# Synthesis of 2,3-Epoxyperfluoroalkanes by Means of Oxidation of Fluorine-Containing Olefins

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## Abstract

A set of problems and directions of the accelerated development of methods to synthesize perfluoroalkane-2,3-epoxides by means of the oxidation of fluorine-containing olefins is considered. Attention to perfluoroalkane-2,3-epoxides is due to their promising use in obtaining fluorinated materials for a wide range of practical applications: for example, as monomers for obtaining polyfluorinated polyethers, for manufacturing fluorinated membranes for electrochemical processes. The effect of the nature of oxidizing agent, radical initiators and the structure of a perfluoroolefin on the yield of the target product and on the formation of polymerization products is investigated. The application areas are proposed.

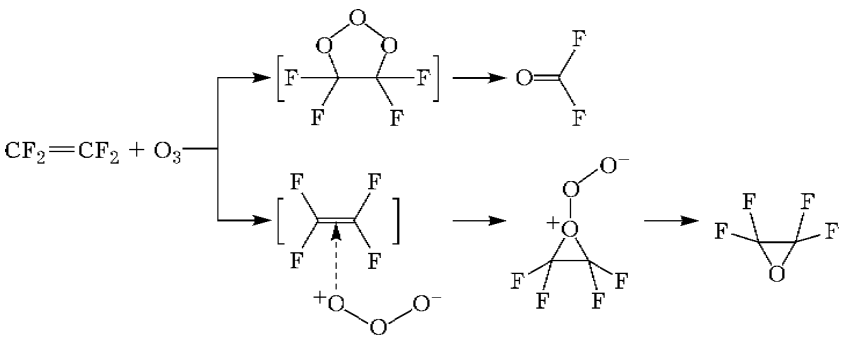
## INTRODUCTION

Onrush of the chemistry of fluorinated organic compounds is caused by increasing need for novel materials for the development of new technical equipment. The scope, level of scientific advances and the level of their industrial realization make the chemistry of fluorinated organic compounds a powerful self-consistent scientific and technical direction in organic chemistry [1, 2]. Complete substitution of hydrogen atoms with fluorine in an organic molecule causes a sharp change in the properties of compounds, which allows one to use them in many processes and to develop the fluorinated materials of the new generation with improved characteristics.

Small heterocycles attract attention due to their high reactivity and their role in biosynthesis. In addition, the simplicity of opening a three-membered cycle containing an oxygen atom provides possibilities to carry out polymerization and heterocyclization. On the one hand, these compounds act as monomers and intermediate products for the synthesis of perfluorinated ethers. The latter compounds are widely used in developing new materials for technology: compounds with high thermal stability, ability to undergo chemical vulcanization, ion exchange and catalytic activity, as well as various heterocyclic compounds [3].

The first member of the homologous series of perfluorinated α-oxides (tetrafluoroxirane) is very unstable and can be characterized only at low temperatures. Tetrafluoroxirane was synthesized by the direct oxidation of tetrafluoroethylene initiated by UV radiation, in the presence of a small amount the agent (for example, bromine) removing the radical from the reaction [4]. Decomposition of this oxide proceeds autocatalytically and often leads to isomerization giving trifluoroacetic fluoride [5]. For example, α-oxide of tetrafluoroethylene was obtained by the oxidation of tetrafluoroethylene with ozone in acetonitrile at a temperature of −75 °C or in Freon 113 at 0 °C and normal pressure [5] (Scheme 1).

Contrary to the above, the presence of perfluoroalkyl groups in the epoxide cycle stabilizes the system. Because of this, perfluoroalkane-



Scheme 1.

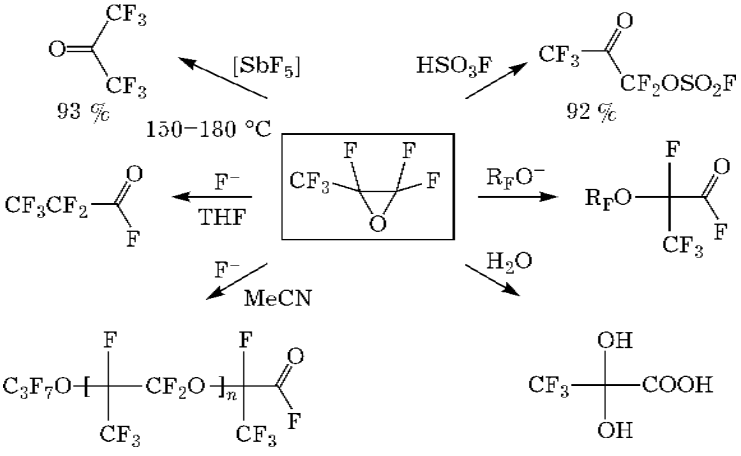
2,3-epoxides of this kind turn out to be rather stable and can be isolated in the individual form at usual temperature. Diversity of reactions involving perfluoroalkane-2,3-epoxides can be demonstrated with hexafluoropropylene oxide as an example [6] (Scheme 2).

The oxides of tetrafluoroethylene and hexafluoropropylene are important intermediate products in organofluoric synthesis; they are interesting for use as valuable monomers [1]. In the recent years, the technology of the production of hexafluoropropylene oxide has been introduced into industry. The possibility of polymerization of this monomer has defined attention to this class of compounds, which is evidenced by a large number of patent publications on perfluorinated polyehters [3]. However, this question is not considered in the review.

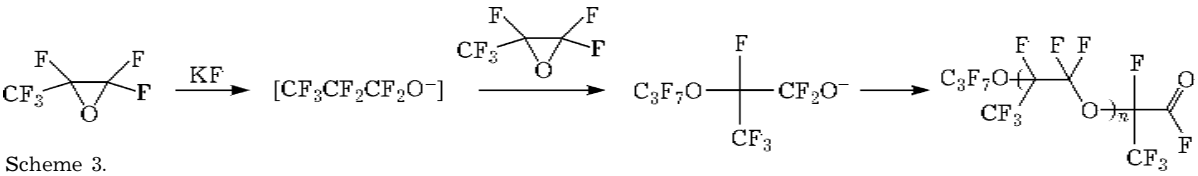
The reaction of perfluoroalkane-2,3-epoxide with fluoride ion as a nucleophilic agent leads to the generation of perfluoroalkoxy anion which interacts with the initial epoxide and forms carboxylic acid fluoride with the perfluoropolyether chain (Scheme 3).

This is a very important aspect, because this is how the end functional group C(O)F is formed; this group allows one to carry out the synthesis of fluorinated surface-active compounds and fluorinated polymers with heterocyclic fragments in the chain for various purposes [7].

Perfluoroalkane-2,3-epoxides undergo polymerization which allows one to obtain surface-



Scheme 2.



Scheme 3.

active compounds, perfluoropolyether oil, solvents, modifying agents for friction faces, lubricants with very high thermal and chemical stability, dielectric coatings, *etc*. [8]. In spite of the availability of the industrial basic compound – hexafluoropropylene oxide – the rise and development of new science-intensive and efficient technologies for the production of these materials still remains an urgent task.

One of the methods to obtain the compounds containing a three-membered cycle with oxygen atom is oxidation of perfluoroolefins [7, 9]. Various oxidizers can be used for this purpose: a complex of HOF with MeCN, oxygen, ozone, hydrogen peroxide, peroxide of *m*-chlorobenzoic acid, NaOCl in $MeCN/H_2O$ [1], though the yield of target products varies and is not always satisfactory.

#### OXIDATION OF PERFLUOROOLEFINS WITH OXYGEN

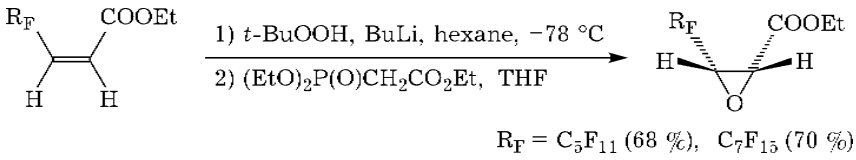
One of the industrial methods of obtaining hexafluoropropylene oxide is oxidation of hexafluoropropylene with oxygen in an inert solvent at a temperature of ~140 °C and a pressure of ~40 atm [10, 11]. However, conversion of hexafluoropropylene under these conditions reaches 70 %, while the yield of the oxide calculated for the reacted olefin does not exceed 70 %. Low conversion of hexafluoropropylene during oxidation leads to substantial losses of the target product at rectification stage because their boiling points are almost identical. In the case of the oxidation of tetrafluoroethylene with oxygen, the necessary conditions are the presence of a radical initiator and temperature within the range 135–150 °C [12], while chlorotrifluoroethylene forms epoxide at low temperature (–80 °C, 10 h) [13].

The recently spread approach is based on the oxidation of tetrafluoroethylene and hexafluoropropylene with oxygen in the presence of an initiator (the most promising initiator being elemental fluorine) in an inert solvent [14–18]. The process of obtaining hexafluoropropylene oxide is carried out at a temperature of 150 °C and a pressure of 40 atm in a reactor made of stainless steel; Freon 113 is used as a solvent. The conversion of hexafluoropropylene is 95 %; the yield of hexafluoropropylene oxide is 85 % within the time acceptable in the existing industrial technologies [19–24]. Oxidation process is initiated by elemental fluorine, which provides higher productivity of the reactor unit [25]. At the same time, the use of fluorine as an initiator of the chain process is a difficult problem because fluorine can cause a chain explosion of the reaction system hexafluoropropylene–oxygen–fluorine [26].

It should be kept in mind that the side products of the low-temperature liquid-phase oxidation of hexafluoropropylene with oxygen are either oligomers of perfluoropolyetherpolyperoxide in the structure of which the prevailing links are either ether groups $-C_3F_6O-$ or the products of transformation of hexafluoropropylene oxide, for example hexafluoroacetone, fluoroanhydrides of perfluorinated carboxylic acids ($CF_3COF$, $CF_3O(CF_2O)_nCF_2COF$) which are of practical importance.

Oxidation of the corresponding perfluoroolefins with oxygen in the presence of initiators (halogens, trifluoromethylhypofluorite, which are able to undergo homolytic dissociation at low temperatures) in an inert solvent at elevated temperature leads to the formation of perfluorinated epoxides [4]. For instance, tetrafluoroethylene in the amount of 0.1–15 vol. % in Freon 113 or in fluorochlorocarbon liquid is easily oxidized to form tetrafluoroethylene oxide [4]. Gaseous perfluoroolefin is supplied into the oxidizer flow under the layer of an inert solvent. In the case of the oxidation of hexafluoropropylene, the yield of hexafluoropropylene oxide is 77 % for the conversion of 78 %, while the yield of tetrafluoroethylene oxide is somewhat higher (87 %, with the conversion of 93 %). A similar method can be used to increase the yield of perfluoroalkane-2,3-epoxides and the degree of conversion of the initial perfluoroolefins, which allows one to develop a reliable industrial technology of these valuable products. From the technological point of view, the process is more acceptable with respect to its productivity; it is characterized by substantially lower peroxide content.

Oxidation of hexafluoropropylene in the liquid phase is carried out in the presence of a heated metal surface at a temperature not lower than 170 °C in Freon 113 solution with simultaneous heat removal from the reaction zone




$R_F = C_5F_{11}$ (68 %), $C_7F_{15}$ (70 %)

Scheme 4.

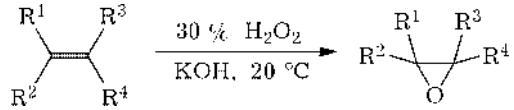
[27]. Conversion is 100 %; the yield of hexafluoropropylene oxide is 75–85 %.

Oxidation of hexafluoropropylene with molecular oxygen in the presence of catalysts, mainly fluorides of alkaline metals, leads to the formation of hexafluoropropylene oxide [28].

It should be noted that the presence of a hydrogen atoms at the multiple bond does not hinder the formation of epoxide cycle, though the yield of target products is lower [29] (Scheme 4).

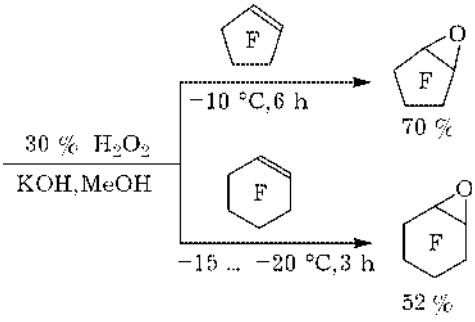
## METAL HYPOHALOGENITES AS ACTIVE EPOXIDE-FORMING REAGENTS

Direct nucleophilic epoxidation of internal perfluorinated olefins with clearly expressed electrophilic properties under the action of hydrogen peroxide in alkaline media leads to the formation of 2,3-epoxyperfluoroalkanes, but this process is characterized by the instability of results and is not always efficient [30]. For instance, oxidation of perfluoroolefins under the action of 30 % hydrogen peroxide in aqueous methanol in the presence of NaOH, $Na_2CO_3$, KOH or BaO at 20 °C leads to the formation of 2,3-epoxyperfluoroalkanes [30]:

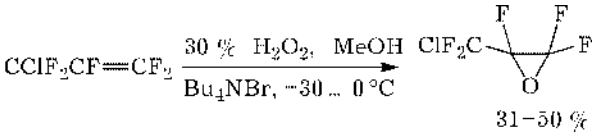



| $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|
| F | F | $C_4F_9$ | F |
| $CF_3$ | F | F | $C_2F_5$ |
| $(CF_3)_2F$ | F | F | $CF_3$ |
| $CF_3$ | F | $CF_3$ | $CF(CF_3)_2$ |
| F | F | F | $(CF_2)_4CHF_2$ |
| F | F | F | $CF(CF_3)_2$ |

Cyclic perfluoroolefins can also be epoxidated under the action of this system [31, 32]. A disadvantage of this method is low conversion, which hinders the isolation of target products because their physical properties are close to those of the initial compounds:



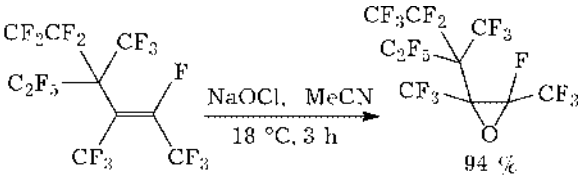

Quaternary ammonium salts (tetrabutylammonium bromide or hexadecyltrimethylammonium bromide) can be used as a base [33]:




Good synthetic possibilities of the hypohalogenite epoxidation of polyfluoroalkenes for obtaining polyfluorinated α-oxides of different structure were demonstrated [20, 34–37]. The essential effect of the structure of the initial olefin on the mechanism of its interaction with hypohalogenite ions was also stressed. It was established that the yield of α-oxides from epoxidation of internal and cyclic perfluoroolefins is close to quantitative one [34–36], while in the case of terminal perfluoroolefins the yield somewhat decreases as a result of side and secondary processes [34, 35, 37].

Nucleophilic epoxidation under the action of hypohalogenites of alkaline metals and alkaline earths proceeds successfully in organic solvents (aliphatic alcohols, ketones, acetonitrile, diglyme) and gives the corresponding 2,3-epoxyperfluoroalkanes with a high yield [20, 38–40]. For example, perfluoro-3,4-dimethyl-4-eth-

ylhexene-2 is epoxidated with aqueous NaOCl in acetonitrile forming 2,3-epoxyperfluoroalkanes in wich the configuration of substituents corresponds to the initial perfluoroolefins [42]:




At the same time, the key role is played by the structure of perfluoroalkene to be epoxidated and by the presence of substituents at the multiple bond differing from fluorine atom. The presence of chlorine or bromine atoms in a or b positions of a fluoroalkene causes a decrease in the selectivity of epoxidation [22, 23]. For example, epoxidation of 3-chloro(bromo)heptafluoro-1-butenes and 3,4-dichlorohexafluoro-1-butene in aqueous solutions of sodium hypohalogenites is accompanied by the opening of the carbon skeleton at the double bond and by the formation of sodium salts of polyfluorocarboxylic acids as side products [41]. The yield of 1,2-epoxides depends on the process temperature and reaches its maximum at 5–10 °C, while it decreases with temperature rise and the formation of the products of alkaline hydrolysis is promoted (Scheme 5).

Notice that the molecules of terminal fluoroolefin oxides are of high polarization, which is used in syntheses with their participation.

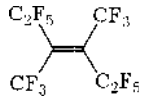
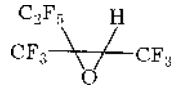
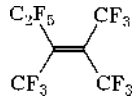
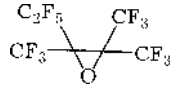
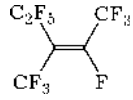
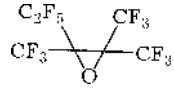
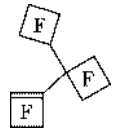
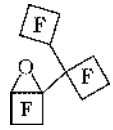
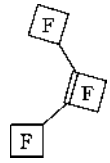
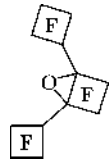
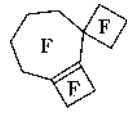
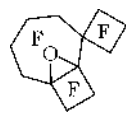
Table 1 shows some parameters of reactions leading to the synthesis of α-oxides from perfluoroolefins [9].

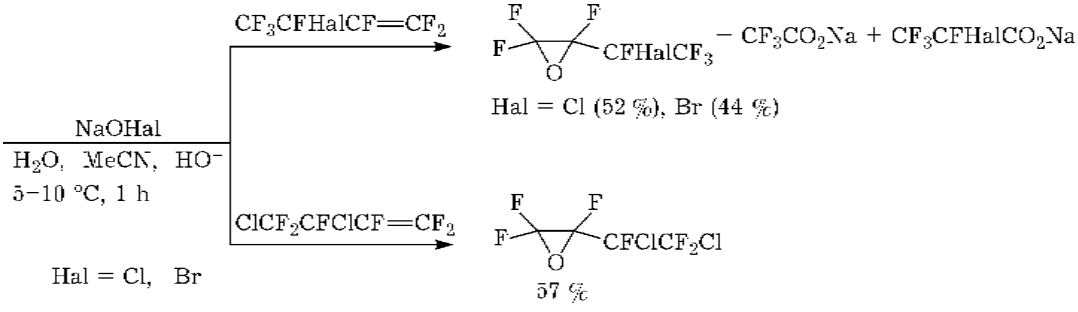
Reactions with sodium hypochlorite in alkaline medium in the presence of acetonitrile is an example of epoxidation which proceeds through nucleophilic addition by $OCl^-$ anion, followed by the substitution of chlorine under the action of intermediate carbanion [9, 43–50].

It is interesting to stress the fact that the oxidation of perfluoro-3,4-dimethylhexene-3 with sodium hypochlorite does not lead to perfluoro-3,4-dimethyl-3,4-epoxyhexane; instead,

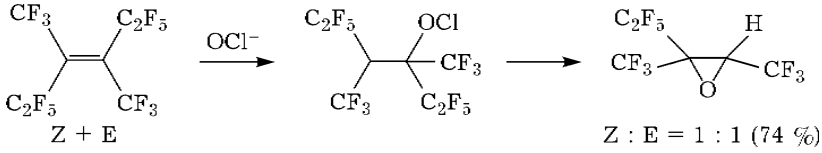
TABLE 1

Oxidation of perfluoroolefins with sodium hypochlorite (NaOCl, MeCN, 20 °C, 40 h) [9]

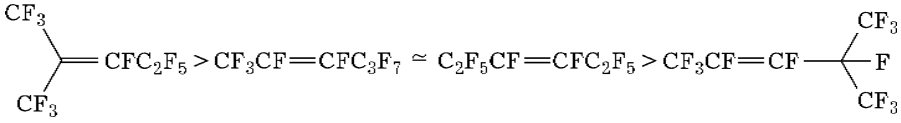
| Perfluoroolefin | Epoxide | Yield Z(E), % |
|---|---|---|
|  |  | 31 |
|  |  | 20 (80) |
|  |  | 28 |
|  |  | 62 |
|  |  | 64 |
|  |  | 28 |




Scheme 5.




Scheme 6.



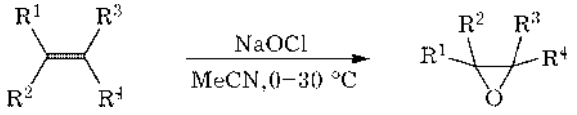

Scheme 7.

3,4-epoxyperfluoro-3-methylpentane is formed (Scheme 6).

Oligomers of tetrafluoroethylene [([$R^1$][$R^2$]C=C[$R^3$][F]): trimer $R^1 = C_2F_5$, $R^2 = R^3 = CF_3$, pentamer $R^1 = (C_2F_5)_2(CF_3)C$, $R^2 = R^3 = CF_3$ and a mixture of the isomers of hexamer $R^1 = (C_2F_5)_2(CF_3)C$, $R^2 = (C_2F_5)(CF_3)(F)C$, $R^3 = F$] – react with NaOCl in acetonitrile forming the corresponding epoxides [42]. *Trans*-perfluorohexene-3 gets epoxidated with this reagent with a rather high yield (84.5 %) giving *trans*-3,4-epoxyperfluorohexane [51].

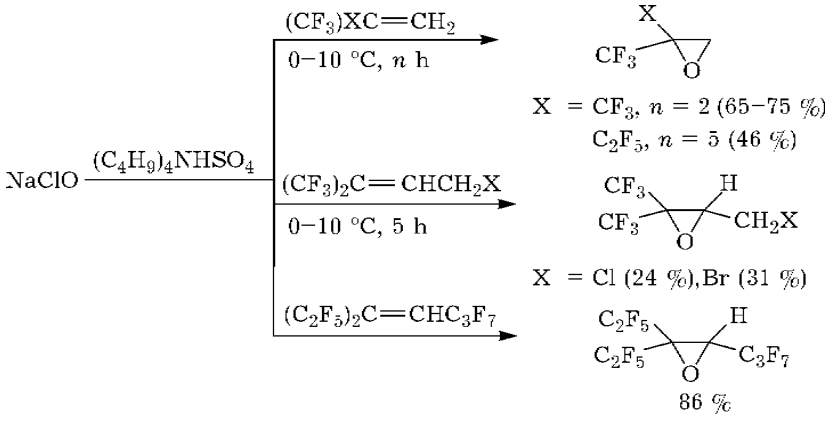
Epoxidation of *cis*- and *trans*-internal perfluoroolefins in water solutions of hypohalogenites of alkaline metals and alkaline earths in an alkaline medium is carried out in the presence of aprotic solvents [44, 48, 49, 51]. In the general case, the yield of 2,3-epoxyperfluoroalkanes varies within the range 69–94 %, depending on the structure of perfluoroolefin used [44]. Rather widely used reagents are hypochlorites $M(OX)_n$ (M = Na, K, Ba, Ca; X = Cl, Br; $n$ = 1, 2) [44].

The yields of α-oxides from epoxidation of internal and cyclic perfluoroalkenes are close to quantitative ones; in the case of terminal perfluoroalkenes the yield somewhat decreases due to side and secondary processes [20, 38, 39, 42, 51]. The oxidation of internal perfluoroolefins by the action of sodium or calcium hypochlorite in acetonitrile proceeds at 0–30 °C. The amount of perfluoroalkyl substituents at the multiple bonds affects the yield of 2,3-epoxyperfluoroalkanes. For example, an activity sequence was deduced for isomeric perfluorohexenes (Scheme 7).

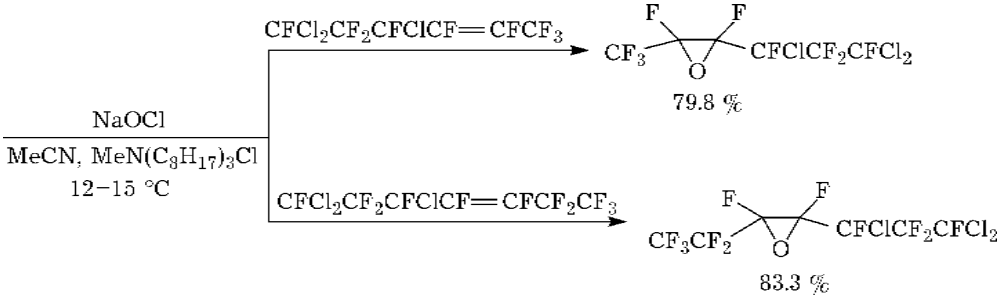



| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield, % | Reference |
|---|---|---|---|---|---|
| $CF_3$ | F | F | $CF_3$ | 90.5 | [49] |
| $C_2F_5$ | F | F | $CF_3$ | 91.5 | |
| $CF_3$ | F | $C_3F_7$ | F | 94 | |
| $C_2F_5$ | F | F | $C_2F_5$ | 91 | |
| $(CF_3)_2CF$ | F | F | $CF_3$ | 89 | |
| $C_5F_{11}$ | F | F | $CF_3$ | 95 | |
| $CF_3$ | F | $H(CF_2)_3$ | F | 92 | |
| $CF_3$ | F | F | $C_2F_5$ | | [42] |
| $CF_3$ | F | F | $C(CF_3)_3$ | | |
| $C(CF_3)(C_2F_5)_2$ | $CF_3$ | F | $CF_3$ | 94 | |
| $C(CF_3)(C_2F_5)_2$ | F | F | $C(CF_3)(C_2F_5)_2$ | | |
| $C_2F_5$ | F | F | $C_2F_5$ | 84.5 | [51] |
| $CHF_2$ | F | F | $CF_3$ | 70 | [48] |
| $CF_3$ | F | F | $CF(CF_3)_2$ | | [52] |
| $CF_3$ | F | $CF(CF_3)_2$ | $CF(CF_3)_2$ | | |
| $CF_3$ | $CF_3$ | $CF_3$ | F | | |
| $CF_3$ | $CF_3$ | F | $C_2F_5$ | | |
| $CF_3$ | $CF_3$ | $C_2F_5$ | $CF(CF_3)_2$ | | |

Partially fluorinated epoxides are obtained under the action of metal hypohalogenites on the corresponding fluoroolefins under the conditions of interphase catalysis [45], including Aliquat$^R$-336 (tricaprylyl methylammonium chloride) and $(C_4H_9)_4NHSO_4$ [46] (Scheme 8).



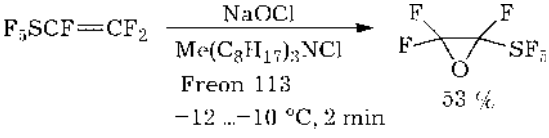

Scheme 8.



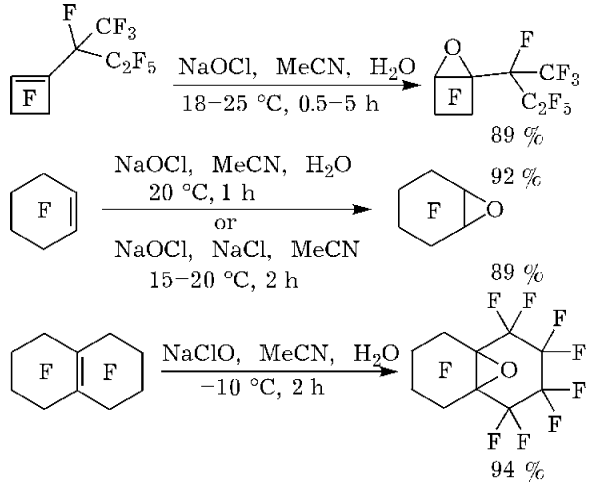

Scheme 9.

Instead of KOH, quaternary ammonium salts can be used as catalysts of interphase transport [53] (Scheme 9).

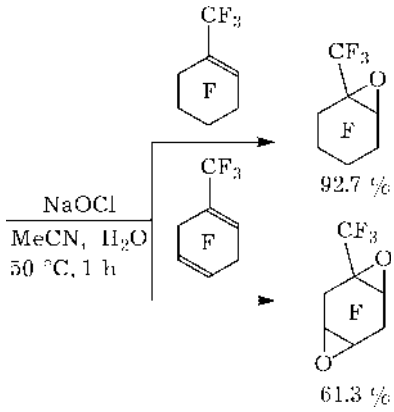
Substitution of fluorine at the double bond for the substituents of different nature, as a rule, does not prevent oxidation and the formation of α-oxide, which can be demonstrated for $SF_5$ group as an example [47]:



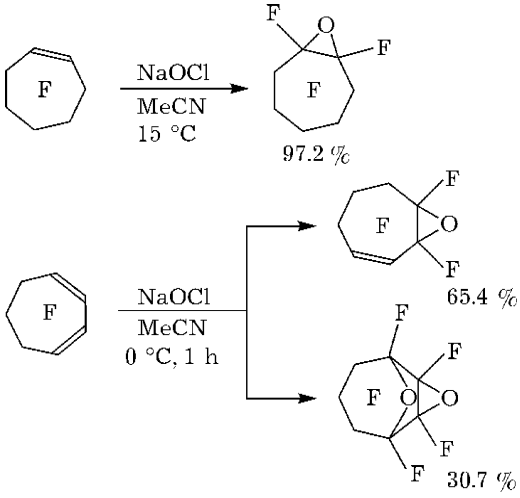

Cyclic perfluorinated olefins are oxidized by sodium hypochlorite in aqueous acetonitrile at 0–20 °C, too; they give the corresponding epoxides with a high yield [38, 54–56]. It is interesting to stress that a spatially hindered double bond(perfluorobicyclo-[4.4.0]-dec-1(6)-ene) is oxidized, too, and gives epoxide with the yield of 94 % [57]:




1-Trifluoromethylnonafluorocyclohexene-1 and 1-trifluoromethylheptafluorocyclohexa-1,4-diene under the action of sodium hypochlorite in acetonitrile form mono- and diepoxides, respectively [58]:



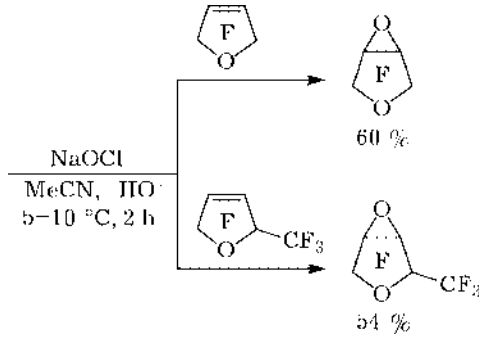

Decafluorocycloheptadiene is transformed under the action of this system into decafluoro-1,2-epoxycycloheptene-3 or into decafluoro-(1,2)(4,5)-diepoxycycloheptane [59]:




It should be noted that cyclic perfluoroolefins are epoxidated easier than non-cyclic analogs [21].

Some heterocyclic compounds are subject to epoxidation, too. For example, perfluoro-4-ethyl-2,3,4,5-tetramethyloxolene-2 under the action of the aqueous solution of NaOCl in acetonitrile is transformed into 2,3-epoxyperfluoro-4-ethyl-2,3,4,5-tetramethyloxolane [56]:


Epoxidation of oxolenes with the aqueous solution of sodium hypochlorite in acetonitrile leads to the formation of compounds containing the oxirane and oxolane cycles at the same time in the molecule [60]:




Unlike internal and cyclic perfluoroolefins for which epoxidation with sodium hypochlorite proceeds almost quantitatively, epoxidation of oxolenes leads to the formation of a mixture of products, including the salts of polyfluorohydroxycarboxylic acids (for example, $CHF_2OCF_2CFClCO_2Na$) [60].

Calcium hypochlorite ($Ca(OCl)_2$) in acetonitrile turned out to be a very efficient nucleophilic epoxidating reagent for multiple bonds in heterocycles; all the multiple bonds containing fluoroalkyl substituents are involved in the process, while benzene ring is left intact [64] (Scheme 10).

The action of calcium hypochlorite on perfluoro-3,4-dimethylhexa-2,4-diene leads to the formation of diepoxide [62] which rearranges into the corresponding derivative of 1,4-dioxa- neat 200 °C [63] (Scheme 11).

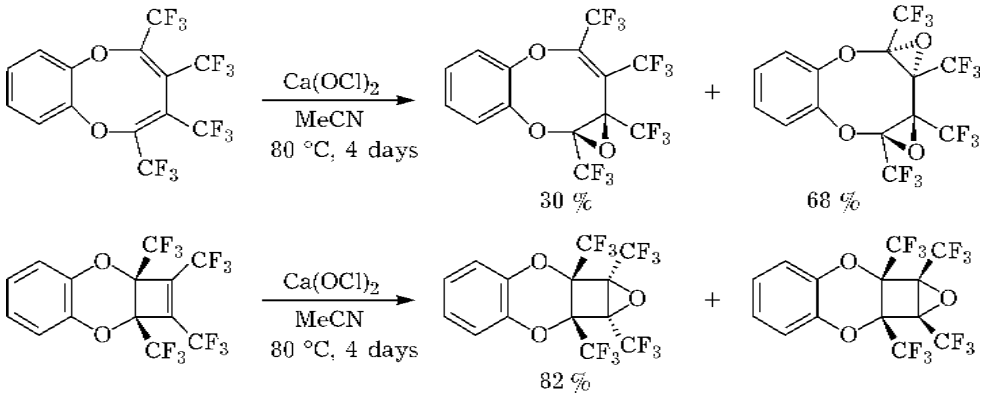
However, no formation of derivative heterocyclic compound occurs during heating the diepoxide up to 350 °C for 48 h [61] (Scheme 12).

Similar properties are exhibited by lithium *tert*-butylhydroperoxide, which was used for epoxidation of electron-unsaturated olefins [64, 65] (Scheme 13).

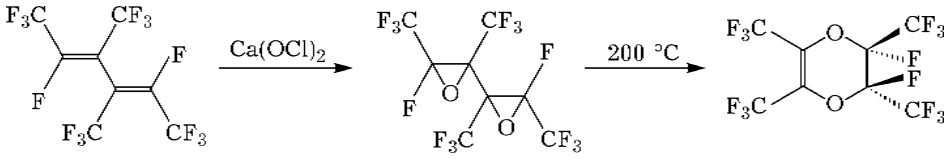
The application of this approach to the systems containing fluorine atoms enriches widely our knowledge of the properties of olefin system. The role of the reagent itself is important too. For instance, for some cases calcium hypochlorite is ineffective for epoxidation of fluorine-containing olefins, unlike lithium *tert*-butoxide [63, 66].

## EPOXIDATION WITH OTHER OXIDIZERS

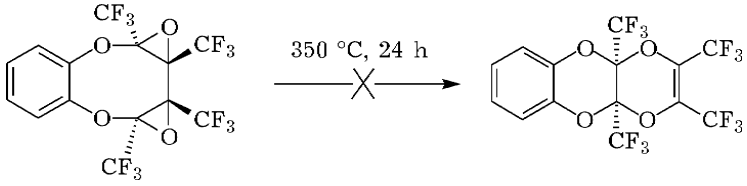
Alkaline epoxidation of perfluorolefins has been most widely accepted in the practice of



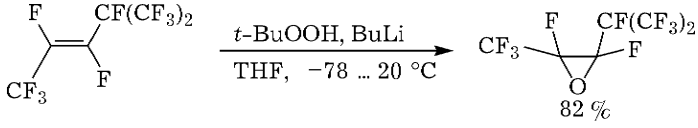

Scheme 10.




Scheme 11.




Scheme 12.

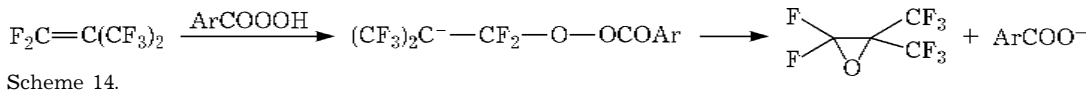



Scheme 13.

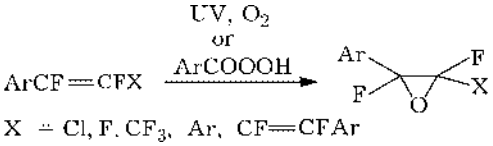
organic synthesis [67–69]. It should be noted that aromatic peracids also turn out to be efficient reagents; in this case a peracid acts as a nucleophilic reagent. For instance, octafluoroisobutylene forms epoxide under the action of aromatic peracids [70] (Scheme 14).

Oxidation of fluorine-containing stilbenes with oxygen under UV irradiation in the presence of chlorine or perbenzoic acid leads to the formation of the products of epoxidation (Scheme 15).

Photooxidation of hexafluoropropylene in the condensed phase at a temperature of −60 °C gives oligomers like $-O(CF(CF_3)CF_2O)_n-(CF(CF_3)CF_2OO)_m-$ with the yield above 90 %, while the yield of the products of decomposition ($COF_2$ and $CF_3COF$) is substantially lower. The links in an oligomer are connected with




Scheme 14.



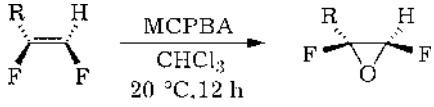

Scheme 15.

each other in a head-to-tail manner; mean polymerization degree ($n + M$) is 30–40. Tetrafluoroethylene is oxidized with oxygen of the air in an inert solvent like difluorodichloromethane with the formation of the polymeric product – perfluoropolyethylene oxides with the mean molecular mass $10^4$–$10^5$ having the structure $-(CF_2CF_2O)_a-(CF_2O)_b-(CF_2CF_2OO)_c-(CF_2OO)_d-$. It should be noted that with an increase in temperature to the room one the concentration of peroxides decreases.

Liquid-phase oxidation of perfluoroolefins and polyfluorinated dienes is performed with oxygen of the air using irradiation with UV light. However, as a rule, a mixture of products is formed in this process. For instance, oxidation of perfluorohexa-1,5-diene leads to the formation of both the target product and other epoxides [16]. The effect of process duration on the conversion of the initial substrate and on the ratio of mono- to diepoxides is clearly seen: at 25 °C, for 32 h the conversion is 100 %, no monoepoxide is formed, while the diepoxide content is equal to 64.6 % (Scheme 16).

However, this method has some substantial disadvantages, including low process productivity, complicated technological arrangement, low efficiency of the sources of UV radiation, which limits the development of industrial technology of hexafluoropropylene oxide and polymeric materials based on this compound.

For perfluoroolefins with less clearly exhibited electrophilic properties, for example for a series of difluoroethylene derivatives, epoxidaiton process proceeds rather smoothly under the action of *m*-$ClC_6H_4CO_3H$ [71], while for the trimer of hexafluoropropylene $[(CF_3)_2CF]_2C=CFCF_3$ no oxidation occurs under the action of 30 % $H_2O_2$ (25 °C, 1–3 days), aqueous $CF_3CO_3H$ (25 °C, 1–3 days), 1 equivalent of *m*-$ClC_6H_4CO_3H$ (MCPBA) in MeCN (25 °C, 5 days) and pyridine-N-oxide in MeCN ((25 °C, 2 h) [72]:

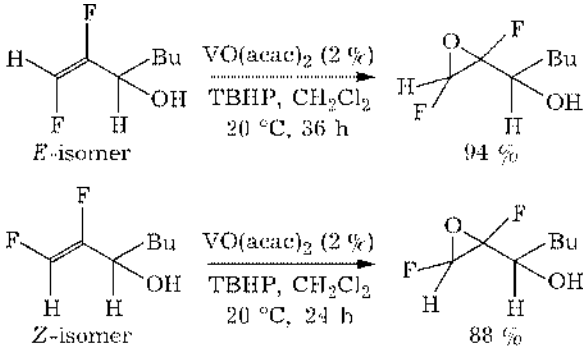


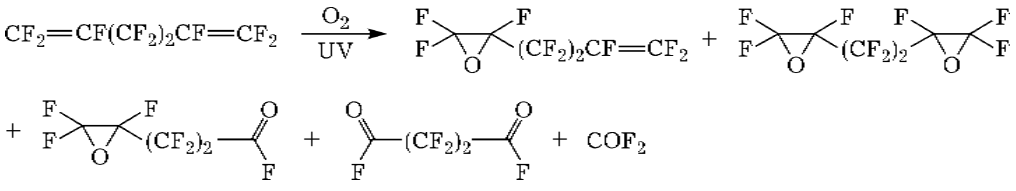

R = 1-adamantyl 81 %
Cyclohexyl 72 %
*tert*-butyl 55 %

At the same time, N-oxide of trimethylamine turned out to be a very efficient epoxidating reagent for processes performed in dimethylformamide (Table 2).

The authors of [72] showed the efficiency of epoxidation of perfluoroolefins under the action of trimethylamine-N-oxide and iodozobenzene. The data on epoxidation of perfluoro-2-methyl-3-isopropylpentene-3 with various reagents are shown in Table 2. The action of trimethylamine-N-oxide on various perfluoroolefins is shown in Table 3.

α,β-Difluoroallyl alcohols (Z and E isomers) are epoxidated under the action of vanadyl acetylacetonate $VO(acac)_2$ in the presence of *tert*-butylhypoperoxide (TBHP) with diastereoselectivity for the Z isomer (the yield being 83 %) [73, 74]. Hypoperoxides are used when

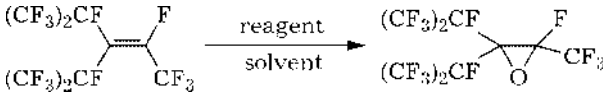



Scheme 16.

TABLE 2

Epoxidation of perfluoro-4-methyl-3-isopropylpent-2-ene with various reagents [72]




| Reagent | Amount, equiv. | Solvent | $T$, °C | Time | Yield, % |
|---|---|---|---|---|---|
| $(CH_3)_3N{-}O$ | 1 | DMF | 25 | 30 min | 100 |
| | 1 | $H_2O$ | 60 | 3 days | 89 |
| | 2 | $H_2O$ | 20 | 8 days | 1 |
| N-methylmorpholine-N-oxide | 2 | $H_2O$ | 60 | 7 days | 44 |
| | 2 | $H_2O$ | 110 | 16 h | 22 |
| | 1.5 | MeCN | 20 | 2 h | No reaction |
| $PhPO_3$ | 1.5 | DMF | 20 | 1 days | « « |
| PhIO | 1.5 | DMF | 25 | 1 h | 100 |
| NaOCl | 1.5 | MeCN | 25 | 15 h | 100 |
| Urea–$H_2O_2$ in the presence of $M_3N$ | 0.1 | DMF | 25 | 3 h | 81 |

TABLE 3

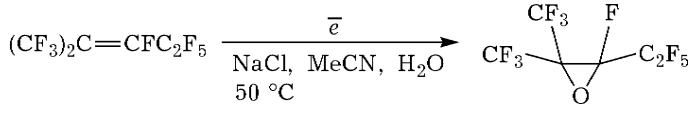
Epoxidation of some perfluoroolefins with equimolar amount of trimethylamine-N-oxide [72]

| Perfluoroolefin | Solvent | $T$, °C | Time | Yield, % |
|---|---|---|---|---|
| (*E*)-$(CF_3)_2CFCF{=}CF(CF_3)C_3F_7$ | DMF | 20 | 2 h | 63 |
| | $H_2O$ | 60 | 3 days | – |
| $(CF_3)_2C{=}C(C_2F_5)CF(CF_3)_2$ | DMF | 20 | 1 h | 97 |
| | $H_2O$ | 60 | 3 days | – |
| $(CF_3)_2C{=}CFC_2F_5$ | DMF | 20 | – | – |
| | DMF | −30 | 1 h | 98 |
| (*E*)-$(CF_3)_2CFCF{=}CFCF_3$ | DMF | −30 | 2 h | – |

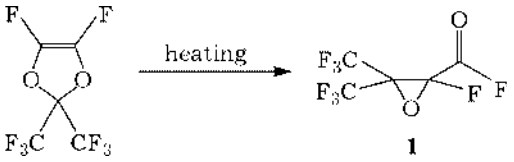
epoxidation is carried out with $VO(acac)_2$ and $Ti(OPr^i)_4$ [75].

Oxidation of perfluoroolefins can also be carried out electrochemically. Electrolysis of perfluoro-2-methylpentene-2 in NaCl–MeCN–$H_2O$ electrolyte in a glass diaphragm-free electrolytic cell with a platinum anode (current intensity 4 A, current density 2 kA/m$^2$) and nickel cathode at 50 °C results in the formation of perfluoro-2-methylpentene-2 oxide of the purity of 99 %, with the yield as a function of current 22.2 %, substance yield 93 % (4 A/h passed) (Scheme 17).

Another method is based on thermal rearrangement of fluorinated 1,3-dioxols. For example, thermolysis of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxol gives the corresponding epoxide I [76] (Scheme 18).

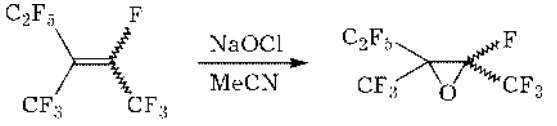



Scheme 17.




Scheme 18.

Internal perfluoroolefins are able to exist in different geometric isomerism, so they can undergo isomerization at the double bond under the effect of bases. Because of this, the stereochemical aspect of epoxidation is important, since the effect of the spatial positions of substituents at the double bond serves as a criterion of the mechanism of its oxidation. It was established previously [44] that the interaction of *trans*-perfluoroalkenes with hypohalogenite ions proceeds with the conservation of the configuration and with predominant formation of the *trans*-isomers of the corresponding 2,3-epoxyperfluoroalkanes. This conclusion was confirmed also with other objects, in particular with epoxidation of a series of the oligomers of tetrafluoroethylene and hexafluoropropylene [20, 42, 62]. However, in some cases a deviation from this rule is observed. For instance, for the oxidation of a mixture of *cis*- and *trans*-isomers of perfluoro-3-methylpentene-2 with the help of NaOCl, according to the data obtained by the authors of [42] and [9], the ratio of geometric isomers does not correspond to that in the initial olefin:




Z : E = 10 : 90
Z : E = 20 : 80

Z : E = 35 : 65 [36]
Z : E = 27 : 73 [9]

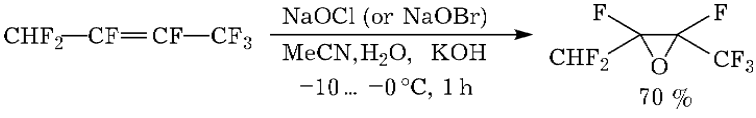
It should be stressed that the basic investigations in this area were carried out for the oxidizers like hypohalogenite ions. It was shown in [48] that both geometric isomers of partially fluorinated butene are epoxidated with the conservation of configuration. Thus, epoxidation of a mixture of the isomers of Z and E configuration of 1-hydroheptafluorobutene-2 with aqueous NaOCl in the presence of acetonitrile leads to the formation of a mixture of isomers of 1-hydro-2,3-epoxyheptafluorobutane with the isomer ratio Z : E = 54 : 46, that is, with the conservation of configuration (Scheme 19).

The effect of the structure of a perfluoroolefin on the final product of its reaction with the aqueous solution of sodium hypochlorite was demonstrated with many examples. Due to the insignificant difference in the induction constants of perfluoroalkyl groups in internal perfluoroolefins, no noticeable shift of the electron density of the double bond occurs; hypochlorite ion starts to form bonds with two carbon atoms of the double bond simultaneously. It is likely that the formation of the transition state similar to a cyclic σ-complex takes place (Scheme 20).

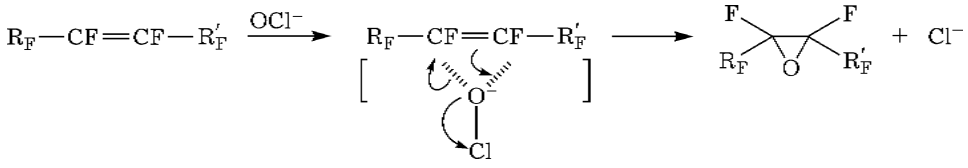
The observed stereospecificity of the epoxidation of perfluoroolefins with sodium hypochlorite and its high selectivity toward the formation of epoxides agree with such a transition state.

## CONCLUSIONS

Analysis of the reviewed data on the methods of synthesis of perfluoroalkane-2,3-ep-




Scheme 19.




Scheme 20.

oxides shows that researchers pay attention to this class of compounds because they are intermediate products for obtaining new fluorinated materials. An important practical feature of these reactions is the use of perfluoroolefins produced on an industrial scale. High reactivity of this class of compounds and their availability allow one to develop fluorinated materials with new properties on the basis of perfluoroalkane-2,3-epoxides. Prerequisites and application of fluorinated materials on this basis determine advances in technology.

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