 105.

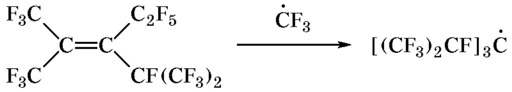


Scheme 106.



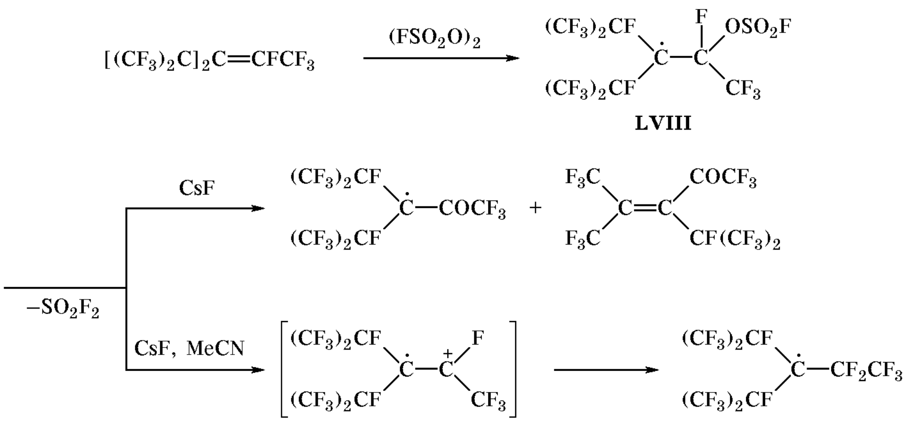
The fact that trifluoromethyl radical is capable of reacting with perfluoroolefins at the double bond to to give stable fluoroalkyl radical [203, 219] suggests the possibility for formation of other stable radicals using different, probably “hot” radicals (Scheme 107).

Scheme 107.



In fact, branched perfluoroolefins [dimers and trimers derived from hexafluoropropylene and perfluoro(4,4-dimethyl-2-pentene] react with peroxydisulfuryl difluorides to afford stable α-fluorosulfonyloxytetrafluoroethylperfluoro(diisopropylmethyl) radical **LVIII** [227–232] which was isolated in the pure state in more than 80% yield [233, 234] (Scheme 108). The stability of radical **LVIII** is enhanced due to its branched structure [226]. Less branched perfluoro(4-methyl-2-pentene) with the same reagent also forms stable radical **LIX** in the absence of oxygen (Scheme 109). It should be noted that the presence of unpaired electron does not hinder reaction at the other functional group of the same molecule. The reaction with CsF gives keto radical via elimination of sulfonyl fluoride. When the same reaction is carried out in acetonitrile, a stable radical is obtained as a result of replacement of the OSO_2F group by fluorine [227–230]. By the action of SbF_5 at 45–60°C without a solvent, radical **LVIII** is converted into perfluoro(ethyldiisopropylmethyl) radical **LX** via replacement of the FSO_3 group by fluorine [235, 236] (Scheme 110). The anionic mobility of the FSO_3 group in the initial radical was attributed to stabiliza-

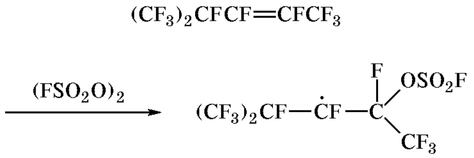
Scheme 108.



LVIII

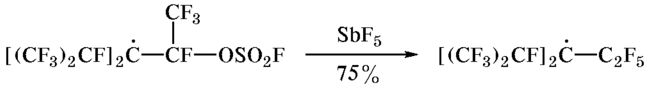
tion of the conjugate carbocation by vicinal paramagnetic center [235].

Scheme 109.



LIX

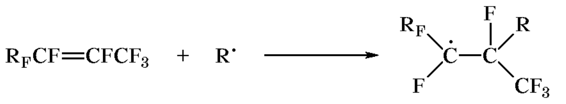
Scheme 110.



LVIII LX

Perfluoroolefins having branched alkyl groups react with intermediate radicals generated from dimethoxy(methyl)vinylsilane or diethoxy(methyl)vinylsilane by UV irradiation at –10 to –20°C, yielding stable radicals [236] (Scheme 111).

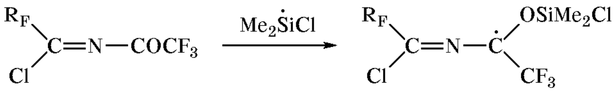
Scheme 111.



R_F = $CF(CF_3)_2$, $C(CF_3)_3$, $CF_2CF(CF_3)_2$;
R = [CH_2=$CHSi(Me)(OCH_2X)(OCH_2X)$] (X = Me, Et).

Radical addition of vinylsilane to branched perfluoroolefins may be regarded as a method for introduction of fluorinated substituents. Stable radicals were also obtained from fluorinated imidoyl chlorides [237] (Scheme 112).

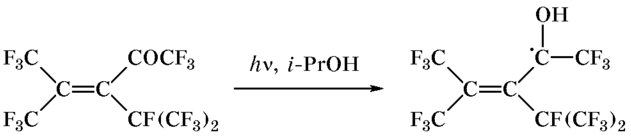
Scheme 112.



R_F = CF_3, $CF_3CF_2CF_2$.

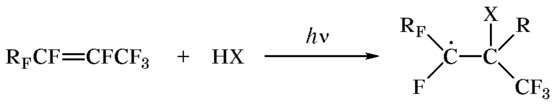
These radicals are stable at room temperature, but they are detected by ESR spectroscopy at reduced temperature. The reactions are initiated by photolysis in the presence of Et_3SiH in 2-propanol [238] (Scheme 113).

Scheme 113.



UV irradiation of solutions of silicon hydrides in perfluoroolefins leads to formation of relatively stable *syn*-adducts **LXI** (lifetime 5–10 h) [239] (Scheme 114). On addition of di-*tert*-butyl peroxide, the signal intensity under irradiation increases by a factor of 10 to 30. The intermediate formation and reactivity of radicals **LXI** are determined by steric shielding of the radical center.

Scheme 114.

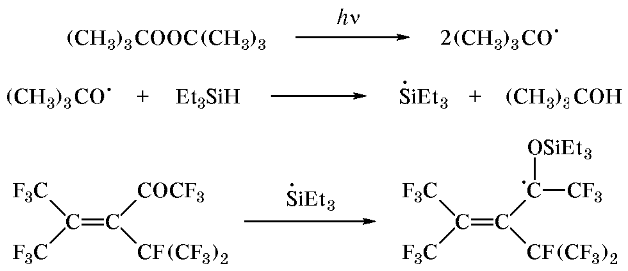


LXI

RF = $CF(CF_3)_2$, $C(CF_3)_2CF(CF_3)_2$; X = $SiCl_3$, $SiMeCl_2$, $SiMe_3$, $SiEt_3$; R_F = $C(CF_3)_3$; X = $SiCl_3$, $SiMeCl_2$, $SiMe_3$, $SiEt_3$; R_F = $CF(CF_3)_2$, $C(CF_3)_3$; X = HP(O)(OR) (R = Me, Et, Pr).

Analogous results were obtained by UV irradiation in the presence of dialkyl hydrogen phosphites. Structurally similar allyl radical **LXII** is formed in the reaction of perfluoroolefin with a silicon-centered radical (Scheme 115).

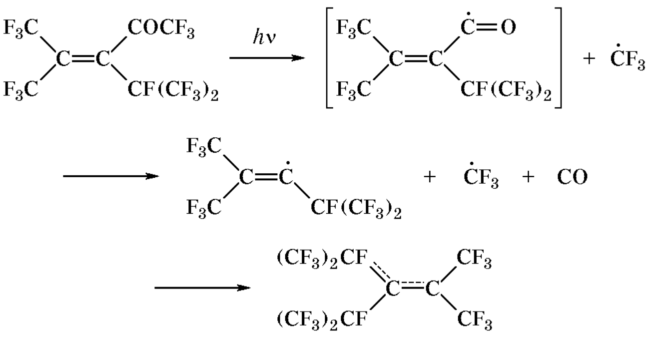
Scheme 115.



LXII

Photolysis of the same olefin in the absence of hydrogen donor also gives allyl radical **LXIII** with an analogous structute (Scheme 116).

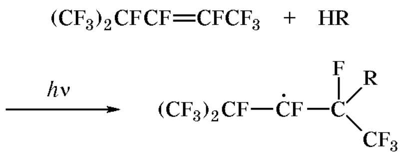
Scheme 116.



LXIII

The lifetime of such allyl radicals is about 1 h [239], which is inconsistent with the data obtained in [240] for analogous radicals. Stable radicals **LXIV** are formed by irradiation in alcoholic solution of perfluoroolefins which cannot be regarded as sterically hindered [241] (Scheme 117). Addition of di-*tert*-butyl peroxide (5 vol %) increases the ESR signal by a factor of 10 to 40.

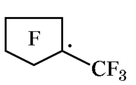
Scheme 117.



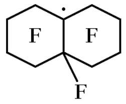
LXIV

$R = CH_2OH, CH(CH_3)OH, C(CH_3)_2OH.$

Perfluoroalkyl radicals **LXV** and **LXVI** having cyclic substituents are stable up to 220°C; they were obtained by photolysis of the corresponding bromides in the presence of $Hg(C_2B_{10}H_{11})_2$ [242]:



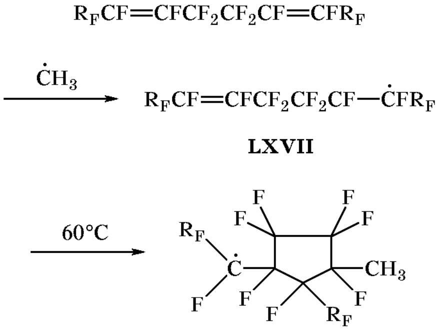
LXV



LXVI

Perfluorinated alkenyl radicals **LXVII**, generated by the action of methyl radical (which is formed in the photolysis of di-*tert*-butyl peroxide) on terminal perfluoroolefins, are converted into relatively stable radicals **LXVIII** via cyclization at the double bond located in position *4* or *5* with respect to the radical center [243, 244] (Scheme 118).

Scheme 118.

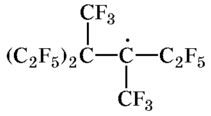


LXVIII

$R_F = C(CF_3)_3.$

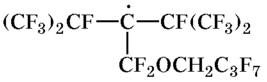
The reaction of perfluoro(2-methyl-2-pentene) with di-*tert*-butyl peroxide at 140°C or at 20°C under UV irradiation yields 30% of 1,1,1,3,5,6,6,7,7,7-decafluoro-2,5-dimethyl-3-pentafluoroethyl-2,4,4-tris(trifluoromethyl)heptane [245]. Intermediate radical $(CF_3)_2CMe\dot{C}FC_2F_5$ was identified by the ESR spectrum. Such radicals are models for studying the structure and reactivity of cyclic tertiary perfluorinated radicals in which motion of substituents at the radical center is restricted on the ESR time scale. From the character of the kinetic curves (obtained in the temperature range from 20 to 120°C) and the dependence of the stationary signal amplitude on the light intensity, the following kinetic parameters for radical dimerization were derived: $k_{20} = 10^2$ l/mol, $E^{\neq} =$ 3.4 kcal/mol. These data suggest that sharp decrease of the rate constant for dimerization of cyclic radicals relative to those found for acyclic fluorinated radicals [222, 245] is explained by not only steric shielding but also stereochemical rigidity of the radical center. Restricted motion of substituents at the radical center could hamper a radical pair to attain a configuration favorable for dimerization in a solvent cage.

Stable perfluoroalkyl radicals were also obtained by other methods based on reactions of perfluoroolefins with various radicals. Electrochemical fluorination of perfluoroolefins and their alkoxy and alkylamino derivatives gave highly stable radicals **LXIX**–**LXXI** [246]:



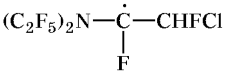
$(C_2F_5)_2C(CF_3)-\dot{C}(CF_3)-C_2F_5$

LXIX



$(CF_3)_2CF-\dot{C}(CF_2OCH_2C_3F_7)-CF(CF_3)_2$

LXX



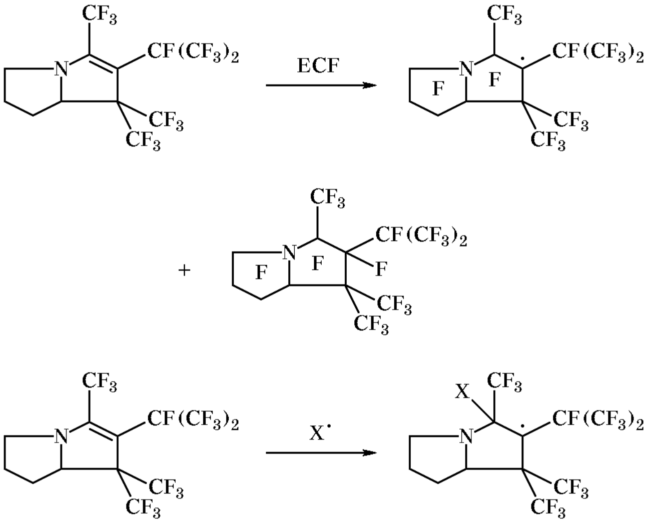
$(C_2F_5)_2N-\dot{C}F-CHFCl$

LXXI

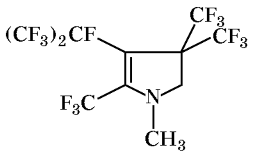
In the absence of oxygen, these radicals are stable above 140°C for several minutes, so that they can be characterized by ESR spectra.

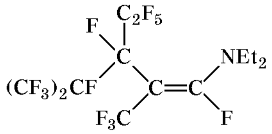
Gervits *et al.* [247, 248] studied electrochemical fluorination of sterically strained branched polyfluorinated pyrrolizidine by ESR spectroscopy and detected a stable radical at a concentration of no less than 5% (lifetime >1 month) among the products insoluble in hydrogen fluoride (Scheme 119). Such radicals are fairly stable, and they can be obtained by the action of elemental fluorine or other radicals [e.g., $\dot{C}H_3$ or $^{\cdot}P(O)(OMe)_2$] on perfluoroolefins. Likewise, stable radicals were detected during electrochemical fluorination of the following compounds:

Scheme 119.



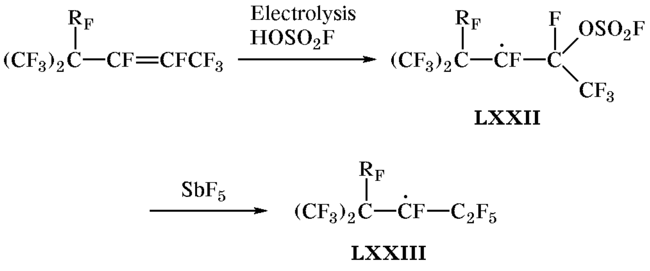
X = F, P(O)(OMe)$_2$, Me; ECF stands for electrochemical fluorination.





Electrolysis of perfluoroolefins in fluorosulfonic acid gives a stable fluorosulfonyloxyperfluoroalkyl radical (2–3%, according to the ESR data) [227–230, 232], in which the FSO_3 group is replaced by fluorine atom by the action of SbF_5. As a result, new stable radical **LXXIII** is obtained (SU 2000 vitreous–carbon anode, titanium cathode, I = 0.6 A, 0.5 h; current-based yield 75%; Scheme 120). The replacement of FSO_3 group in β-fluorosulfonyloxyperfluoroalkyl radicals by fluorine under the action of SbF_5 is a general reaction. It is explained by stabilization of the positively charged carbon atom at which the substitution occurs by paramagnetic center. This stabilization ensures anionic mobility of the fluorosulfonate group [232].

Scheme 120.

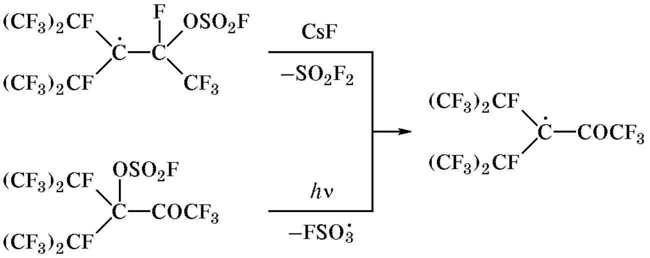


R_F = F, CF_3 [249], *iso*-C_3F_7, *tert*-C_4F_9 [227].

The boiling points of the radical generated by electrochemical fluorosulfonylation of hexafluoropropylene trimer, initial olefin, and further transformation product are considerably different, and the radical can be isolated in the analytically pure state.

As compared to fluorination, the synthesis of perfluorinated aliphatic radicals by fluorosulfatation of fluorinated olefins seems to be more attractive, for this procedure leads to formation of FSO_3-substituted species which can be involved in further chemical transformations. By the action of cesium fluoride fluorosulfonyloxy radical was converted into stable perfluoro(acetyldiisopropylmethyl) radical. The latter was also detected in the photolysis of fluorosulfonyloxy ketone (Scheme 121).

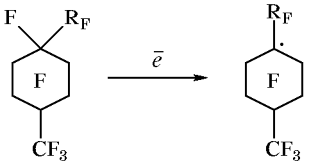
Scheme 121.



Thus, it becomes possible to accomplish chemical transformations of aliphatic carbon-centered radicals with retention of the radical moiety.

Ono *et al.* [250] obtained stable perfluoro(3-ethyl-2,4-dimethyl-3-pentyl) radical by electrochemical fluorination of hexafluoropropylene trimer in the presence of NaF. The most extensively used procedure for preparation of stable perfluoroalkyl radicals is based on radiolysis of perfluoroparaffins having a tertiary carbon atom [211, 213, 214, 249, 251–256]. The procedure is simple, general, and sometimes the only possible one. Long-lived radicals are formed as a result of abstraction of fluorine atom from a ring [243] (Scheme 122).

Scheme 122.



R_F = $CF(CF_3)_2$, $C(CF_3)_3$.

UV irradiation of perfluorinated compounds can also be applied. However, the photolytic technique turned out to be low effective because of sensitivity of the resulting radicals to light. For example, the concentration of long-lived radicals formed by photolysis of hexafluoropropylene trimer is lower by three orders of magnitude than in the radiolysis of the same substrate [213]. Radicals can also be obtained by abstraction of fluorine atom from a tertiary carbon atom.

VI. CONCLUSION

The data given in the present review indicate continuously increasing interest in the development of new approaches to introduction of perfluorinated fragments into organic molecules and transformation of simple substituents into complex functional groups. Considerable advances achieved in this line show that in some cases the developed procedures can be regarded as alternatives to the well known classical methods. Wide use of internal perfluoroolefins in reactions occurring in the presence of fluoride ion should be noted. Such processes are clearly more advantageous from the viewpoint of their application to large-scale preparations. Implementation of new technologies is expected to discover new reactions and transformations leading to fluorine-containing compounds. Taking the above into account, the present review is mostly an attempt to demonstrate new approaches, potentialities of new reagents, and new ideas which have been put into practice of organic synthesis. In addition, an effort was made to highlight new trends and main directions of studies in the field of synthesis of organofluorine compounds having various molecular fragments and functional groups. Undoubtedly, these problems are interesting not only for chemists working on fluorine-containing compounds but also for specialists in the field of organic synthesis as a whole. It is seen that in some cases perfluorinated organic compounds are convenient, and sometimes unique models for the formulation and solution of a number of fundamental problems of theoretical organic chemistry.

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