

# Synthesis and Application of the Products of the Interaction of Sulphuric Anhydride with Perfluoroolefins

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## Abstract

A set of the problems and directions of the accelerated development of the methods of synthesis of fluorine-containing  $\beta$ -sultones by means of the interaction of sulphur trioxide with perfluorinated olefins is considered in connection with the outlooks for their wide use to obtain fluorinated materials for a broad range of practical applications. For instance, they are used as semi-products to obtain polyfluorinated sulpho- and carboxylic acids which are involved in the manufacture of fluorinated membranes for electrochemical processes. The effect of substituents at the unsaturated bond on the formation of a four-membered cycle and the effect of Lewis acids on obtaining unsaturated fluorosulphates. The areas of application are described.

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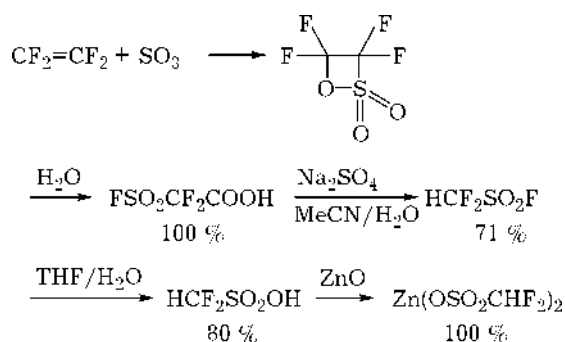
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## INTRODUCTION

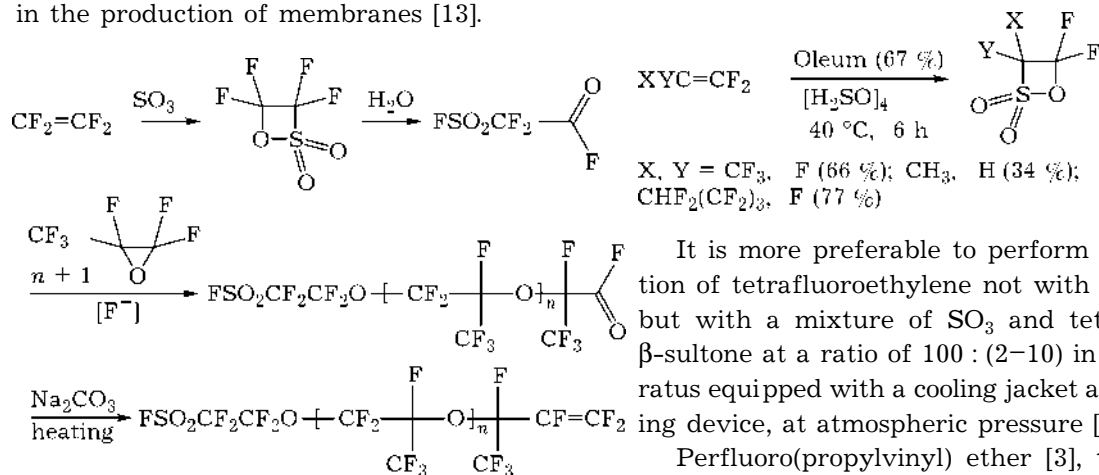
Fluorinated  $\beta$ -sultones are important products of the chemistry of organofluoric compounds. Their development started due to the fundamental works of the scientific school of I. L. Knunyants [1–4]. Later other researchers joined these investigations [5–8]. Many sultones are used as semi-products to obtain surface-active substances, electrolytes for lithium batteries, alkylating reagents *etc.* This class of compounds has become especially urgent for the synthesis of perfluorinated ionomer membranes (Nafion<sup>TM</sup>) which are composed of a perfluorinated polymeric chain with perfluoroalkyl sulphonate group [9].

The reactions of sulphuric anhydride with fluorinated alkenes allows one to obtain  $\beta$ -fluorosultones,  $\beta$ -fluorosulphites, fluorine-containing cyclic sulphites and sulphonates. Substituting sulphotrioxidation of perfluorinated unsaturated and fatty aromatic compounds and electrochemical fluorosulphation of fluoroolefins in  $\text{HSO}_3\text{F}$  gives one the possibility to obtain fluorosulphates possessing fluoroalkenylating and fluoroalkylating properties.

Perfluorinated  $\beta$ -sultones are interesting by their ability to open the cycle under the action of water and thus form fluorosulphonyldifluoroacetic acid which finds practical application as a catalyst, as well as for the synthesis of fluorinated membranes [10–12].



An intermediate fluoroanhydride of fluoro-sulphonyldifluoroacetic acid is used to synthesize the substituted trifluorovinyl ether applied in the production of membranes [13].



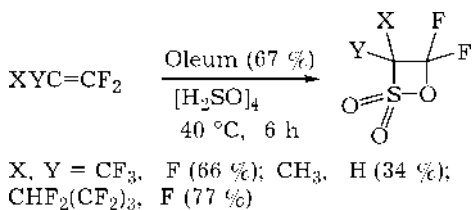
#### SYNTHESIS AND PROPERTIES OF FLUORINE-CONTAINING $\beta$ -SULTONES

Inorganic acids, such as  $\text{HSO}_3\text{F}$ ,  $\text{H}_2\text{SO}_4$  (or  $\text{SO}_3$ ) easily add to partially fluorinated olefins [14]; under rigid conditions at  $200^\circ\text{C}$  they add also to perfluoroolefins [15, 16] with the formation of the products of addition to the unsaturated bond.

It is important to note that only freshly distilled  $\text{SO}_3$  allows one to obtain successfully fluorinated sultones in its reaction with fluoroolefins. Commercially available sulphuric anhydride of Sulfan grade, as well as the solid polymeric form of  $\text{SO}_3$  (trimer) are inefficient due to the

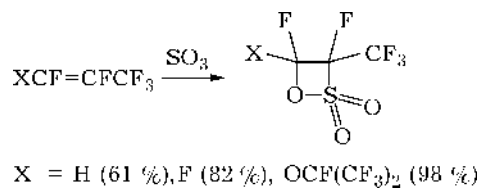
low yield of sultone and the formation of a number of side products. At the same time, it is difficult to work with the free oxide of sulphur (VI) because of its ability to polymerise (to prevent polymerisation, monomeric and liquid  $\text{SO}_3$  should be stored at a temperature of  $45^\circ\text{C}$ ). Nevertheless, the examples of efficient use of  $\text{SO}_3$  were reported in the review [1] and in [14].

Terminal fluoroolefins, such as hexafluoropropylene, 2H-pentafluoropropylene, 6H-perfluorohex-1-ene, perfluoro(propylvinyl) ether and tetrafluoroethylene, react with oleum (67%) with the formation of  $\beta$ -sultones similarly to monomeric liquid  $\text{SO}_3$  [17].

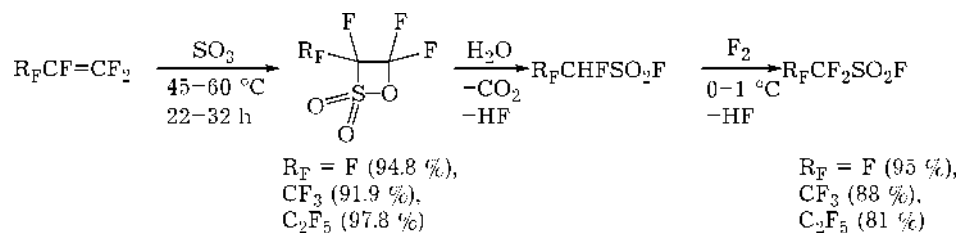


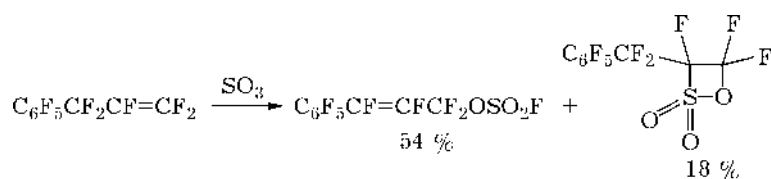
It is more preferable to perform the reaction of tetrafluoroethylene not with pure  $\text{SO}_3$  but with a mixture of  $\text{SO}_3$  and tetrafluoro- $\beta$ -sultone at a ratio of 100 : (2–10) in an apparatus equipped with a cooling jacket and a mixing device, at atmospheric pressure [18].

Perfluoro(propylvinyl) ether [3], tetrafluoroethylene [17, 19] and  $\text{CF}_2=\text{CFSF}_5$  [20] enter a non-catalytic reaction with  $\text{SO}_3$  forming the corresponding  $\beta$ -sultones.



The authors of patent [21] developed the method of obtaining perfluoroalkanesulphofluorides using  $\beta$ -sultones obtained by treating perfluoroolefins with sulphuric anhydride at a temperature of  $45\text{--}85^\circ\text{C}$ ; after hydrolysis with water they give monohydroperfluoroalkanesulphofluorine. Fluorination of the latter com-





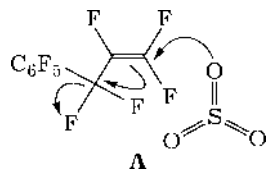
Scheme 1.

pound with elemental fluorine at 0–30 °C leads to the formation of perfluoroalkanesulphofluoride (Scheme 1).

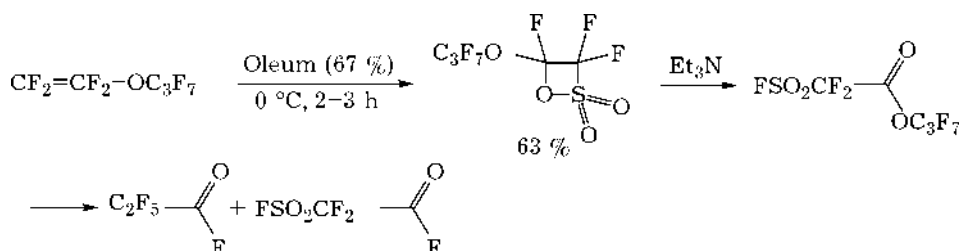
In the case of hexafluoropropylene, the reaction with  $\text{SO}_3$  is strongly exothermal, so the process should be conducted at rather low temperature. For example, the interaction of 67 % oleum with hexafluoropropylene is carried out at first at –45 °C, then temperature is increased to 43 °C; after 13 h,  $\beta$ -sultone of hexafluoropropylene is obtained with the yield of 62 % [22]. The reaction of perfluoro(propylvinyl) ether with  $\text{SO}_3$  proceeds at 0 °C within 2–3 h with the formation of the corresponding  $\beta$ -sultone with a high yield [17]. The same reaction carried out at 20 °C gives  $\beta$ -sultone with the yield of 68 % within 10 min.

Perfluoroallyl benzene reacts with  $\text{SO}_3$  especially easily [4]. However, in this case one obtains a mixture of stereo isomers of perfluoro- $\gamma$ -phenylallylfluorosulphate (the ratio of *cis*- to *trans*-isomers is 93 : 7) and  $\beta$ -sultone (see Scheme 1).

The high content of the *trans*-isomer may be explained by the realisation of the synchronous mechanism with the participation of a cyclic transition state **A**:

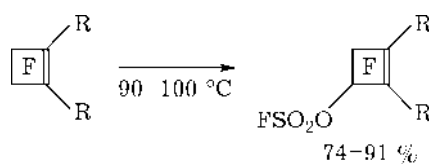


The formation of  $\beta$ -sultones is accompanied by different processes. For instance, the interaction of  $\text{SO}_3$  with terminal fluoroolefins results in the products of cycloaddition- $\beta$ -sultones [23, 24],

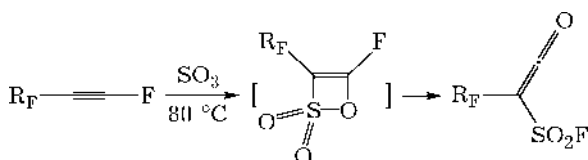


Scheme 2.

while the processes characteristic of cyclic fluoroolefins are those involving substitution of fluorine at the double bond.

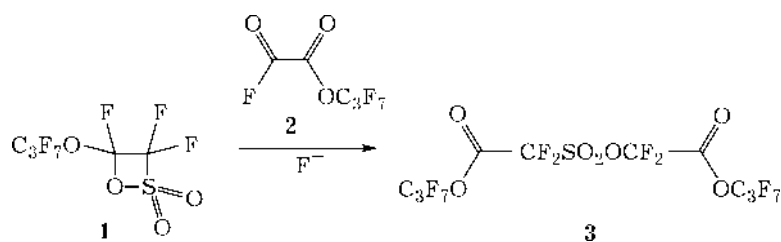


Perfluoroacetylenes easily react with  $\text{SO}_3$  at 80 °C forming perfluoroalkylfluorosulphonyl ketones with the yield of 86–90 %, perhaps through the intermediate formation of unsaturated  $\beta$ -sultone [25].

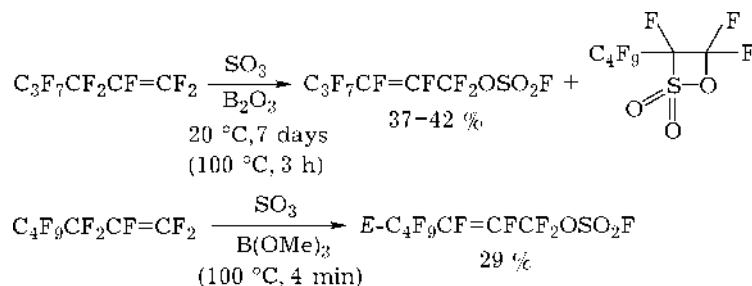


Tetrafluoroethane- $\beta$ -sultone may decompose even at such a low temperature as 150 °C with the formation of carbonyl fluoride, sulphur dioxide and perfluorocyclopropane. It was shown [26] that difluorocarbene is an intermediate product in this reaction and can be fixed with the help of fluorinated olefins, vinyl ethers and acyl fluorides. Thermal decomposition is characteristic also of other perfluoro- $\beta$ -sultones. This process may become the main reason of explosions of the mixtures of sultone with  $\text{SO}_3$ .

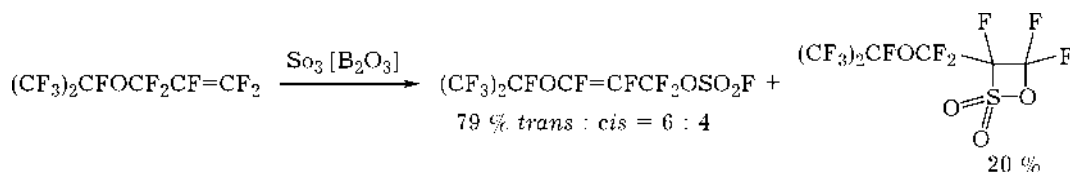
$\beta$ -Sultone obtained according to the reaction of perfluoro(propylvinyl) ether with  $\text{SO}_3$  decomposes under the action of triethylamine with the formation of unstable  $\text{FSO}_2\text{CF}_2\text{COOC}_3\text{F}_7$  which gives the fluoride of pentafluoropropionic acid and the fluoride of fluorosulphonyldifluoroacetic acid [17] (Scheme 2).



Scheme 3.



Scheme 4.



Scheme 5.

$\beta$ -Sultones easily open at the O-SO<sub>2</sub> bond under the action of nucleophilic reagents. For example, perfluorodiethers **3** form by the condensation of heptafluoropropylfluorooxalate **2** with  $\beta$ -sultone **1** in the presence of fluoride ion [17]. Fluorooxalate under the action of fluoride ion generates the corresponding alkoxy anion that acts as a nucleophilic agent and opens the four-membered ring of  $\beta$ -sultone (Scheme 3).

Electrochemical fluorination of the sultone, formed in the interaction of tetrafluoroethylene with  $SO_3$ , in anhydrous hydrogen fluoride gives trifluoromethanesulphonyl fluoride, carbonyl fluoride and sulphuryl fluoride [27]. Pentafluoroethylsulphonyl fluoride and perfluorobutanesulphonyl fluoride are obtained similarly [27].

#### INTERACTION OF PERFLUOROOLEFINS WITH $SO_3$ , CATALYSED BY LEWIS ACIDS

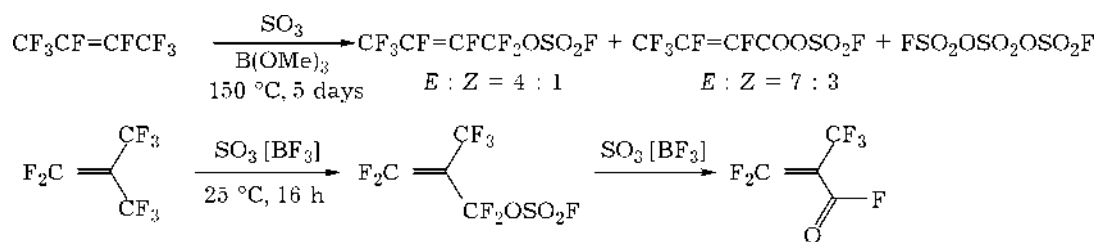
When electron accepting substituents decreasing the mobility of fluorine atoms in these positions are introduced into an olefin molecule, increasingly rigid electrophilic catalysis is needed

to insert  $SO_3$  at the unsaturated bond. The use of Lewis acids in the reactions of perfluoroolefins with  $SO_3$  causes also changes in the process direction. In this case, the main direction of the reaction becomes not cycloaddition but substituting sulphotrioxidation; the formation of unsaturated fluorosulphates with the general formula  $RCF=CFCF_2OSO_2F$  occurs. Later on the sequence of activity of substituents of sulphotrioxidation was established:  $R_F < F \approx R_F O < C_6F_5$ .

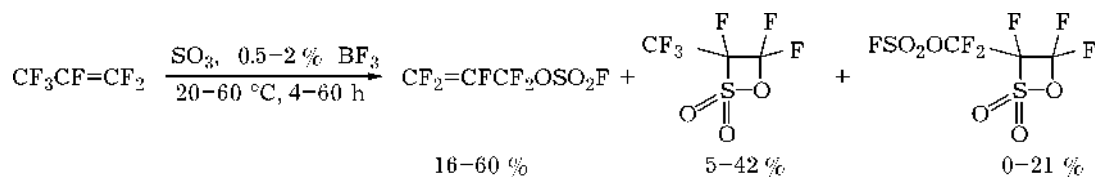
Thus, in the presence of catalysts (boron-containing compounds  $BF_3$ ,  $B_2O_3$ ,  $B(OMe)_3$ ), along with  $\beta$ -sultones, unsaturated fluorosulphates in the form of *trans*-isomers are formed, which was demonstrated for many terminal perfluoroolefins as examples [28, 29] (Scheme 4).

As a rule, a mixture of products is formed in the reaction of perfluoroisopropylvinyl ether with  $SO_3$  in the presence of boron-containing compounds. This fact is an evidence of the realisation of two directions [22] (Scheme 5).

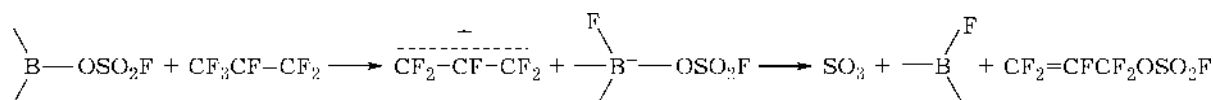
With temperature rise, only unsaturated fluorosulphates are formed. This was shown for the example of perfluorobut-2-ene [29]; with the change of the catalyst for  $BF_3$ , this direc-



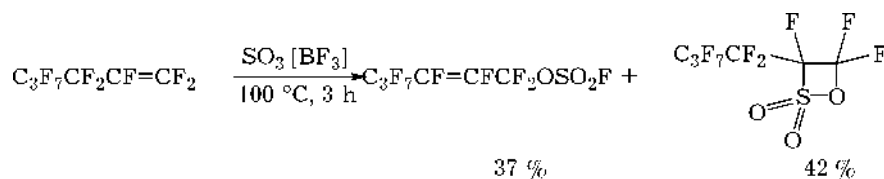
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

tion is observed even at low temperature (for example, in the interaction of  $\text{SO}_3$  with perfluoroisobutylene [30]). It should be noted that with  $\text{SO}_3$  taken in excess, this process may be completed with the formation of the fluoroanhydride of fluorometacrylic acid (Scheme 6).

Some perfluoroolefins (for example, hexafluoropropylene, 2-hydropentafluoropropylene [31] and (2,3-dichloropropyl)trifluoroethylene [32, 33]) react with sulphuric anhydride in the presence of  $\text{BF}_3$  regioselectively giving the corresponding mixtures of  $\beta$ -sultones and perfluorinated unsaturated fluorosulphonates (Scheme 7).

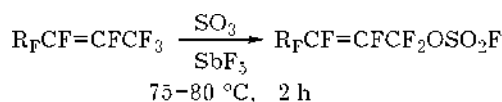
The mechanism of fluorosulphate formation with the participation of perfluoroallyl cation was postulated in [24] (Scheme 8).

Evidently, the decisive factor in the synthesis of fluorosulphates is the allyl mobility of fluorine atoms in the allyl position, determined by the stability of the corresponding carbenium ions.

At the same time, as a rule, such catalysts as  $\text{BF}_3$ ,  $\text{SbF}_3$ ,  $\text{SbF}_5$  lead to the formation of

either a mixture of products or only fluorosulphates, which is determined by the number of substituents at the unsaturated bond [2] (Scheme 9).

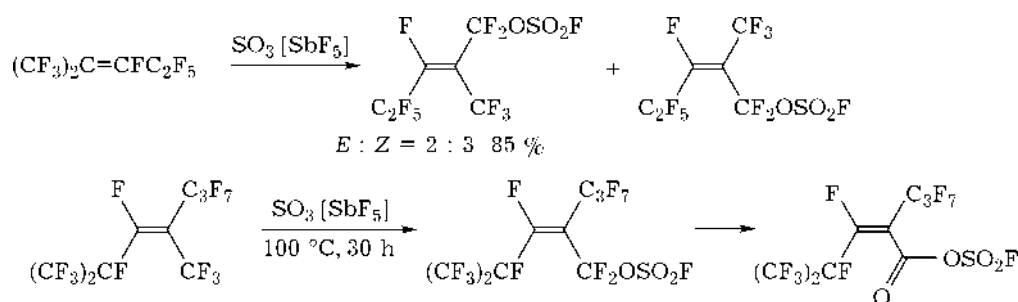
In the case of internal  $\Delta^2$ -perfluoroolefins, it is necessary to use  $\text{SbF}_5$  because the reaction does not proceed with  $\text{BF}_3$ . The corresponding allylfluorosulphates are formed in the process [2, 34].



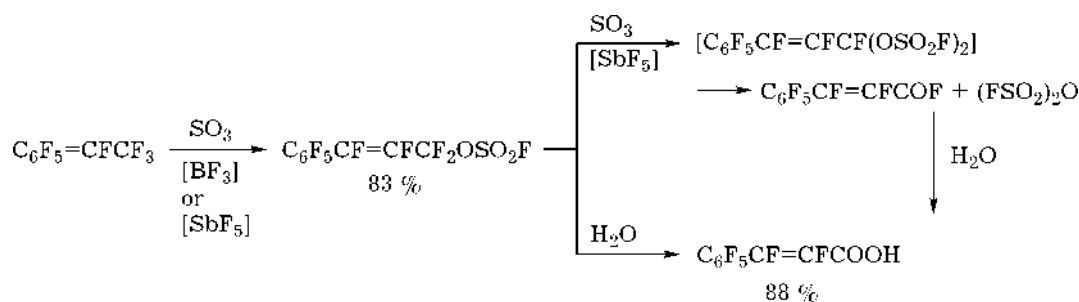
$\text{R}_F = \text{C}_2\text{F}_5$  (87%),  $n\text{-C}_3\text{F}_7$  (93%),  $i\text{-C}_3\text{F}_7$  (93%),  $i\text{-C}_4\text{F}_9$  (89%),  $n\text{-C}_5\text{F}_{11}$  (87%)

The efficiency of the reaction of perfluoroolefins with  $\text{SO}_3$  is determined by the amount of acceptor substituents at the allyl system [35] (Scheme 10).

The action of  $\text{SO}_3$  on *trans*-perfluoro-4-methylpent-2-ene in the presence of 1%  $\text{SbF}_5$  results in the formation of *trans*-perfluoro-4-methylpentene-2-ylfluorosulphate with the yield of 95% (conversion 37%); the action on *trans*-



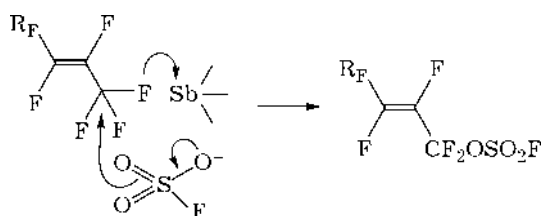
Scheme 10.



Scheme 11.

perfluoro-4,4-dimethylpentene-2 gives *trans*-perfluoro-4,4-dimethylpentene-2-ylfluorosulphate with the yield of 89 % (conversion 78 %) [2]. These transformations are based on the electrophilic attack of  $\text{SO}_3$  or its complex with  $\text{SbF}_5$  at the allyl fluorine atom, followed by the interaction of thus generated carbenium ion with fluorosulphate anion [2, 34].

The stereoisomeric composition of perfluoroalkene-2-ylfluorosulphates formed in the interaction of perfluoroalkenes-2 with  $\text{SO}_3$  in the presence of  $\text{SbF}_5$  completely corresponds to the stereoisomeric composition of the initial olefin. On this ground, it was concluded that the substitution of fluorine atom by  $\text{FSO}_3$  group proceeds through the cyclic transition state [34, 36].



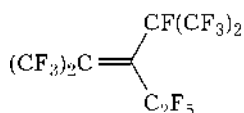
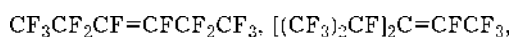
The pentafluorophenyl group stabilizes carbenium ions, which allows one to carry out the substituting sulphotrioxidation under softer conditions than those for perfluoroalkenes-2 [36]. For example, the reaction of perfluoropropenylbenzene with  $\text{SO}_3$ , with  $\text{BF}_3$  as a catalyst, proceeds at 75–80 °C with the formation of

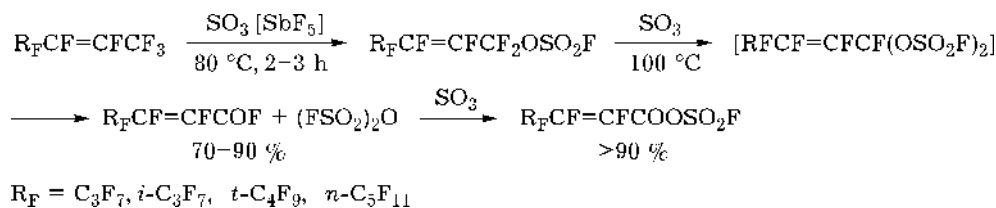
perfluoro- $\gamma$ -phenylallylfluorosulphate with the yield higher than 80 % (Scheme 11).

In the case of catalysis with a stronger Lewis acid ( $\text{SbF}_5$ ), the reaction is even more efficient (it starts at room temperature); perfluoro- $\gamma$ -phenylallylfluorosulphate is formed. With temperature rise to 95–100 °C, it is transformed into perfluorocinnamoylfluorosulphate. Hydrolysis of the latter compound leads to perfluorocinnamic acid (yield 88 %) [36].

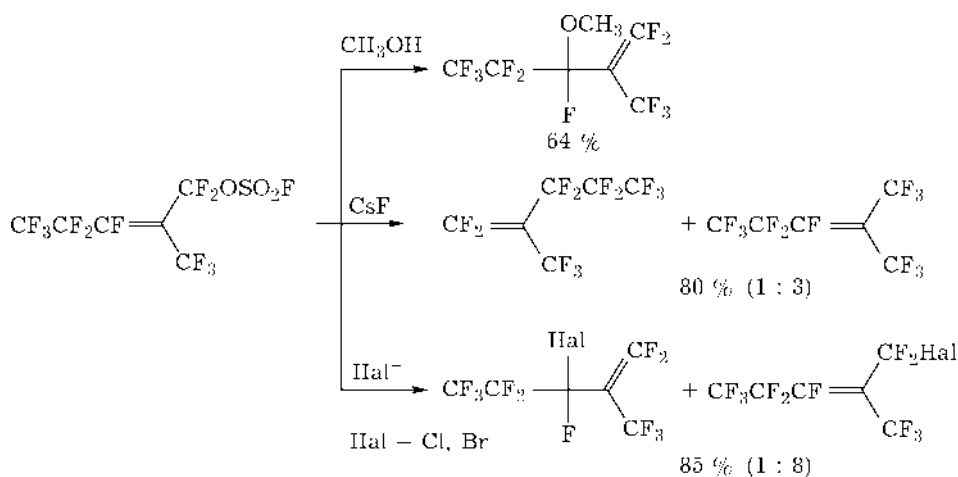
The interaction of internal perfluoroolefins with  $\text{SO}_3$  in the presence of  $\text{SbF}_5$  results in the formation of perfluoroalken-2-ylfluorosulphates; the reaction is not accompanied by the migration of the double bond; the stereoisomeric composition exactly corresponds to that of the initial fluoroolefin. Transomers react somewhat more rapidly than *cis*-isomers do [30, 37–42].

A necessary condition for the substituting sulphotrioxidation of perfluoroalkenes-2 is the presence of at least four fluorine atoms in the charge positions of the allyl triad. Because of this, the following olefins do not enter the reaction with  $\text{SO}_3$  in the presence of  $\text{SbF}_5$  (up to 10 % mass) within temperature range 120–190 °C:





Scheme 12.

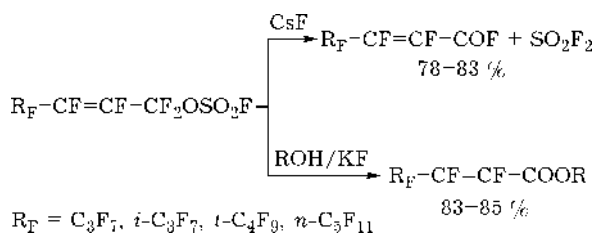


Scheme 13.

So, the functionalisation of allyl  $CF_3$  group in higher perfluoroolefins is thus carried out.

In the case of the use of excess  $SO_3$  and the catalytic amount of  $SbF_5$ ,  $\alpha,\beta$ -unsaturated perfluorocarboxylic acids are formed: for the two-fold excess of  $SO_3$ , perfluoroalkenylfluorides are formed, for the three-fold excess perfluoroalkenylfluorosulphates are obtained [34]. Formally, this is in fact saponification of  $CF_3$  group (Scheme 12).

It turned out that perfluoroalkenylfluorides are also obtained in the interaction of perfluoroalkene-2-ylfluorosulphates with  $CsF$  at the sulphur atoms, while the esters of  $\alpha,\beta$ -unsaturated perfluorocarboxylic acids are formed under the action of alcohols in the presence of  $KF$  [23].



On this basis, a general method of obtaining  $\alpha,\beta$ -unsaturated perfluorocarboxylic acids was developed.

However, it should be kept in mind that the reaction of nucleophilic reagents with alkenylfluorosulphates obtained by the interaction of hexafluoropropylene dimers with  $SO_3$  leads not to the corresponding acids but to the substituted terminal perfluoroolefins [24] (Scheme 13).

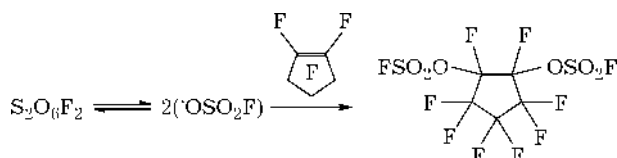
Other nucleophilic reagents also may be used for this purpose. For example, fluoroanhydride of trifluoroacrylic acid was obtained from perfluoroallylfluorosulphate  $CF_2=CF CF_2 OSO_2 F$  under the action of  $KBr$  or  $NaBr$  in ether (diglyme, sulpholane) [43].

Taking into account the importance of perfluoroalkylfluorosulphates as semi-products of organofluoric synthesis, it is reasonable to consider other methods of their synthesis. The processes of perfluoroolefin interaction with peroxydisulphuryldifluoride ( $FSO_2O$ )<sub>2</sub> and their electrolysis in the solution of fluorosulphonic acid are worth considering.

#### INTERACTION OF PERFLUOROOLEFINS WITH PEROXYDISULPHURYLDIFLUORIDE

The reactions of perfluoroolefins with radicals are rather well investigated and are the key processes for the synthesis of various

fluorinated compounds. In particular, peroxydisulphuryldifluoride ( $\text{FSO}_2\text{O}$ )<sub>2</sub> seems an efficient source of  $\text{FSO}_2\text{O}^\cdot$  radicals that may attach to the double bond of fluoroolefins. It should be noted that these reactions proceed very rapidly [44, 45].



This ability is used to carry out fluorosulphation of fluoroolefins, for example such key compounds as tetrafluoroethylene, hexafluoropropylene and their dimers and trimers [46, 47]. For instance, the interaction of ( $\text{FSO}_2\text{O}$ )<sub>2</sub> with the trimer of hexafluoropropylene **4** for the reagents ratio of 1 : 2 leads to the formation of an intermediate stable  $\alpha$ -fluorosulphatotetrafluoroethyl-bis(perfluoroisopropyl)methyl radical **5** with the yield of 81 %. The transformation of the latter under the action of ( $\text{FSO}_2\text{O}$ )<sub>2</sub> in excess gives bis(fluorosulphate) **6** [48] (Scheme 14).

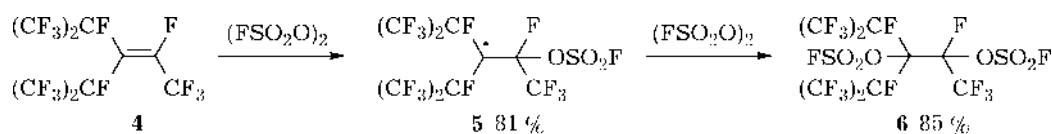
However, unlike for the trimer of hexafluoropropylene **4** of the shown structure, one did not succeed in obtaining stable radical particles by means of fluorosulphation of its other isomers (**7**, **8**). The main products of the

transformations in these reactions are bis(fluorosulphates) **9** and **10**, respectively (Scheme 15).

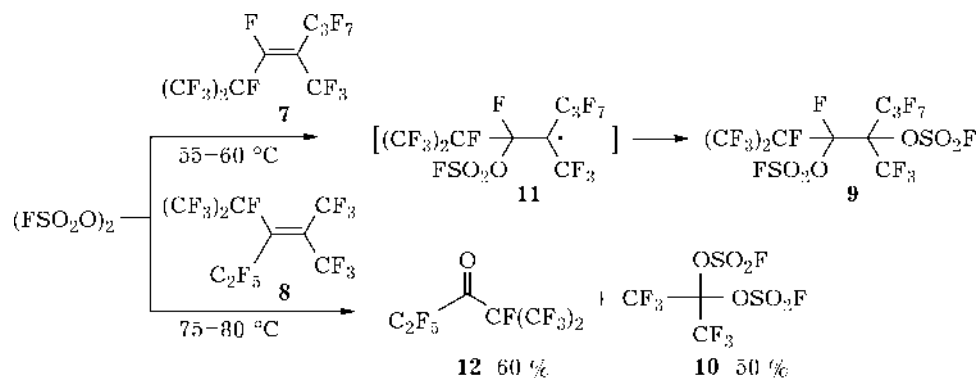
The author of [48] explains the absence of stable intermediate radicals by the effect of perfluoroisopropyl group, causing a sharp decrease in the rate of  $\text{FSO}_2\text{O}^\cdot$  radical addition at the double bond of fluoroolefin **7**, while the rate of formation of radical **11** becomes smaller than the rate of its recombination with  $\text{FSO}_2\text{O}^\cdot$  radical. In the case of isomeric fluoroolefin **8**, the reaction proceeds only at higher temperature (75–80 °C), and the process is accompanied by splitting the molecule at the C=C bond, which leads to the formation of ketone **12** and *hem*-bis(fluorosulphate) **10**.

#### ELECTROCHEMICAL METHOD OF $\text{FSO}_2\text{O}^\cdot$ RADICAL GENERATION AND ITS REACTIONS WITH PERFLUOROOLEFINS

Since peroxydisulphuryldifluoride ( $\text{FSO}_2\text{O}$ )<sub>2</sub> is a difficultly available and dangerous reagent, an electrochemical method of obtaining it was developed. It is formed due to the oxidation of the anion of fluorosulphonic acid  $\text{FSO}_3^-$  to form  $\text{FSO}_2\text{O}^\cdot$  radical and its further interaction with perfluoroolefin or its derivative. Such an approach may serve as a convenient preparative method to synthesize various bis(fluorosulphates).



Scheme 14.



Scheme 15.



However, total yield of this process is small, and the concentration of vicinal bis(fluorosulphates) in the mixture of products reaches 88–90 %. For instance, electrolysis of  $\text{HSO}_3\text{F}$  in diaphragm-free electrolyzers in the presence higher perfluoroalkenes-2 of the isostructure leads to the major products: vicinal bis(fluorosulphates) **13**, **14**; isomeric ketofluorosulphates **15**–**17** and cyclic sulphates **18**, **19** are formed as the side products with a small yield [49] (Scheme 16).

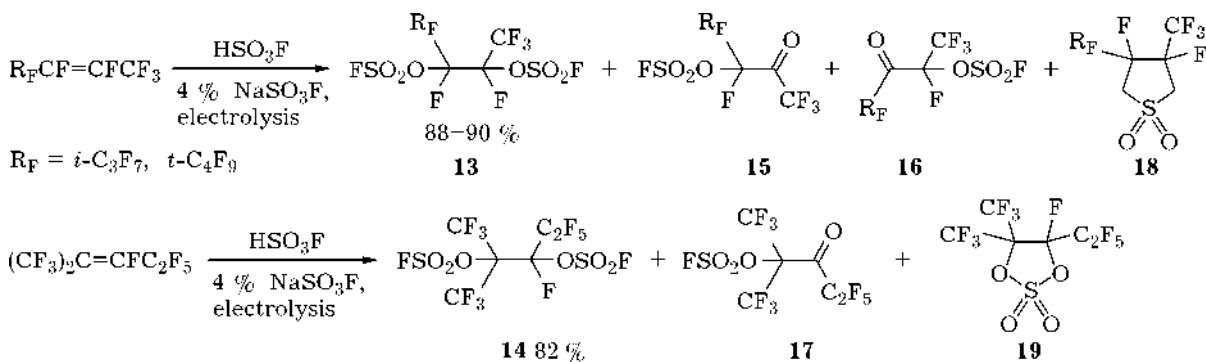
Unlike this, the linear perfluoroalkenes-2 and perfluorocyclohexene under similar conditions, along with the expected products (vicinal bisfluorosulphatoperfluoroalkanes, ketofluorosulphates and cyclic sulphates), also give substantial amounts (up to 25–40 %) of the products of fluorosulphatodimerisation [50, 51]. Conditions may be created in the  $\text{HSO}_3\text{F}$  medium under which dimerization of the formed fluorosulphatoperfluoroalkyl radicals successfully

competes with the addition of  $(\text{FSO}_3)_2$  to perfluoroolefin-2 (Scheme 17).

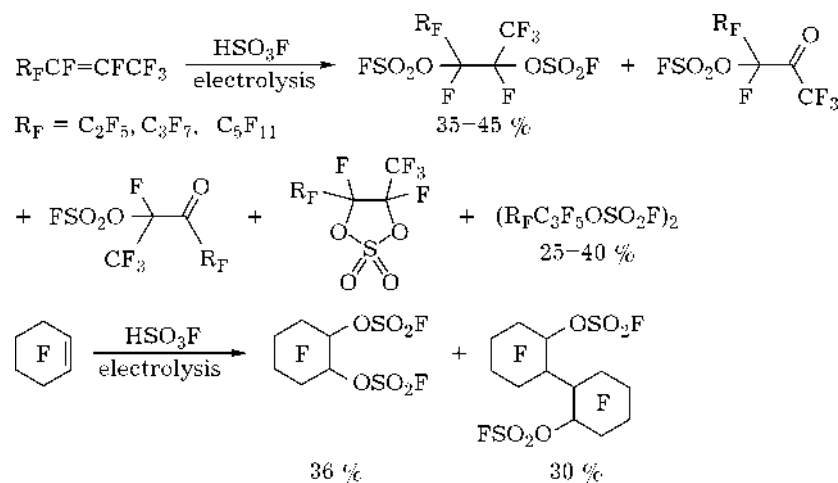
The authors of [50] think that the reason is different solubility of fluoroalkenes in  $\text{HSO}_3\text{F}$ .

Some substituted perfluoroolefins, for example **20**, **21**, also undergo fluorosulphation during electrolysis in  $\text{HSO}_3\text{F}$  forming bis(fluorosulphates) **22** and **23**, respectively (Scheme 18).

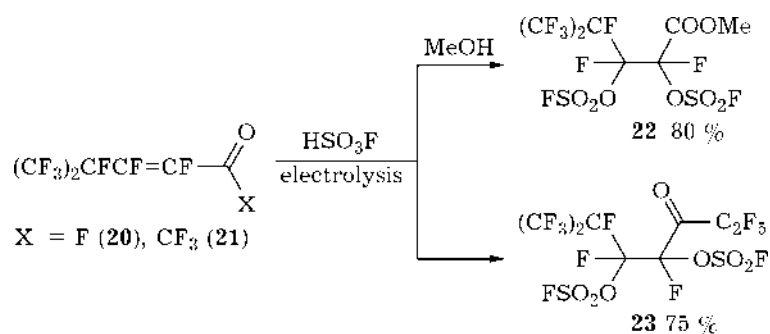
Electrolysis of perfluoroallylbenzene in  $\text{HSO}_3\text{F}$  initially leads to its isomerisation into perfluoropropylbenzene (a mixture of *cis*- and *trans*-isomers is formed); then the latter compound undergoes addition of  $\text{FSO}_2\text{O}^\cdot$  radical at the double bond forming the major reaction product -  $\alpha,\beta$ -bis(fluorosulphonyloxy)perfluoropropylbenzene **24**, and small amounts of high-boiling polyfluorosulphates **25**, **26** due to the attack of  $\text{FSO}_2\text{O}^\cdot$  radical at the carbon atom of C–F bond of the benzene ring [52] (Scheme 19).



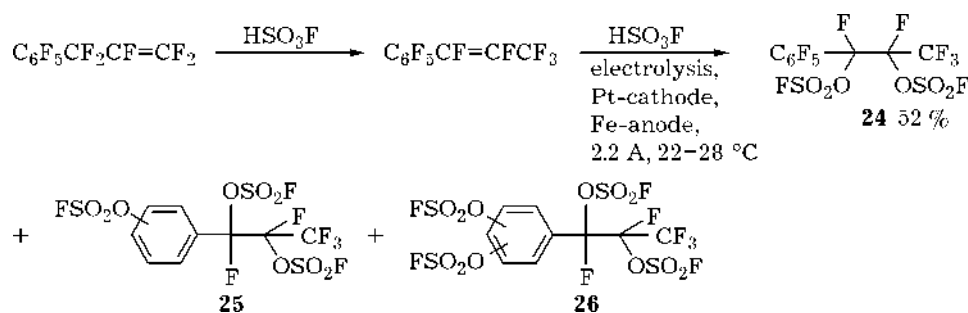
Scheme 16.



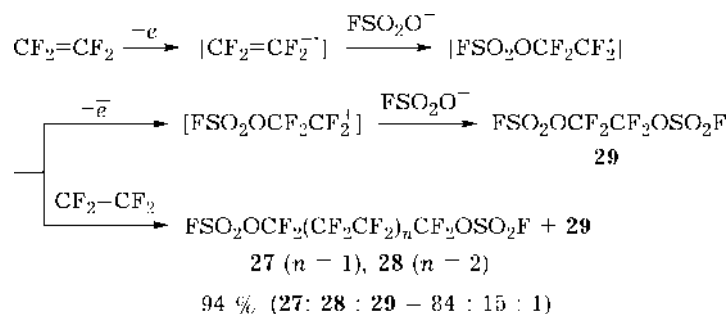
Scheme 17.



Scheme 18.



Scheme 19.



Scheme 20.

When considering the data on the electrochemical fluorosulphation of perfluoroalkenes in fluorosulphonic acid, special attention was paid to the chemical interaction of the fluorinated organic substrate with the electrochemically generated radical  $\text{FSO}_2\text{O}^\cdot$ . At the same time, the formation of fluoroalkylsulphates is also possible *via* other mechanisms, in particular as a result of anode oxidation of a fluorinated organic molecule to the cation radical, and the cathode process of the reduction of fluoroolefin to anion radical in the medium of  $\text{HSO}_3\text{F}$ . For example, the electrolysis in  $\text{HSO}_3\text{F}$  at the potential excluding the formation of  $\text{FSO}_2\text{O}^\cdot$  (1.35 V with respect to the reversible hydrogen electrode in the same solvent) in the presence of tetrafluoroethylene, the authors of [53] obtained a mixture of fluorosulphates **27-29** (Scheme 20).

It is assumed to use this (alternative) route to carry out preliminary anode oxidation of a fluoroolefin, then the interaction of the formed cation radical with  $\text{FSO}_3^-$  anion. It is evident that the realisation of one or another route of

TABLE 1

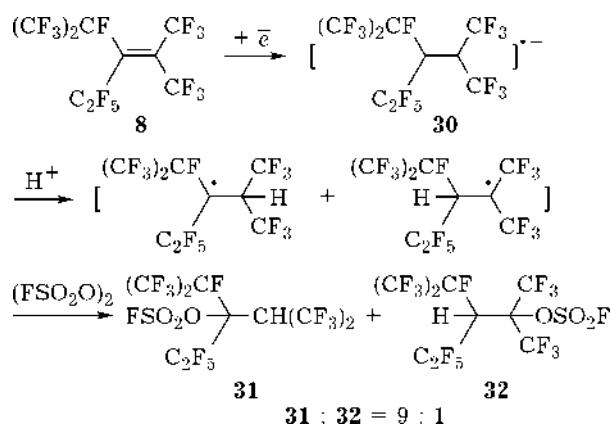
Semi-wave potentials of the oxidation of some fluoroolefins

Compound	$E_{1/2}$ , V	
	GC	Pt
$\text{CF}_2=\text{CF}_2$	1.3	1.2
$\text{CF}_3\text{CF}=\text{CF}_2$	1.9	1.8
$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}=\text{CF}_2$	1.9	1.8
$(\text{CF}_3)_2\text{CFCF}=\text{CFCF}_3$	>2.0	>2.2

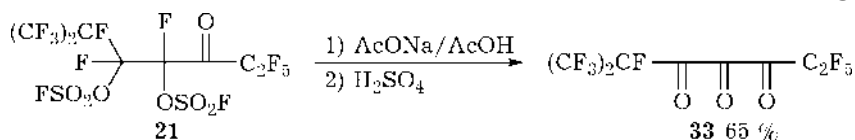
*Note.* The potentials of the start of discharge of fluorosulphate anion in  $\text{HSO}_3\text{F}/0.25 \text{ M KSO}_3\text{F}$  on smooth platinum is <2.2 V, on glass carbon <1.95 V [53].

fluoroolefin fluorosulphation by means of the electrolysis in  $\text{HSO}_3\text{F}$  will depend on the difference in the potentials of oxidation of fluorosulphate anion and the fluoroolefin. Table 1 shows the data on the half-wave potentials of the oxidation of some fluoroolefins and the potentials of the start of discharge of fluorosulphate anion in  $\text{HSO}_3\text{F}$  on smooth platinum (Pt) and glass carbon (GC) [53]. For platinum, this difference is 1.0 V.

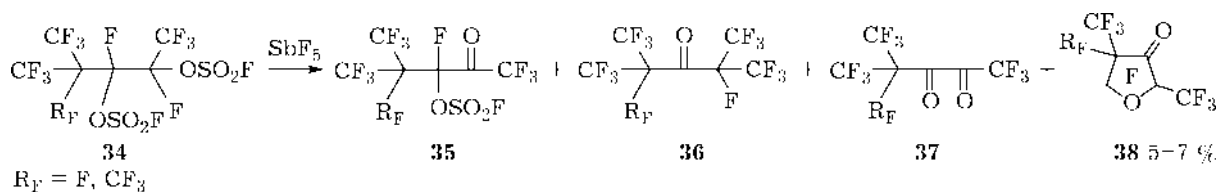
For electrochemical fluorosulphation of the olefin **8** with four voluminous fluoroalkyl groups, due to the steric hindrance for the addition of  $(\text{FSO}_2\text{O})_2$  at the double bond, olefin **8** reduces at the cathode to form anion radical **30**; its further transformations lead to the formation of hydrogen-containing fluorosulphato-perfluoroalkanes **31** and **32** [48].



$\alpha,\omega$ -Bis(fluorosulphato)perfluoroalkanes are valuable semi-products for the synthesis of perfluoroalkane carboxylic acids and their fluoroanhydrides having high practical importance [54]. For instance, they open the way to the synthesis of difficultly available perfluoroal-

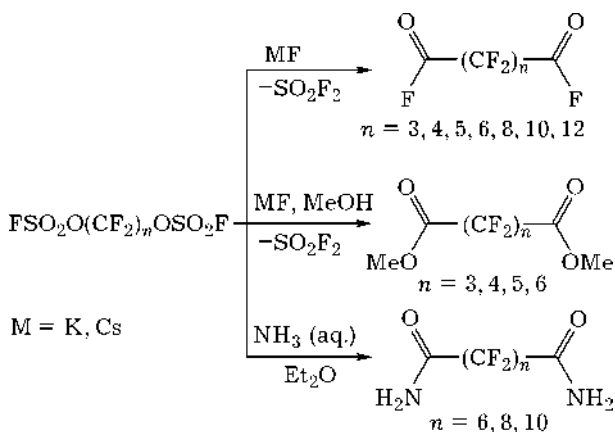


Scheme 21.



Scheme 22.

kanedicarboxylic acids and their derivatives. Decomposition of  $\alpha,\omega$ -bis(fluorosulphato)perfluoroalkanes is carried out in the presence of alkaline metal fluorides, in methanol and ammonia, which leads to the formation of the corresponding fluoroanhydrides, esters and amides of acids.



Splitting of  $\alpha,\beta$ -bis(fluorosulphatoketone) **21** in the medium of a protonating solvent (alcohol or acid), for example the system  $\text{AcONa/AcOH}$ , followed by the treatment of the formed semi-ketals with concentrated sulphuric acid, leads to the formation of perfluoroethylisopropyltriketone **33** [55] (Scheme 21).

The interaction of bis(fluorosulphates) **34** with  $\text{SbF}_5$  leads to obtaining  $\alpha$ -fluorosulphatoketones **35** as the major reaction products, while heating with  $\text{SbF}_5$  leads to the formation of  $\alpha$ -diketones **36**, **37** [51]. Oxolanone **38** is also formed as a side product with a low yield (Scheme 22).

## CONCLUSIONS

The considered information provide evidence of the increasing attention of researchers to

the development of the new methods of addition of perfluorinated fragments into the molecules of organic compounds and the transformation of simple substituents into complicated functional groupings. It should be noted that perfluoroolefins are widely used as initial substrates for many reactions leading to interesting and important semi-products. These processes have clear advantages and actual possibilities for use in industrial technologies. This allows one, first, to solve urgent industrial tasks; second, to carry out applied works on the development of technologies for the production of new promising fluorinated materials.

This review represents an attempt to demonstrate new approaches to the use of the interactions of perfluoroolefins with sulphuric anhydride and some its derivatives, in particular fluorosulphonic acid and peroxydisulphuryldifluoride (FSO<sub>2</sub>O)<sub>2</sub> as an efficient source of FSO<sub>2</sub>O radical for the development of methods to synthesize a number of perfluorinated organics containing various molecular carcasses and functional groups. Of course, the questions connected with the realisation of these ideas and approaches are of interest not only for chemists working in the area of organofluoric compounds but also for experts in the area of organic synthesis. It is necessary to stress that perfluorinated organic compounds, due to some their characteristics, are convenient and sometimes unique models for formulating and solving a number of fundamental questions of theoretical organic chemistry. This allows one to solve also the applied problems for which a substantial advance has been outlined during the recent years.

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