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INTERNAL PERFLUOROOLEFINS IN A SYNTHESIS OF FLUOROORGANIC COMPOUNDS

G.G. FURIN

Institute of Organic Chemistry, 630090, Novosibirsk, Russia

ABSTRACT

Experimental data in the last decade on the synthesis of fluoroorganic compounds by the reaction of internal perfluoroolefins with nucleophilic reagents and a direct fluorination with elementary fluorine or electrochemical fluorination of the most important classes of organic compounds have been generalized and synthesized. This overview covers the principles governing the orientation and reactivity of fluorinated alkenes towards nucleophiles, fluoride ion as a nucleophile and reactions with nitrogen-, oxygen- and sulfur-centred nucleophiles. It has been demonstrated that the reaction of internal perfluoroolefins with N-nucleophilic reagents issues in the production of terminal perfluoroolefins whose interaction leads to the formation of enamines. Factors which affect the stability and reactivity of these compounds are discussed as examples of their application for the preparation of partially fluorinated organic compounds containing N-, O-, P- and S-atoms. This treatment summarized new experimental data, as well as their theoretical description, on the use of C-nucleophiles and C-carbcations from internal perfluoroolefins in the synthesis of fluoroorganic compounds. Examples of application of the perfluorinated carbcations to the synthesis of perfluorinated olefins, cyclic systems and oxygen-containing heterocyclic compounds are considered. The mechanisms of these transformations are discussed. A new approach to the generation of the stable perfluorinated alkylradicals from internal perfluoroolefins is discussed and experimental data are given on its reaction with the varies substances. The overview discusses the modern methods for the fluorination of elementary fluorine internal perfluoroolefins and their derivatives. The problems related to the production of high quality perfluorinated organic materials are analyzed. We have also set out the trends in the development of methods and technology for obtaining fluoroorganic compounds. Instances of the practical application of various perfluorinated substances in industry and medicine are given, rational techniques for producing them are suggested and trends in the development of this technology are considered.

CONTENTS

2.5. Isomerization of internal perfluoroolefins.

The isomerization of terminal perfluoroolefins to internal ones takes place under the influence of fluoride-ion [183,184].

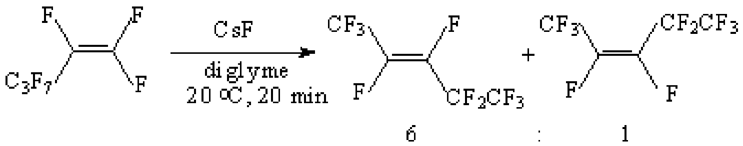
$$CCl_2FCF_2CFClCF_2CF=CF_2 \xrightarrow{F^-} trans\text{-}Cl_2FCCF_2CFClCF=CFCl$$

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

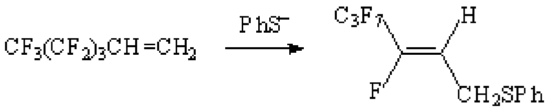
(93-96 %)

n = 2 cis:trans = 19:81
n = 6 cis:trans = 6:94

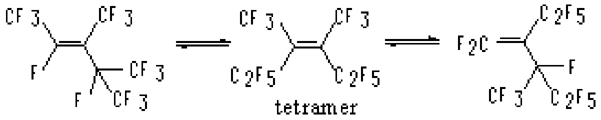
For example, the rapid isomerization of perfluoro-1-pentene to thermodynamically more stable isomer occurs in the presence of cesium fluoride [185].



The reactions of allylic displacement occur readily and with a stereo-chemistry steric control [186].



The last product reacts with formation, as a rule, a mixture of isomeric internal perfluoroolefins. For example, the isomerizations of tetrafluoroethylene tetramer under influence of fluoride-ion proceed with the isomers (**52**) and (**53**) formation [187].



52 **51** **53**

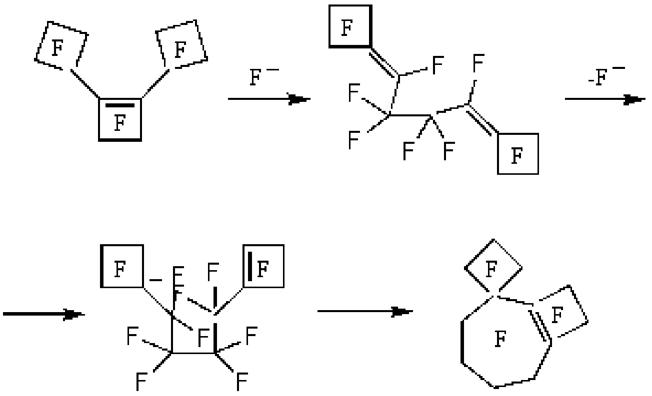
The nucleophilic reagents react with internal perfluoroolefins and the elimination of fluoride-ion take place. The result of this process is the formation of others isomers. If the rate of reaction with a nucleophile for such isomers is higher then for initial olefin, the result of reaction is the complex mixture. It should be taken into account at realization of these processes.

Both type of isomerization are possible at the action of fluoride-ion on ramified internal perfluoroolefins (with double bond participation) and rearrangement with migration of CF_3^-. The authors of [17] found the intermediate trifluoromethyl anion in the reaction with perfluoropyrimidine. The new perfluoroolefins with unexpected structure may be produced [12].

$$(CF_3)_3CCF{=}CFCF_3 \xrightarrow[\text{sulpholan}\quad 150\text{-}160\ ^{o}C,\ 5\ h]{CsF} [\,(CF_3)_2C{=}CFCF_2CF_3 + {}^{-}CF_3\,] \longrightarrow$$

$$\longrightarrow (CF_3)_2CFCF{=}C(CF_3)_2$$

The generation of carbanions under the influence of fluoride-anion can to give the transformation of initial structure. So, at the reaction of CsF with trimer of a perfluorocyclobutene a complex cycle is formed [18,19]:



Isomerization also can be carried out by transformation of C-carbcation, which generate, for example, by the action of SbF_5on perfluoroolefin. Thus, terminal perfluoroolefins (perfluoropent-1-ene, perfluoro-hex-1-ene etc.) at the action of SbF_5(catalytic amounts) smoothly isomerizate to corresponding *trans*-perfluoroolefins with double bond in position 2 (yield 80-85 %) [16, 188-190].

$$CF_2{=}CFCF_2R_F \xrightarrow[20^{o}C]{SbF_5} CF_3CF{=}CFR_F$$

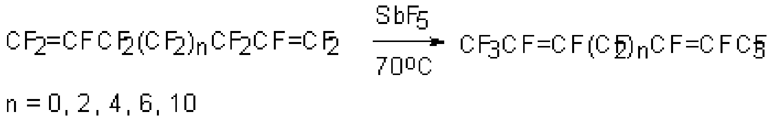
$$(CF_3)_2CFCHFCF_2CF{=}CF_2 \xrightarrow[20^{o}C]{SbF_5} (CF_3)_2CFCH{=}CFCF_2CF_3$$

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

Other catalytic agents (for example $AlCl_xF_y$) are effective in these processes too [191].

$$(CF_3)_2CFCF{=}CFCF_3 \xrightarrow[25\ ^{o}C,\ 24\ h]{AlCl_xF_y} (CF_3)_2C{=}CFC_2F_5$$

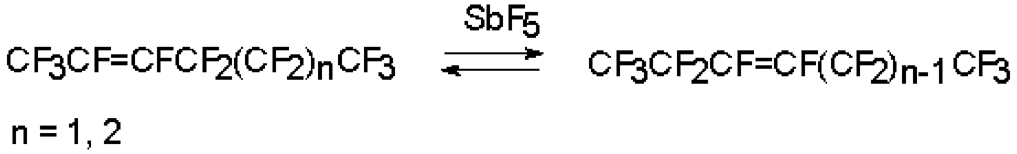
The rearrangement of erfluoroisopropylethylene to tris(trifluoromethyl)-ethylene at heating up to 30-40 ^oC was observed [188-190]. If molecule had two terminal double bond, they isomerizate simultaneously with formation of 80-90 % E, E-isomers and 10-20 % E, Z-isomer [192,193].



$$CF_2{=}CFCF_2(CF_2)_nCF_2CF{=}CF_2 \xrightarrow[70^oC]{SbF_5} CF_3CF{=}CF(CF_2)_nCF{=}CFCF_3$$

n = 0, 2, 4, 6, 10

When boiling perfluorohex-2-ene (perfluorohept-2-ene) reacts with SbF_5 and equilibrium mixture containing 75-80 % of olefin (**54**) and 20-25 % of (**55**) is observed [194].

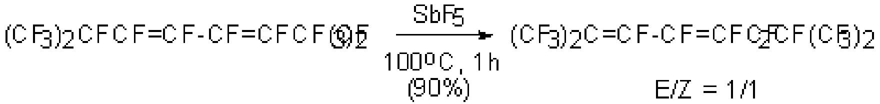


$$CF_3CF{=}CFCF_2(CF_2)_nCF_3 \overset{SbF_5}{\rightleftharpoons} CF_3CF_2CF{=}CF(CF_2)_{n-1}CF_3$$

n = 1, 2

55 **54**

The shift of double bond is also observed in the reactions of some perfluorinatered dienes with SbF_5 [195]. So, perfluoro-2-methylpent-2,4-diene in the reaction with SbF_5at temperature 0-5 ^oC isomerizate to perfluoro-2-methylpent-1,3-diene. Last quantitatively isomerizate to tris(trifluoromethyl)fluoroallene at 20-25 ^oC



$$(CF_3)_2CFCF{=}CF{-}CF{=}CFCF(CF_3)_2 \xrightarrow[100^oC,\ 1h\ (90\%)]{SbF_5} (CF_3)_2C{=}CF{-}CF{=}CFCF_2CF(CF_3)_2 \quad E/Z = 1/1$$

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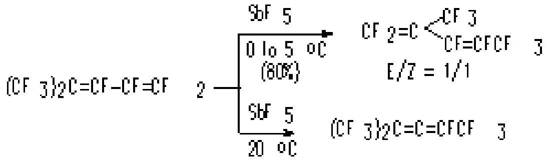
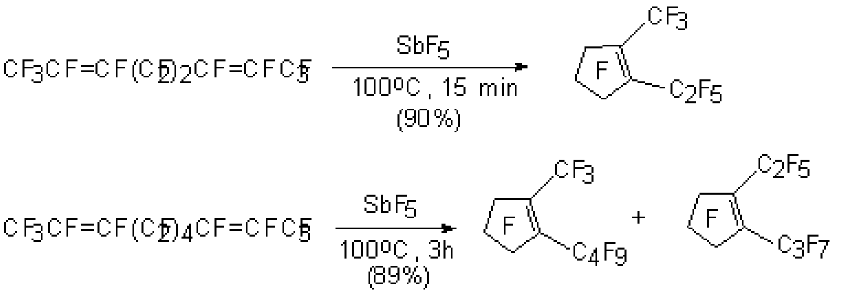


German with co-workers was shown [191-196], that the realization of an intramolecular cyclization with formation of perfluoroalkylcyclopentene is the important moment.



3 : 7

Perfluorinated dienes at presence of SbF_5 also yield the derivative of cyclopentene in soft conditions. However, if diene contains only CF_3 of group, the cyclic product is not formed at room temperature, whereas perfluoro-1,2-dimethylcyclobutene was produced at temperature 100^oC [196].

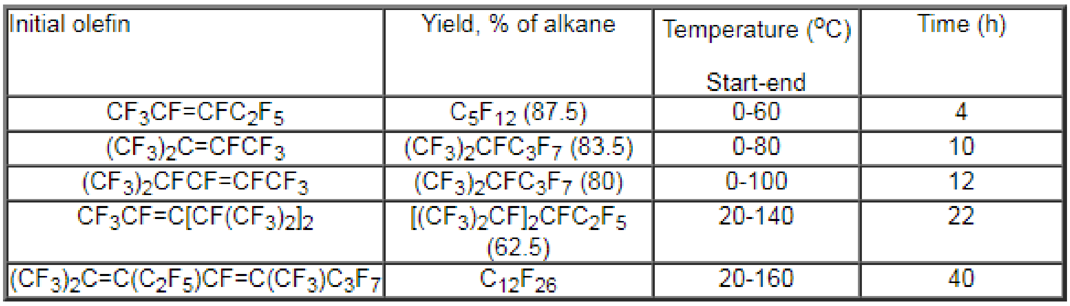
3. Synthesis of perfluorinated compounds from internal perfluoroolefins and elementary fluorine.

The significant part of works is devoted to processes of double bond fluorination. This way is vary important for producing of perfluorinated paraffins and freons [197-203]. The expected highly exothermic nature of the reaction of $F_2$with olefins discouraged many experimental workers. Reactions of organic compounds with fluorine gas are dangerous and require special equipment. Often the yields of the desired product in these reactions are poor and low selectivity is observed because the fluorine gas has high reactivity.

Merritt [204-207] showed that it is not impossible to add the fluorine to certain simple olefins. His technique was, however, quite unusual and rather inconvenient. It seems that the major obstacle for realization of this reaction is the fact that the F-F bond is weak and can be readily separated to very reactive fluorine radicals. A number of indirect methods have been developed for producing of vicinal difluoro compounds to circumvent the direct fluorination. Some success was achieved with adding $F_2$to perfluoroalkenes. The result was the formation of the corresponding perfluoroalkanes. So, tetrafluoroethylene reacts with element fluorine both in gas-phase and in liquid-phase (Freon 114) conditions at 80^{o}C, and gives the hexafluoroethane with yield 87.8 % [208-210]. Taking into account, that hexafluoroethane use as quality propellants, working bodies for refrigerating machines and for dry etching of semiconductors, this method is perspective for industrial scale [211]. Similarly, perfluoro-2-methylpent-2-ene and perfluoro-4-methylpent-2-ene or their mixture react with elemental fluorine both in liquid phase at -120^{o}C - -30^{o}C and without solvent resulting the perfluoro-2-methyl-pentane with a quantitative yield [212]. Author of [213] have developed effective techniques for a production of polyfluorinated compound from polyfluoroolefins and fluorine gas in liquid phase. According to this method, 100 % fluorine gas react in mild condition (reaction temperature: -64 - +58^{o}C; reaction pressure: atmospheric) without explosion or combustion of the initial substances.

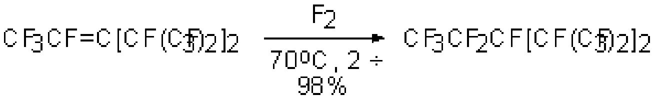
Preparation of the branched perfluoroalkanes was carried out with mixture of 20 % $F_2$and 80% N_2[214] or 100 % F_2[215] in liquid-phase absorption column system (Table 3).

Table 3. Fluorination of perfluoroolefins (slight excess of F_2)[215].



Initial olefin	Yield, % of alkane	Temperature (^{o}C) Start-end	Time (h)
$CF_3CF=CFC_2F_5$	C_5F_{12} (87.5)	0-60	4
$(CF_3)_2C=CFCF_3$	$(CF_3)_2CFC_3F_7$ (83.5)	0-80	10
$(CF_3)_2CFCF=CFCF_3$	$(CF_3)_2CFC_3F_7$ (80)	0-100	12
$CF_3CF=C[CF(CF_3)_2]_2$	$[(CF_3)_2CF]_2CFC_2F_5$ (62.5)	20-140	22
$(CF_3)_2C=C(C_2F_5)CF=C(CF_3)C_3F_7$	$C_{12}F_{26}$	20-160	40

Perfluoro-2-methylpentane can be used as a hydraulic liquid, dielectric and heat-carrier. This method has appeared convenient for reception of others perfluoroparaffins from various perfluoroolefins. So, trimer of a hexafluoropropylene react with elemental fluorine and perfluoro-3-isopropyl-4-methylpentane is produced with 86 % yield [216]. Fluorination by elemental fluorine at -40 - -120^{o}C in inert solvents ($CFCl_3$, CF_2Cl_2) also gives perfluorinatered products with high yields [79,217-220]. Perfluoro-3-isopropyl-2-methylpentane was produced at 70^{o}C with quantitative yield [221].



$$CF_3CF=C[CF(CF_3)_2]_2 \xrightarrow[70^{o}C\text{ , }2\ \div\ 98\,\%]{F_2} CF_3CF_2CF[CF(CF_3)_2]_2$$

Others perfluoroolefins and their derivative also give perfluorinatered products, for example, such perfluoroolefins as :

$(iso\text{-}C_3F_7)_2C{=}CFCF_3$,

$(CF_3)_2C{=}C(C_2F_5)CF(CF_3)_2$,

$CF_3CF{=}C(CF_3)C(CF_3)_2(C_2F_5)_2$,

$(CF_3)_2C{=}C[CF(CF_3)_2]CF(CF_3)OCH_2C_3F_7\text{-}n$,

$(CF_3)_2CFC(C_2F_5){=}CFCF_3$,

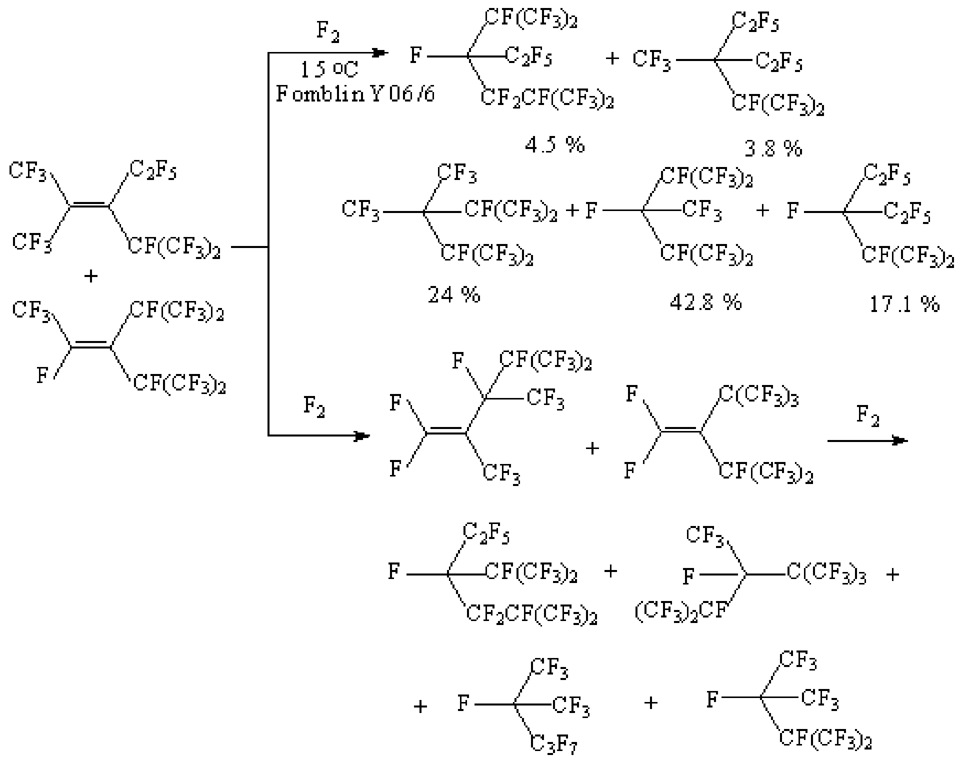
perfluoro-2,2-propanebicyclo [5.2.0.]non-1(7)-ene [212,221],

$(CF_3)_2CFCF(C_2F_5)C(CF_3){=}CF_2$,

$CF(CF_3)_2C[C(CF_3)_3]{=}CF_2$[218].

Thus, fluorine react at -78^{o}C in alcohol only with multiple bond and vicinal products are formed, while the epoxy compounds is observed at 0^{o}C in acetonitrile. The $CF_3^{\cdot}$ readily detach and new perfluoroolefins is formed. They can, firstly, yield radicals themselves and, secondly, lead further to perfluoroparaffins with altered carbon skeleton. These results have led to processes of destruction and isomerization of perfluoroparaffins.

The reaction of perfluoro-3-ethyl-2,4-dimethylpent-2-ene and perfluoro-3-isopropyl-4-methyl-pent-2-ene with fluorine in Fomblin Y06/6 in the presence of UV light was studying by the authors of [220]. Perfluoro-2,3,3,4-tetramethylpentane and perfluoro-2,3,4-trimethyl-pentane were the main products of reaction together with small amounts of other known compounds **60-62**. Therefore perfluoro-2,3,3,4-tetramethylpentane has a potential as a new initiator for vinylic polymerization. But photochemical isomerization of perfluoropent-2-ene isomer yield two terminal olefins: perfluoro-3-ethyl-2,4-dimethyl-pent-1-ene **63** and perfluoro-2-iso-propyl-3,3-dimethylbut-1-ene **64**, which are not the unsaturated counterparts of photo induced fluorination of main products. Fluorination of **63** and **64** gives, respectively, **60** and perfluoro-2,2,3,4-tetramethylpentane **65**, together with other decomposition products.



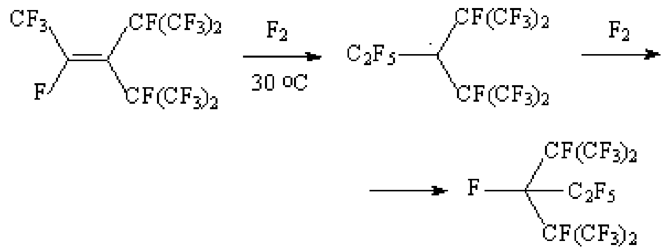
The terminal olefins $(CF_3)_2CFCF(C_2F_5)C(CF_3)=CF_2$and $(CF_3)_2CFC[C(CF_3)_3]]=CF_2$were fluorinated and highly branched perfluoroalkanes was obtained. They provide the perfluoroalkyl radicals, which are the initiators for monomers polymerization [218]. Other perfluoroolefins: $(CF_3)_2CFC(C_2F_5)=C(CF_3)_2$and $[(CF_3)_2CF]_2C=CFCF_3$were fluorinated under UV radiation with producing $(CF_3)_2CCF(CF_3)CF(CF_3)_2$, $(CF_3)_2CFC(CF_3)_2CF_2CF_2CF_3$and $(CF_3)_2CFCF_2CF_2CF_3$(yields 26, 50, 24 %, respectively).

Direct gas-phase fluorination of hexafluoropropene trimers, perfluoro-3-ethyl-2,4-dimethyl-pent-2-ene and perfluoro-3-isopropyl-4-methylpent-2-ene, at 130 -150°C in the presence of copper and nickel yields the first stable perfluororadical, which was found by Scherer [222].

So the stable radical can undergo $n \rightarrow \sigma^*$ transition of the unpaired electron with forming a very unstable species which can rearrange by two ways:

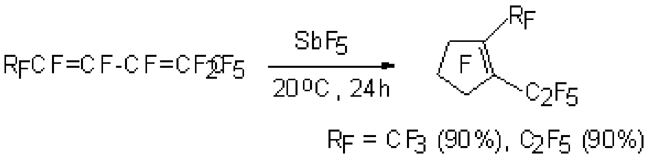
1. *The main pathway is the β-elimination of $CF_3\cdot$ radical from the CF_3CF_2group with terminal alkene formation (perfluoro-2-isopropyl-3-methylbut-1-ene), which react with $F_2$and intermediate perfluoro-2,3,4-trimethylpentan-3-yl is formed. The last one can react with $F\cdot$ radical or $CF_3\cdot$ radical with formation of perfluoro-2,3,4-trimethylpentane and perfluoro-2,3,3,4-tetramethylpentane;*
2. *theβ-elimination of $CF_3\cdot$ radical with formation of intermediate perfluoro-3-isopropylpentan-3-yl; last one can react with $F\cdot$ radical or $CF_3\cdot$ radical with formation of perfluoro-2-methyl-3-ethylpentane and perfluoro-2,3-dimethyl-3-ethylpentane.*

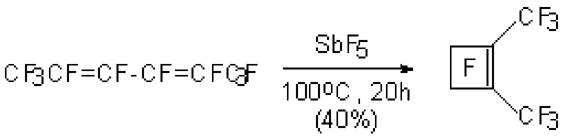
Perfluoro-3-isopropyl-2-methylpent-3-ene was fluorinated and 98 % yield of perfluoro-3-isopropyl-2-methylpentane was obtained [201,223,224]. When the temperature of fluorination is higher than 170°C the process proceeds non-selectively with formation mainly the carbon and tetrafluoromethan. An obvious change in the products type is observed when using the special catalyst Ni/support: perfluoro-2-methyl-3-isopropylpentane as the main product at 130°C is obtained [224].



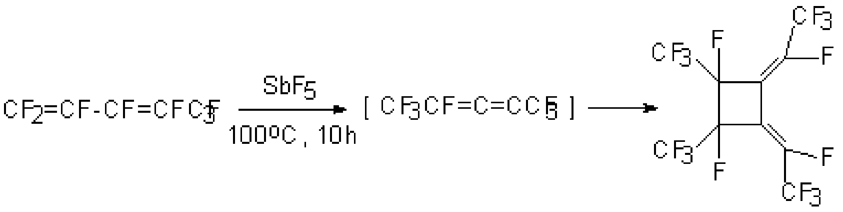
The basic idea is the localization of fluorination acts on the catalyst surface. In the direct gas-phase catalytic fluorination of incompletely fluorinated organic compounds the adsorbed excited intermediate adducts have the possibility to leave the excessive energy to the solid without destruction, resulting the increasing of the selectivity of fluorination. This idea is illustrated by the results of gas-phase direct fluorination of fluoroolefins (dimer and trimer of hexafluoropropylylene). New catalysts allow to obtain excellent results not only in laboratory, but also in industry.

The process of fluorination proceeds by the radical mechanism. The average lifetime of intermediate fluorocarbon radicals in various radical reactions in a liquid at room temperature is much more (10^2 - 10^3 h) than their hydrocarbon analogues.





The presence only one CF_3-group results the formation of cyclobutane system [196]. Probably, the rearrangement of perfluoropent-1,3-diene to perfluoro-1,3-dimethyl-allene with further cyclodimerization is take place.



3.1. New approach to generate superstable radicals and their reactions with internal perfluoroolefins and elementary fluorine.

One of the key problems in the chemistry of free radicals is to ascertain the dependence of the reactivity of radicals on the delocalization of unpaired electron.

Scherer with co-workers [222,225-227] on an example of reactions of perfluoro-3-ethyl-2,4-dimethylpent-2-ene (T2) and perfluoro-3-isopropyl-4-methylpent-2-ene (T3) with fluorine received a superstable and persistent radical of perfluoro-3-ethyl-2,4-dimethyl-3-pentyl (**56**) that confirmed the well established radical mechanism of fluorine attack on perfluoroolefins. It is known that radical **56** is vary stable andcan be isolated and analyzed by the gas chromatography without decomposition. Radical **56** do not react with conc. HCl, conc. H_2SO_4, and oxidizing agents such as oxygen, chlorine, bromine and iodine. The stability of 56 arises not only from the inaccessibility of the radical center becouse of the sterical hindrance, but also from the electronic properties of perfluorosystem. This stable fluoroalkyl radical has large time of life in a solution at 20 °C [222]. The olefin T2 with fluorine atom at multiple bonds has the greater activity in comparison with T3. So, the olefin T2 reacts with a fluorine for 3 hours, whereas an olefin T3 only for 22-24 hours (Table 4) [228].

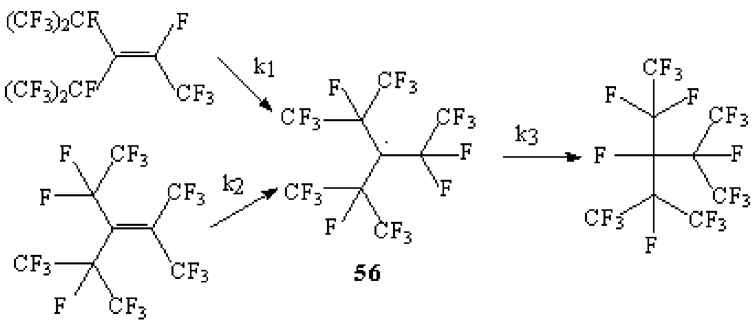


Table 4. Data of gas-chromatography analysis: direct fluorination of olefins (T2 and T3) mixture by elementary fluorine [228]

Time, hours	percentage of reaction mixture, %				
	T2	T3	radical **56**	perfluoroparaffin	unexplored products
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

By these reasons the kinetic measurements of fluorine reaction with olefin T-2 is not possible [228].

The physical data of this radical [225].

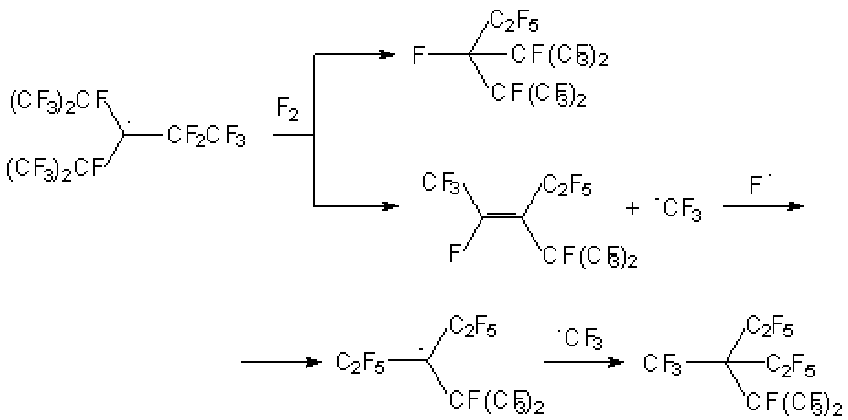
b.p. 37-37.5 °C/35 Torr.

m.p. -28.2 (-28 °C)

Density d_4^{20} 1.845

Parameter of refraction n_D^{20} 1.2872

This radical is stable at room temperature (period half-life 8 years) [222,225-227]. Radical **56** explain the unexpected formation of perfluoro-3-methyl-3-isopropyl-pentane at 104 °C by means of hypothesis that the mechanism involving elimination and re-adduction of CF_3groups exist.



At room temperature radical **56** does not react with water, acids, alkalis, oxygen, chlorine, and bromine. It is necessary to note, that such stable radicals were received from various spatially complicated olefins. Lewis bases such as triethylamine and triphenylpnictogens (Ph_3Pn, Pn = N, As, Sb, Bi) and some soft anions such as iodide or tetraphenyl borate reacted with radical **56** and the perfluoro-3-isopropyl-4-methylpent-2-ene was obtained quantitatively [229]. Even very weak Lewis bases (such as diethyl ether and diethylsulfide) also reacted with radical **56** and the perfluoro-3-isopropyl-4-methylpent-2-ene and additional perfluoro-3-ethyl-3H-2,4-di-methylpen-tane was produced. Hydrogen gas did not reacted with radical **56** without catalyst, but in the presence of Pd, adsorbed on charcoal, smoothly reacted with formation of perfluoro-3-isopropyl-4-methyl-pent-2-ene with quantitative yield (Table 5). Hydrides ($LiAlH_4$, $NaBH_4$, NaH, BH_3(THF complex), Bu_3SnH, Me_2PhSiH) reacted with **56** with formation of perfluoro-3-isopropyl-4-methylpent-2-ene and perfluoro-3-ethyl-3H-2,4-dimethylpentane.

Table 5. Reaction of radical **56** with hydrogen (all unmarked bonds are fluorine) [229].

Conditions	Time	Product distribution (%)					Recovery (%)
		A	B	C	D	56	
H_2	7 days	-	-	-	-	100	100
H_2, 80 °C	33 h	1,6	-	14,8	49,9	13,2	74,2
H_2/cat, 5 % Pd/C	30 min	100	-	-	-	-	100
H_2/cat, 5 % Pd/$BaSO_4$	30 min	100	-	-	-	-	100
Ar/cat, 5 % Pd/$BaSO_4$	5 h	-	-	-	-	100	100
Ar/cat, 5 % Pd/C	4,5 h	25,4	-	-	-	74,6	100

These radicals can exist in a liquid at room temperature during long years.

The authors of [221,226-232] studied the reactions with formation of long-lived fluoroalkyl radical in a solution at 20 °C. Likely, the stabilization of an unpaired electron take place due to the formation of sterically screened radical centers in the process of alkanes or olefins fluorination. Hence, the perfluoroalkyl stable radicals are the particular type of stable radicals with new mechanism of stabilization. The presence of perfluoro groups as substituents enhance the stability of such radicals presumably due to the structure and properties of fluorine atom. These radicals may be used as initiators in polymerization of fluorocontaining monomers. The use of perfluoroalkyl radicals for decreasing of fluorocontaining polymers degradation from radiation will be interesting moment in fluorine chemistry. The use of the perfluoroalkyl radicals in biology as spin-tracer compounds allows to investigate their methabolism. It is interesting to consider the idea of using of perfluoroalkyl radicals as antirad.

It should be noted that stable radicals of this kind have been obtained from various space-hindered olefins [226,227,230-232]. Thus, perfluoroalkenes :

$(CF_3)_2C=C(C_2F_5)CF(CF_3)_2$,

$(iso\text{-}C_3F_7)_2C=CFCF_3$,

$(CF_3)_2CFC(C_2F_5)=CFCF_3$,

$CF_3CF=C(C_2F_5)CF(CF_3)_2$,

perfluoro-2,2-propanebicyclo-[5.2.0]-non-1(7)-ene, $(CF_3)_2CFC(C_2F_5)=CFCF_3$, when react with F_2, form the corresponding long-lived perfluoroalkyl free radicals [212,221]. The interaction of fluorine with olefins :

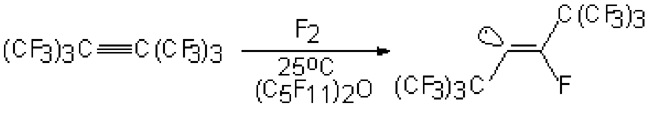
$(CF_3)_2CFCF=CFCF_3$, $(CF_3)_2C=CFC_2F_5$,

$(CF_3)_2C=C(C_2F_5)_2$,

perfluoro-$D^{4a\ (8)}$ -octaline

and perfluoro-1-(1,1-dimethylbutyl)-cyclobutene-1 do not produce similar radicals.

Direct fluorination of perfluoro-*tert*-butylacetylene results the formation of vinyl radicals **57** ($t_{1/2}$ 1 h) [233], identified by ESR spectrum [234,235].



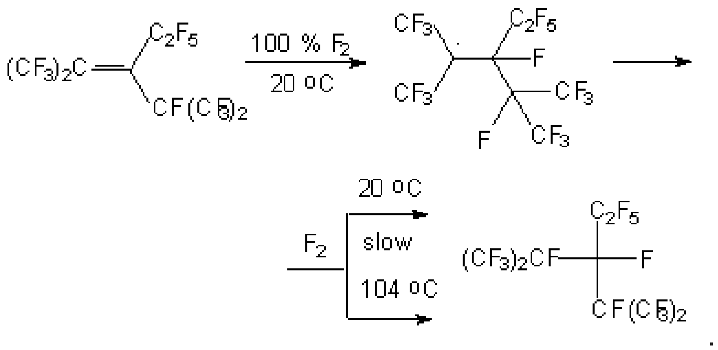
57

This radical is stable when oxygen is absent.

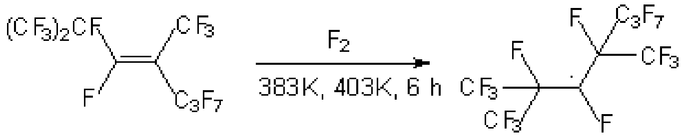
Authors of [221,236-238] studied the processes of fluorination with radical formation. Currently the researches of kinetic and mechanism of a number of radical processes have carried out. For these researches the conditions of long-life radical producing is determined. The authors of [232,238,239] consider the mechanism of formation and structure of long-life perfluorocarbon radicals in the reactions of photolysis, fluorination of the perfluorinatered unsaturated compounds, perfluoroaliphatic and fluorocontaining aromatic compounds, linear perfluoroalkanes and fluorocontaining of polymers [232,238,239].

The elimination of radical $CF_3^{\cdot}$ results the new perfluoroolefins. Firstly, these perfluoroolefins can react with fluorine and give the radicals. Secondly, further can produce the perfluoroolefins with changed carbon skeleton. These works was a new stage in understanding of processes of decomposition and isomerization of perfluoroolefins in fluorination processes and allow carrying out a useful synthesis of some perfluoroparaffins.

The interest of researchers to such radicals constantly increases. The stabilization of free valence in such radicals usually is caused by a delocalization of electronic density or on p-system of an aromatic ring, or on orbitals of heteroatoms (oxygen, nitrogen etc.) [240,241]. The presence of spatial shielding from volumetric groups promotes this stabilization. The new radical practically is not capable to mutual recombination in solutions at room temperature [241-243]. The analysis of structure of radical **56** shows that the inability of recombination defines only by intramolecular isolation of free valence.

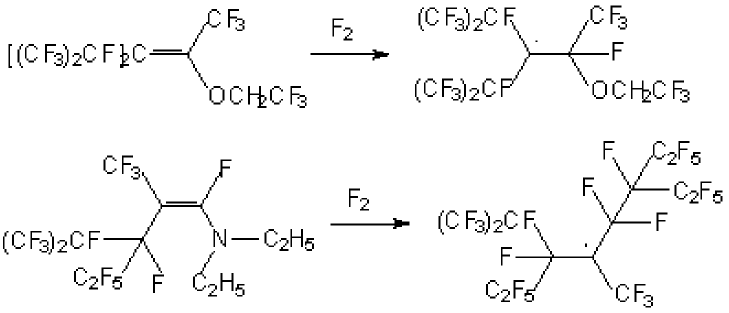


In all cases the spatial isolation of radical center during formation of intermediate perfluorocarbon radicals interferes with their recombination and lowers their reactionary ability in the subsequent stage of a recombination with atom of fluorine [230,244,245].



This radical thermally is more stable in comparison with $\{[(CF_3)_2CF]_2C\text{-}C_2F_5\}$. When heating radical produce $CF_3^{\cdot}$radical, which react with trimer of a hexafluoropropylene $CF_3CF=C[CF(CF_3)_2]_2$with formation of $[(CF_3)_2CF]_3C^{\cdot}$.

The long-life radicals also are formed during fluorination of hexafluoropropylene trimer or its derivatives, which contain phenoxy- [230], diethylamino- aβ,trifluoroethoxy group [244].



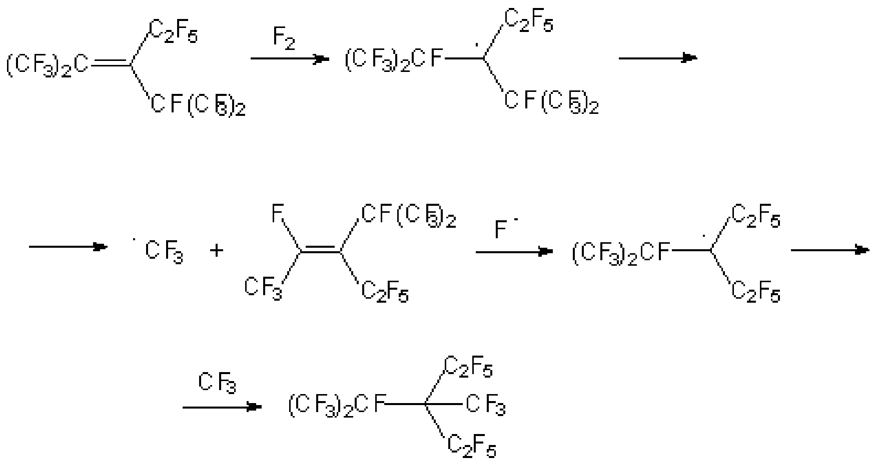
Steady fluorocarbon radicals can be applied as spin labels and for reception of the 2D-images in ESR tomography [244].

It was established, that the greatest influence on a speed of radicals dimerization render the steric shielding of radical center and the speed of radicals rotary diffusion [246].

The interesting opportunities were opened in the reaction of fluorine with perfluoroolefins. So, at -78 °C in alcohol fluorine attach to double bond with formation of remote vicinal products, whereas at 0 °C in a water-acetonitrile mixture fluorine react with formation of epoxy-compounds. The elimination of $CF_3^{\cdot}$ radical results the new perfluoroolefins, which:

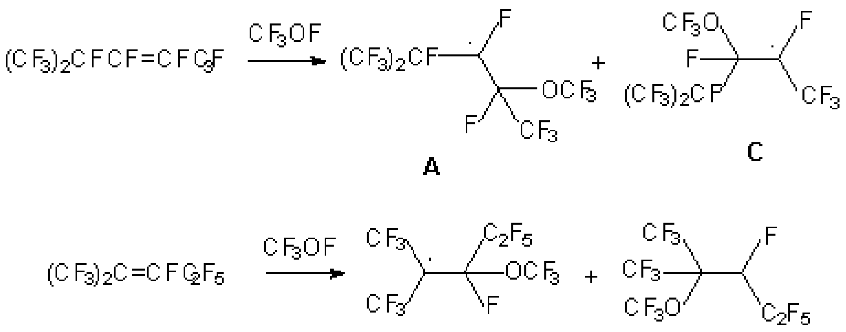
1. Can produce radicals.
2. To react further forming the perfluoroparaffins with altered carbon skeleton.

These works gave a new impulse to understanding of processes of perfluoroolefins decomposition and isomerization during fluorination and allowed to carry out a purposeful synthesis of some



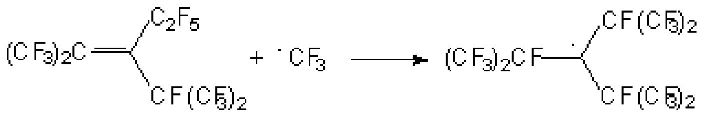
These reactions easily carry out when the processes of a fluorination accompany by ultraviolet light.

Others fluorinating reagents can be used instead of a fluorine for long-life radicals generation. For example, in reaction CF_3OF with perfluoro-2-methyl-2-pentene and perfluoro-4-methylpent-2-ene the stable radicals **A**-**D** are formed as by-products (realization of this process in a cell of a ESR-spectrometer at 330 K and 320 K allow to receive precise signals of radicals **A** and **B** with super thin splitting of fluorine atoms whereas the identification of radicals **C** and **D** was not possible, probably, from their low stability) [247]. It should be note, that this is the first example of fixing of intermediate particles in reactions of olefins with CF_3OF.



The similar pictures takes place in the reaction of CF_3OF and $X(CF_2O)_n(CF_2CF_2O)_mCF_2OF$ with others perfluoroolefins [248]. Thus the method of a ESR in these reactions registered a tertiary and secondary radicals.

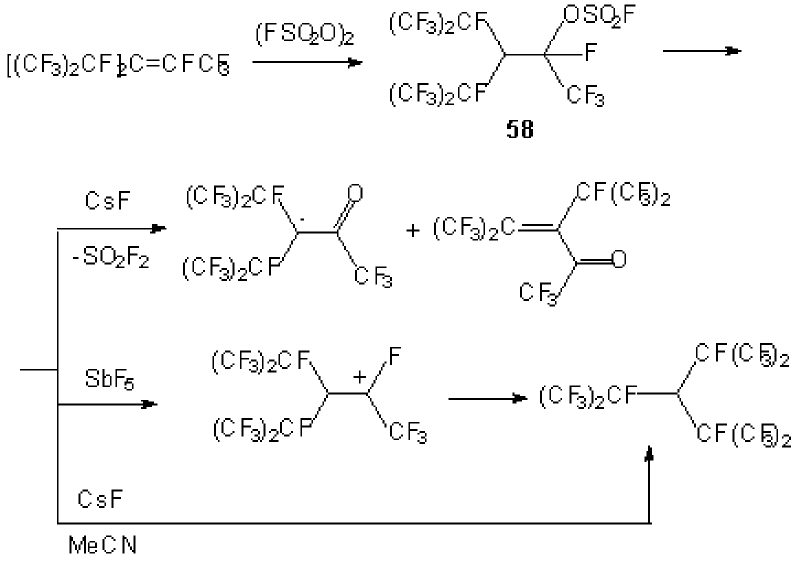
The fact, that trifluoromethyl radical can react with double bond of perfluoroolefin with formation of stable fluoroalkyl radical [221,230] allowed to assume that another stable radicals was formed with using others even "hot" radicals.



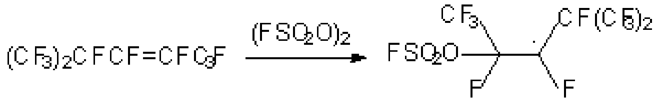
The dynamics of the formation of paramagnetic sites were monitored under identical experimental conditions when mixture of hexafluoropropylene trimer with F_2 was defrosted in ampoule, which was placed into the resonator of the ESR radiospectrometer. The formation of free radicals **56** occurs at 115 K. The poorly resolved doublet of ESR spectrum was appeared. This doublet can be assigned to a radical formed from addition reaction of fluorine atom with double bond of hexafluoropropylene trimer [227]. Free radicals of this type do not recombine even in the liquid state at 293 K, and they have an infinite lifetime:

3.2. Other methods of stable radicals generation and problems of stability and reactivity of perfluoroalkyl radicals.

Really, the reactions of ramified perfluoroolefins (dimers and trimer of a hexafluoropropylene, perfluoro-4,4-dimethylpent-2-ene) with peroxydisulphurildifluorides resulted the stableα-fluoro-sulphonyloxy-tetrafluoroethylperfluoro-di(isopropyl)methyl radical (**58**) [249-254], which was isolated with yield more than 80 % [255,256]. Because of the ramified structure the radical **58** has high stability [235]. Radical **58** can produce the perfluoroisoninyl radical as a product of FSO_3 group substitution under the action of either SbF_5 [248,254] or CsF in acetonitrile [255]. Radical **58** is the first example of new type of fluoroalkylating agents. Their alkylation properties are determined by the stabilizing influence of unpaired electron on the adjacent carbcation center.

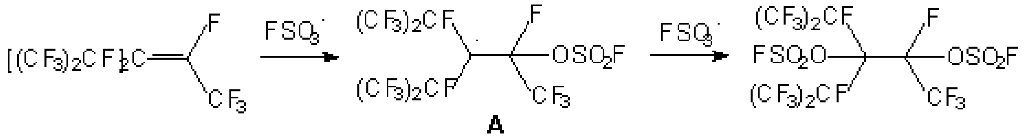

58

It was shown that perfluoro-4-methyl-2-pentene reacted with peroxydisulfuryldifluoride regiospecifically with formation of radical 59, which was stable in the oxygen absence [257,258].


59

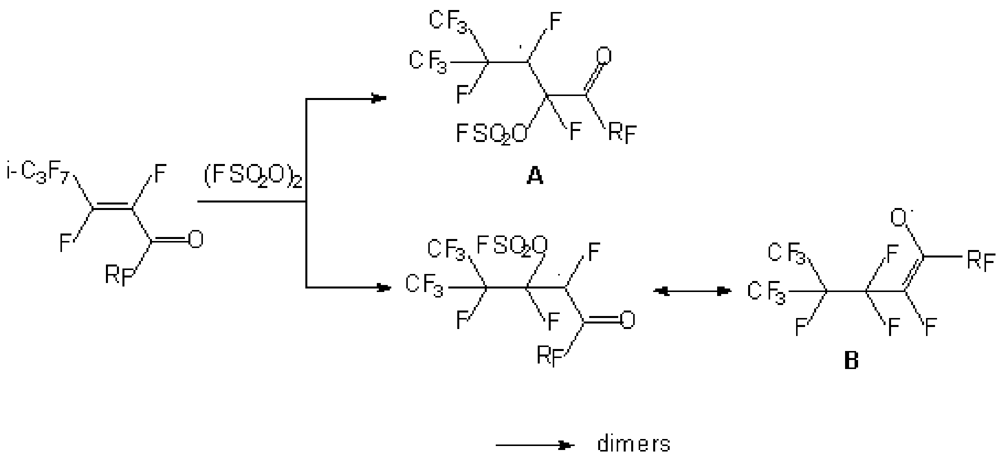
When peroxidisulfuryldifluoride $(FSO_3)_2$ reacts with perfluoro-4-methylpent-2-ene, the radical attacks perfluoro-4-methylpent-2-ene in position 2 with formation of a-fluorosulphatotetrafluoroethylperfluoroiso-propylmethyl radical. Last ones is capable to addition either a secondradical FSO_3 or halogen atoms. But it is not able to undergo the dimerization [259].

In the case of more branched perfluoro-4-methyl-3-isopropylpentene-2 the addition of peroxydi-sulfyryldifluoride led to a stable radical **A**, which was isolated as individual material. The use of more violent conditions results the formation of bis-fluoro-sulfate **B** [257].


A

The presence of functional FSO_3 group carries out the chemical transformations of radical **A** with

The reactions of unsaturated carbonyl compounds iso-$C_3F_7CF{=}COR_F$ (R_F = F, C_2F_5, i-C_3F_7) with $(FSO_3)_2$ yield the considerable amounts (30-35 %) of fluorosulphatodimers [260].



Obviously, dimerization is associated with changing of the radical attack site, which result the thermodynamically more stable radical **B**. Remains can react with formation of the less hindered, and therefore, more reactive O-centered radical. This fact probably determines the dimerization of unsaturated carbonyl compounds.

The kinetic of hydrogen absorption from hydrocarbons by air-stable perfluoroacetyldi-iso-propylmethyl radical was studied by the method of ESR (Table 6) [261].

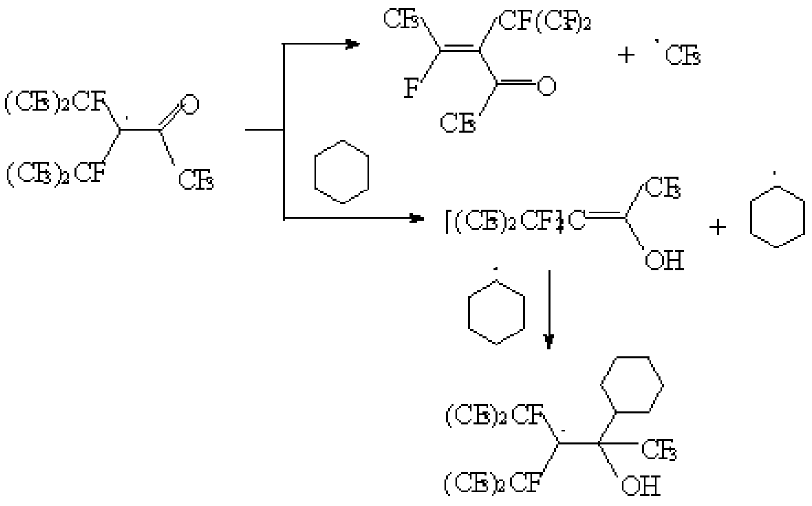
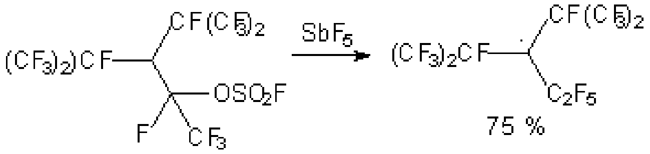


Table 6. The kinetic and thermodynamic data of hydrogen atom detachment from paraffins by α-ketoradical [261].

RH	$k \cdot 10^3$/ $mol^{-1} \cdot L \cdot s^{-1}$ (T/K)	E_a/kcal· Mol^{-1}
Toluene	6.5 (240); 15.0 (260); 53.7 (280); 134.0 (300)	6,3
Hexane	1.6 (280); 5.2 (290); 8.17 (300); 10.3 (10.3)	10,0
Cyclohexane	19.5 (280); 34.2 (300); 87.9 (320), 275 (340)	8,1
Cyclohexene	30 (249); 59.0 (250); 74.0 (260)	5,6
Heptane	3.6 (270), 10.4 (290); 48.1 (320); 75.7 (340)	7,8
Octane	3.4 (300); 5.2 (320); 35 (330); 74 (340); 126 (350)	16,5

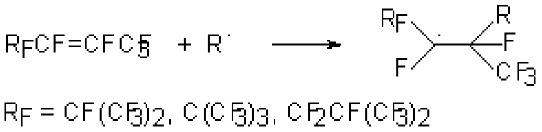
It is interesting, that the radical center does not complicate the reactions ways with other functional groups in all molecules. So, CsF reacts with formation of ketoradical with fluorosulphuryl elimination. If this reaction carries out in acetonitrile, the stable radical is formed as replacement of OSO_2F-group by fluorine [249-252].

The radical (**58**) react with SbF_5 at 45-60 ^{o}C without of solvents and a product of replacement of FSO_3group by fluorine atom (that is perfluorodi-iso-propylmethyl radical (**60**)) is obtained [259,261].



58 **60**

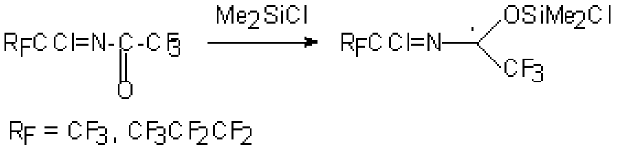
The interaction of intermediate formed from methylvinyl-dimethoxysilane or methylvinyl-diethoxysilane radicals at UV-irradiation and -10 --20 ^{o}C with perfluoroolefins having ramified alkyl groups results the formation of stable radicals [259].



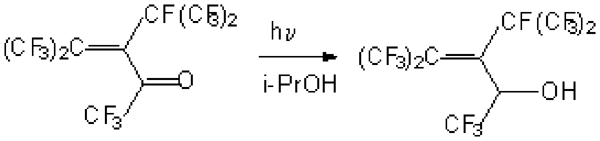
R = $[CH_2=CHSi(Me)(OCH_2X)(OCH_2X)]^{\cdot}$ (X = Me, Et)

The radical reaction of vinylsilane with ramified perfluoroolefins can be the ways of introduction of fluorinated substituents.

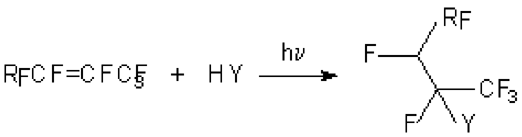
The stable radicals are received from fluorinated imidoylchlorides too [263].



These radicals are stable at room temperature. Reactions proceed as photolysis in isopropyl alcohol with Et_3SiH [264].



The ultraviolet influence on solutions of hydrosilanes in perfluoroolefins results the formation of steady adduct **61**(time of life 5-10 h) [265]. When di-*tert*-butyl-peroxyde was added the signals intensity increased in 10-30 times. The reactionary ability of intermediates obtained from free radical **61** determines by steric shielding of the radical centers.



61

Y = $SiCl_3$, $SiMeCl_2$, $SiMe_3$, $SiEt_3$

R_F= $C(CF_3)_3$

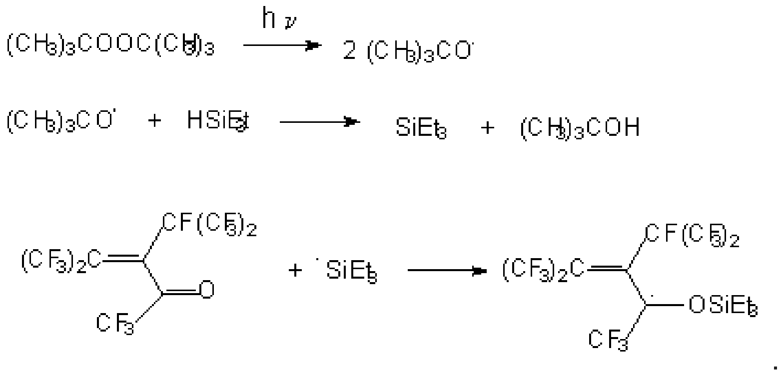
Y = $SiCl_3$, $SiMeCl_2$, $SiMe_3$, $SiEt_3$

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

Y = HP(O)(OR) (R = Me, Et, Pr)

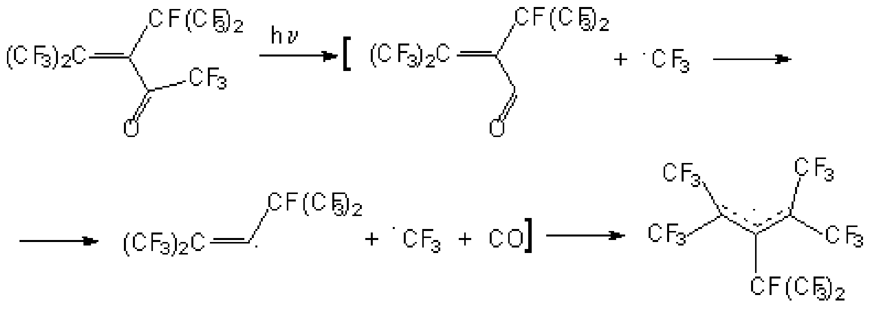
The similar results are received for irradiation of dialkylphosphites too.

Allylic radical of a similar structure **62** is formed when initial olefin reacts with silicon-containing radical.



62

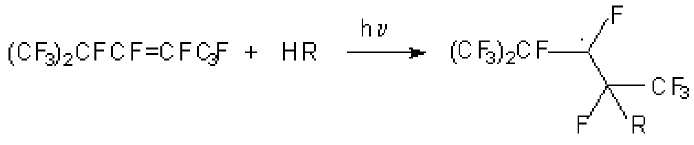
However, photolysis of this olefin without the donors of hydrogen also results the formation of allylic radical with similar structure **63**.



63

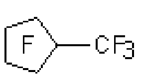
The authors of this work have established, that the lifetime of such allylic radicals is approximately 1 hour. This fact disagrees with the data of such type of radicals described in [266].

The irradiation of perfluoroolefins (even not very spatially complicated) in alcoholic solutions results the formation of steady radicals **64** [267]. Thus, the addition of peroxyde *tert*-butyl (5 % volumetric) increases the signal strength of ESR in 10-40 times..

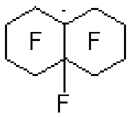


R = CH_2OH, $CH(CH_3)OH$, $C(CH_3)_2OH$

The perfluoroalkyl radicals (65 and 66) with cyclic substituents were received by photolysis of corresponding bromides at presence of Hg $(C_2B_{10}H_{11})_2$ [268]. They were stable up to 220 ^{o}C.

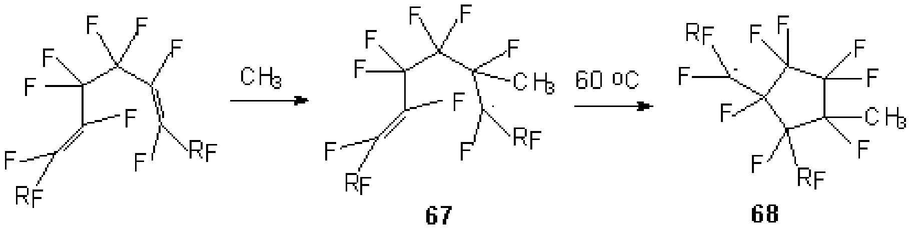


65



66

Perfluorinated alkenyl radical **67** was received by the reaction of terminal perfluoroolefin and methyl radical which was formed from photolysis of di-*tert*-butyl-peroxyde. Radical 67 contain the double bond in position 4 or 5 to the radical center and further turn into the rather stable radical **68** [269,270].



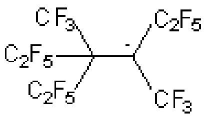
67 **68**

$R_F = C(CF_3)_3$

In the reaction of perfluoro-2-methylpent-2-ene with di-*tert*-butyl-peroxyde at 140 ^{o}C or at 20 ^{o}C (UV light) $(CF_3)_2CMeCHFC_2F_5$ and $(CF_3)_2CHCFMeC_2F_5$ (ratio 1:4) was obtained (30 % yield) [271]. The intermediate radical $(CF_3)_2CMeCFC_2F_5$ was identified by ESR spectrum.

These radicals are the models for study of a structure and reactionary ability of cyclic tertiary perfluorinated radicals. It is established, that the view of received kinetic curves (range of temperatures +20 - 120 ^{o}C), and dependence of signal of stationary amplitude from intensity of light support the idea of radicals dimerization with following kinetic parameters: $k_{20}=10^2$ L/mols, E_{act}= 3.4 kkal/mols. It is assumed that the reduction of dimerization speed constant of these radicals over against the acyclic fluorinated radicals [246, 271] was provided not only by steric factors, but also by the stereo chemical rigidity of radical canter.

The stable perfluoroalkyl radicals were received also by other methods, which include interaction of perfluoroolefins with various radicals. So, at electrochemical fluorinations of perfluoroolefins and their alkoxy- and alkylamino-derivatives the radicals **69** - **71** with high stability are received [272].



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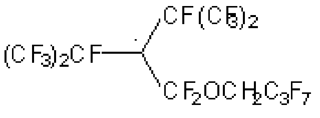

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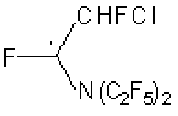
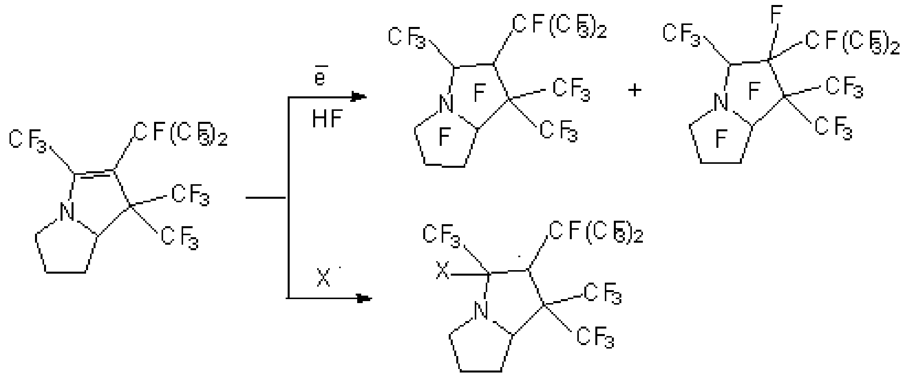


71

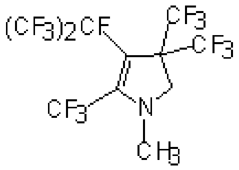
Radicals **69-71** was identified by ESR spectrums.

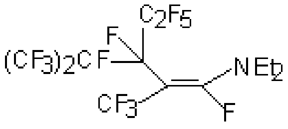
During the electrochemical fluorination of steric ramified polyfluoropyrrolizidine the stable radical (with concentration not less 5 % and time live > 1 month) was recognized in products of reaction by the method of ESR [273, 274]. The radicals of this type rather stable and can be received when perfluoroolefins reacted with either element fluorine, or other radicals, for example, $CH_3^{\cdot}$, $[P(O)(OMe)_2]^{\cdot}$.



X = F , $P(O)(OMe)_2$, Me

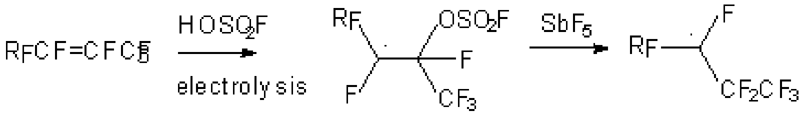
Radicals were fixed during electrochemical fluorination of following compounds:





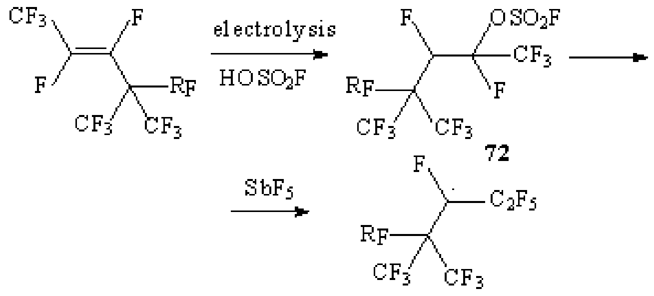
Electrolysis of perfluoroolefins in environment of fluorosulphonic acid produce the stable fluorosulphonyl-oxyperfluoroalkyl radical [249-252, 275].

The characteristic features of this reaction are confirmed by the formation of the perfluoroalkyl radicals from the β-fluorosulfatoperfluoroalkyl radicals under the action of SbF_5 [249].



R_F = i-C_3F_7, t-C_4F_9

SbF_5 replaces FSO_3 group on atom of fluorine, giving a new stable radical **73** (anode - glass - carbon SU 2000, cathode - titanium, 1=0.6 A, t = 0.5 h) (current yield 75 %)



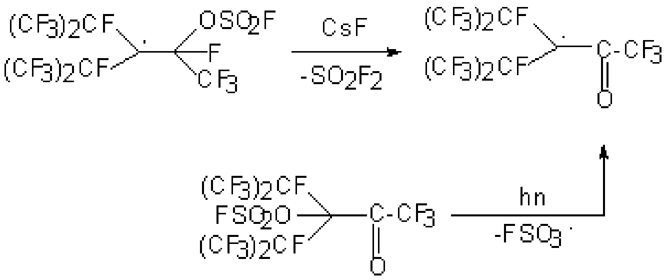
72

73

R_F = F, CF_3 [267], i-C_3F_7, t-C_4F_9 [245]

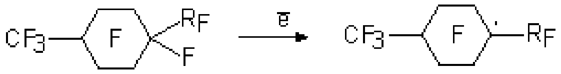
Due to the essential differences in boiling points of radicals, received by electrochemical fluorosulphatation of hexafluoropropylene trimer and the initial olefin as well as a product of the further transformation, radical was isolated.

The method of fluoroolefins fluorosulphatation is attractive becouse allows to receive the fluoroalkyl radicals with functional FSO group which permit their further chemical transformations. So, under the action of CsF this radical was transformed to the stable perfluoroacetyldi-iso-propylmethyl radical (last also was recognize during photolysis of ketofluorosulphate).



The electrochemical fluorination of hexafluoropropylene trimer at presence of NaF produce the stable perfluoro-3-ethyl-2,4-dimethyl-3-pentenyl radical [276].

The method of stable perfluoroalkylic radicals producing by radiolysis of perfluoroparaffins, having tertiary atom of carbon, is most advanced [228,232,239,277-279]. Method is simple and universal. The formation of radicals proceeds with fluorine atom elimination from a cycle [269]. It is possible to use ultraviolet irradiation of perfluorinatered compounds. However photolysis is less effective method then radiolysis. So, during the photolysis of hexafluoropropylene the concentration of radicals was three times less than during radiolysis [232].



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

Conclusion.

The above-mentioned material allows to ascertain the growing interest of the researchers to the new approaches of introduction of perfluorinatered fragments to organic molecules and transformations of the simple substituents to complex functional groups. The significant successes achieved in development of methods, which help to carry out the introduction of fluorocontaining fragments to organic molecules. It is necessary to note that was studied the reactions of wide using internal perfluoroolefins with fluoride-ion. Such processes have advantages and can give the real opportunities of application in industrial technologies. It is expected that realization of this methodology help to open the new reactions and transformations resulting the synthesis of fluorocontaining compounds. Taking into account all above-mentioned, in the review we basically try to show the new approaches, opportunities of new reagents and new ideas, which are realized in the organic synthesis. Besides we aspired to show the tendencies and basic directions of researches in the field of a synthesis of perfluorocontaining organic substances containing a various molecular skeleton and functional groups. Certainly questions concerning the realization of these ideas and processes are attractive not only for the chemists working in field of fluoroorganic compounds, but also for experts of organic synthesis. Thus, perfluoroorganic compound in number moments are convenient, and moreover sometimes they are the unique models for decision of a number fundamental questions of theoretical organic chemistry.

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