Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE-CONTAINING POLYMERS, PERFLUOROEPOXIDES

Perfluoroepoxides were first prepared in the late 1950s by Du Pont Co. Subsequent work on these compounds has taken place throughout the world and is the subject of a number of reviews (1–5). The main use of these epoxides is as intermediates in the preparation of other fluorinated monomers. Although the polymerization of the epoxides has been described (6–12), the resulting homopolymers and their derivatives are not significant commercial products. Almost all the work on perfluoroepoxides has been with three compounds: tetrafluoroethylene oxide (TFEO), hexafluoropropylene oxide (HFPO), and perfluoroisobutylene oxide (PIBO). Most of this work has dealt with HFPO, the most versatile and by far the most valuable of this class of materials (4).

1. Physical Properties

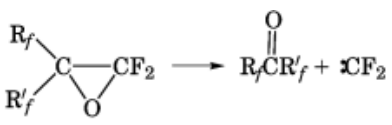
In general, the perfluoroepoxides have boiling points that are quite similar to those of the corresponding fluoroalkenes. They can be distinguished easily from the olefins by ir spectroscopy, specifically by the lack of olefinic absorption and the presence of a characteristic band between 1440 and 1550 cm^{-1}. The nmr spectra of most of the epoxides have been recorded. Little physical property data concerning these compounds have been published (Table 1). The structure of HFPO by electron diffraction (13) as well as its solubility and heats of solution in some organic solvents have been measured (14, 15).

2. Chemical Properties

There are three general reactions of perfluoroepoxides: pyrolyses (thermal reactions), electrophilic reactions, and by far the most important, reactions with nucleophiles and bases.

2.1. Thermal Reactions

Those perfluoroepoxides that contain a CF_2 group in the epoxide ring undergo a smooth decomposition at relatively mild, neutral conditions (140–220°C) to give a perfluorocarbonyl compound and difluorocarbene (16, 17) (eq. **1**).



(1)

where R_f = perfluoroalkyl; R'_f = perfluoroalkyl or fluorine

where R_f = perfluoroalkyl; R'_f = perfluoroalkyl or fluorine. The difluorocarbene produced in this way may react with a variety of compounds (18). Epoxides of internal olefins which do not contain a CF_2 group have much greater stability (19).

Table 1. Physical Properties of Perfluorocarbon Epoxides

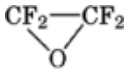
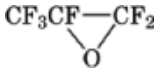
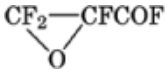
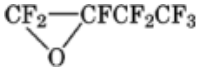
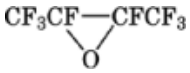
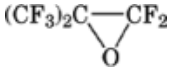
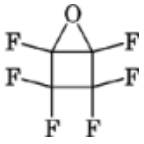
Material	CAS Registry Number	Molecular structure	Bp,[a] °C	Infrared absorption, μm	Reference
tetrafluoroethylene oxide	[694-117-7]		−63.5[b]	6.21	(67, 68)
hexafluoropropylene oxide	[428-59-1]		−27.4	6.43	69
trifluoroglycidyl fluoride	[24419-82-7]		16[c] (extrap.)	6.61 5.35 (COF)	70
perfluoro-1,2-epoxybutane	[3709-90-8]			6.48	21
perfluoro-2,3-epoxybutane	[773-29-5]		0–1	6.63	32
perfluoroisobutylene oxide	[707-13-1]		3[d]	6.66	69
perfluoro-1,2-epoxycyclobutane	[13324-28-2]			6.3	16

Table 1. ***Continued***

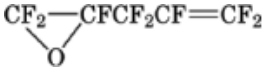
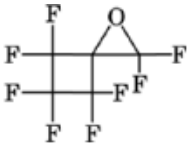
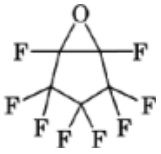
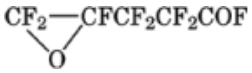
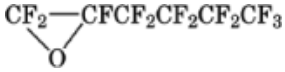
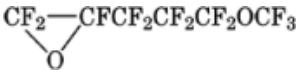
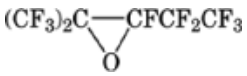
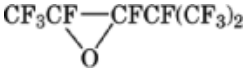
Material	CAS Registry Number	Molecular structure	Bp,[a] °C	Infrared absorption, μm	Reference
perfluoro-4,5-epoxy-1-pentene	[15453-08-4]		37	6.45 5.65 (C=C)	72
perfluoro-1-oxaspiro[2,3]hexane	[53389-66-5]		18–21	6.55	73
perfluoro-1,2-epoxycyclopentane	[710-70-3]		26.5	6.55	61
perfluoro-4,5-epoxyvaleryl fluoride	[140173-04-2]		37–38	6.49	71
perfluoro-1,2-epoxyhexane	[72804-48-9]		55–56	6.45	32
perfluoro-1,2-epoxy-6-oxaheptane[e]	[71877-16-2]		61–62	6.49	74
perfluoro-2-methyl-2,3-epoxypentane	[788-67-0]		57	6.85	69
perfluoro-2,3-epoxy-4-methylpentane	[788-50-1]		53	6.61	69

Table 1. ***Continued***

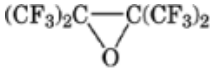
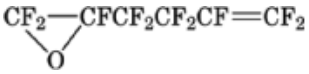
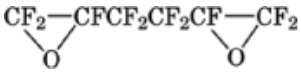
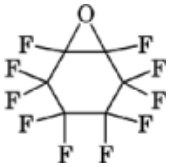
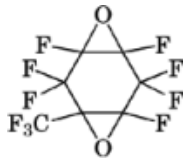
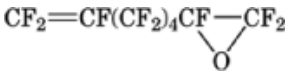
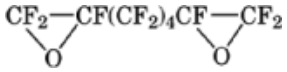
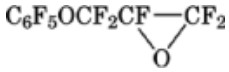
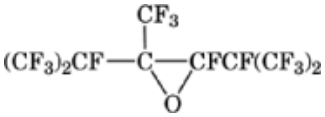
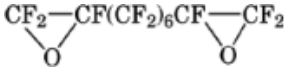
Material	CAS Registry Number	Molecular structure	Bp,[a] °C	Infrared absorption, μm	Reference
2,3-bis(trifluoromethyl)perfluoro-2,3-epoxybutane	[1708-78-7]		53–54		75
perfluoro-5,6-epoxy-1-hexene	[15453-10-8]		57–58	6.45 5.59 (C=C)	71
perfluoro-1,2:5,6-diepoxyhexane	[140173-03-1]		57–58	6.49	71
perfluoro-1,2-epoxy-5-methyl-4-oxahexane	[84424-45-3]		58.5–59	6.47	78
perfluoro-1,2-epoxycyclohexane	[5927-67-3]		54	6.71	79
perfluoro-1-methyl-1,2:4,5-diepoxycyclohexane	[130482-35-8]		77	6.69 6.92	80
perfluoro-7,8-epoxy-1-octene	[72264-78-9]		105		76

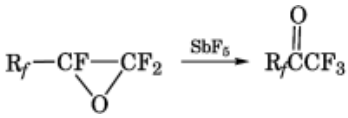
Table 1. ***Continued***

Material	CAS Registry Number	Molecular structure	Bp,[a] °C	Infrared absorption, μm	Reference
perfluoro-1,2:7,8-diepoxyoctane[f]	[13714-88-0]		104	6.45	(76, 77)
perfluorophenylglycidyl ether	[84329-68-0]		61–64 (4 kPa)[g]	6.47	78
perfluoro-3,4-epoxy-2,3,5-trimethylhexane	[2355-27-3]		36–39 (0.13 kPa)[g]	7.21	69
perfluoro-1,2:9,10-diepoxydecane[h]	[13714-90-4]		88 (5.3 kPa)[g]		76

[a] At 101.3 kPa = 1 atm unless otherwise noted in parentheses.
[b] Mp, −118°C.
[c] Heat of vaporization = 28.9 kJ/mol (6.9 kcal/mol).
[d] Mp, 122°C.
[e] n_D^{20} 1.2560; d_4^{20} 1.6441.
[f] n_D^{20} 1.2900; d_4^{20} 1.7220.
[g] To convert kPa to mm Hg, multiply by 7.5.
[h] n_D^{20} 1.3030; d_4^{20} 1.8260.

2.2. Electrophilic Reactions

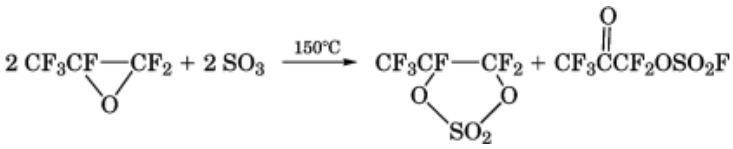
Perfluoroepoxides are quite resistant to electrophilic attack. However, they react readily with Lewis acids, for example SbF_5, to give ring-opened carbonyl compounds (20–22) (eq. **2**).



(2)

The structure of the ketones produced from unsymmetrical internal perfluoroepoxides has been reported (5). The epoxide ring may also be opened by strong protic acids such as fluorosulfonic acid or hydrogen fluoride

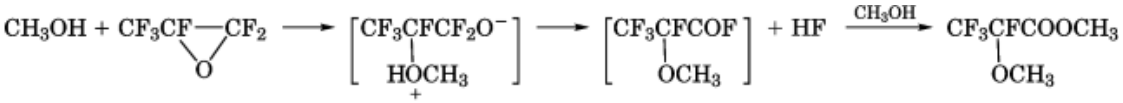
at elevated temperatures (23–25). The ring opening of HFPO by sulfur trioxide at 150°C has been interpreted as an example of an electrophilic reaction (26) (eq. **3**).



(3)

2.3. Nucleophilic Reactions

The strong electronegativity of fluorine results in the facile reaction of perfluoroepoxides with nucleophiles. These reactions comprise the majority of the reported reactions of this class of compounds. Nucleophilic attack on the epoxide ring takes place at the more highly substituted carbon atom to give ring-opened products. Fluorinated alkoxides are intermediates in these reactions and are in equilibrium with fluoride ion and a perfluorocarbonyl compound. The process is illustrated by the reaction of methanol and HFPO to form methyl 2,3,3,3-tetrafluoro-2-methoxypropanoate (eq. **4**).



(4)

TFEO is by far the most reactive epoxide of the series. However, all the reported perfluoroepoxides undergo similar ring-opening reactions. The most important reactions of these epoxides are those with the fluoride ion or perfluoroalkoxides. The reaction of PIBO and the fluoride ion is an example (27). It also illustrates the general scheme of oligomerization of perfluoroepoxides (eq **5**).

(5)

The direction of nucleophilic ring opening of unsymmetrical perfluoroepoxides has been shown to be a function of the nature of the nucleophile and the solvent (23, 28). Although many oligomeric products have been prepared by this procedure and variations of it, no truly high polymers have been obtained (9).

3. Preparation

A large number of methods have been used to prepare perfluoroepoxides (5). All of these methods must contend with the great chemical reactivity of the epoxide product, especially with subsequent ionic and thermal reactions which result in the loss of the desired epoxide.

The reaction of perfluoroalkenes with alkaline hydrogen peroxide is a good general method for the preparation of the corresponding epoxides with the exception of the most reactive of the series, TFEO (eq. **6**).

$$R_fCF{=}CF_2 + H_2O_2 \xrightarrow[\text{solvent}]{OH^-} R_fCF\text{—}CF_2 + H_2O \qquad (6)$$

The alkene is allowed to react at low temperatures with a mixture of aqueous hydrogen peroxide, base, and a co-solvent to give a low conversion of the alkene (29). These conditions permit reaction of the water-insoluble alkene and minimize the subsequent ionic reactions of the epoxide product. Phase-transfer techniques have been employed (30). A variation of this scheme using a peroxycarbimic acid has been reported (31).

Reaction of perfluoroalkenes and hypochlorites has been shown to be a general synthesis of perfluoroepoxides (32) (eq. **7**). This appears to be the method of choice for the preparation of epoxides from internal fluoroalkenes (38). Excellent yields of HFPO from hexafluoropropylene and sodium hypochlorite using phase-transfer conditions are claimed (34).

$$R_fCF{=}CFR_f + {}^-OCl \longrightarrow R_fCF\text{—}CFR_f + Cl^- \qquad (7)$$

The direct oxidation of fluoroalkenes is also an excellent general synthesis procedure for the preparation of perfluoroepoxides (eq. **8**). This method exploits the low reactivity of the epoxide products to both organic and inorganic free radicals.

$$R_fCF{=}CF_2 + {}^1\!/_2\, O_2 \longrightarrow R_fCF\text{—}CF_2 \qquad (8)$$

The oxidation may be carried out with an inert solvent thermally (35), with a sensitizer such as bromine (36), with uv radiation (37), or over a suitable catalyst (38). Principal by-products of all these oxidation processes are the acyl fluoride products derived from oxidative cleavage of the perfluoroalkene (eq. 9).

$$R_f\,CF{=}CF_2 + O_2 \longrightarrow R_f\,COF + COF_2 \qquad (9)$$

Perfluoroepoxides have also been prepared by anodic oxidation of fluoroalkenes (39), the low temperature oxidation of fluoroalkenes with potassium permanganate (40), by addition of difluorocarbene to perfluoroacetyl fluoride (41) or hexafluoroacetone (42), epoxidation of fluoroalkenes with oxygen difluoride (43) or peracids (44), the photolysis of substituted 1,3-dioxolan-4-ones (45), and the thermal rearrangement of perfluorodioxoles (46).

3.1. Tetrafluoroethylene Oxide

TFEO has only been prepared by a process employing oxygen or ozone because of its extreme reactivity with ionic reagents. This reactivity may best be illustrated by its low temperature reaction with the weak nucleophile, dimethyl ether, to give either of two products (47) (eq. **10**).

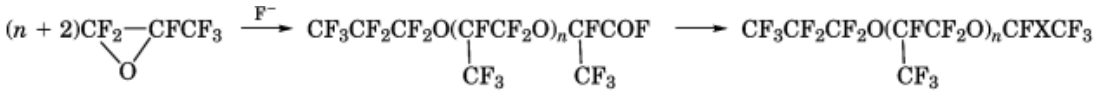
$$CH_3OCF_2CF_2OCH_3 \xleftarrow{-20^\circ C} CH_3OCH_3 + F_2C\text{—}CF_2 \xrightarrow{+25^\circ C} CH_3OCF_2COF + CH_3F \qquad (10)$$

Reaction of TFEO with acid fluorides and the fluoride ion yields oligomers with the structure $R_fCF_2O(CF_2CF_2O)_nCF_2COF$ (47, 48). The epoxide yields a waxy solid polymer when exposed to high energy radiation (47, 49) or when treated with amines at low temperature (47, 50). The extreme chemical reactivity

and facile rearrangement to perfluoroacetyl fluoride have been deterrents to the large-scale development of TFEO. The structure of TFEO has been measured using microwave spectroscopy (51).

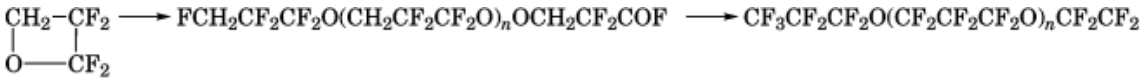
3.2. Hexafluoropropylene Oxide

HFPO is the most important of the perfluoroepoxides and has been synthesized by almost all of the methods noted. Many attempts have been made to polymerize HFPO (6, 8). The most successful has been the reaction of HFPO with fluoride ion at low temperature to give a series of oligomeric acid fluorides which have been end capped to yield stable fluids (eq. **11**, where X = H, F).



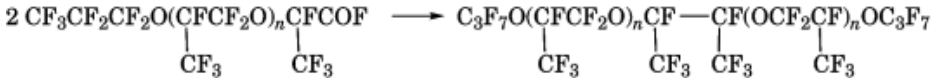
(11)

Materials of this type have been sold by Du Pont Co. under the Freon E and Krytox trademarks. Perfluorinated materials structurally similar to those in equation **11** have been prepared by Ausimont by the low temperature irradiation of either hexafluoropropylene or tetrafluoroethylene with oxygen followed by heating and/or irradiation and have been sold as Fomblin liquids (52). An isomeric polyether, Demnum,prepared by the oligomerization of 2,2,3,3-tetrafluorooxetane followed by fluorination has been commercialized by Daikin (eq. **12**).



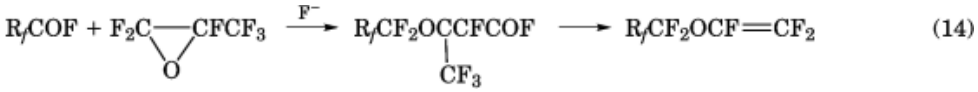
(12)

Higher molecular weight HFPO-based materials have been prepared by reaction with both ends of a perfluorodiacyl fluoride followed by coupling through triazine rings (9). Lower molecular weight HFPO oligomers have been coupled to give inert perfluorinated ethers which are sold as Hostinert liquids by Hoechst-Celanese (eq. **13**).



(13)

HFPO reacts with a large number of acyl fluorides in a general reaction to give 2-alkoxytetrafluoropropionyl fluorides which in turn may be converted to trifluorovinyl ethers (eq. **14**).



(14)

These ethers readily copolymerize with tetrafluoroethylene and other fluoroalkenes to commercially significant plastics, elastomers, and ion-exchange resins such as Teflon PFA, Kalrez, and Nafion (see Fluorine compounds organic–tetrafluoroethylene–perfluorovinyl ether copolymers; Elastomers, synthetic–fluorocarbon elastomers).

Publications have described the use of HFPO to prepare acyl fluorides (53), fluoroketones (54), fluorinated heterocycles (55), as well as serving as a source of difluorocarbene for the synthesis of numerous cyclic and

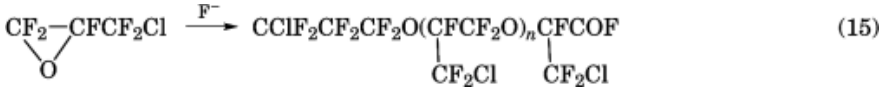
acyclic compounds (56). The isomerization of HFPO to hexafluoroacetone by hydrogen fluoride has been used as part of a one-pot synthesis of bisphenol AF (57). HFPO has been used as the starting material for the preparation of optically active perfluorinated acids (58). The nmr spectrum of HFPO is given in Reference 59. The molecular structure of HFPO has been determined by gas-phase electron diffraction (13).

3.3. Perfluoroisobutylene Oxide

PIBO has been prepared primarily by the addition of difluorocarbene to hexafluoroacetone or by the reaction of alkaline hydrogen peroxide with perfluoroisobutylene. The small amount of published work on PIBO deals with its oligomerization (60), isomerization to perfluoroisobutyryl fluoride (61), conversion to perfluoro-*t*-butyl alcohol (62), and reaction with nucleophiles (63). PIBO has been reported to be as toxic as perfluoroisobutylene (64). The nmr spectrum of PIBO is reported in Reference 65.

4. Other Epoxides

Large numbers of epoxides have been reported that contain only fluorine and carbon bound to the oxirane ring but which contain other halogens, oxygen, hydrogen, and other functional groups in one of the carbon side chains. Although these are not true perfluoroepoxides their syntheses and reactions of their epoxide rings are virtually identical to those of the perfluoro analogues. One example is the reaction of 3-chloropentafluoropropylene oxide with nucleophiles such as fluoride ion (66) (eq. **15**).



(15)

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Related Articles

Fluorine compounds, organic, introduction; Fluorine compounds, organic, tetrafluorethylene-perfluorovinyl ether copolymers; Fluorocarbon elastomers