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# The Addition Reactions of Fluoroalkyl Ethyl Ethers to Perfluoropropene

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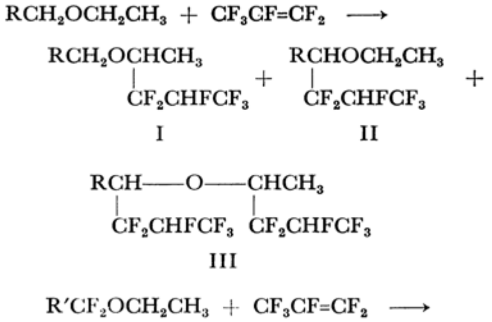
The free-radical reactions of aliphatic or alicyclic ethers to fluoroolefins under $\gamma$-irradiation[1–3] or in the presence of peroxide[4] have been reported to give the 1 : 1 adduct, the ethers with fluoroalkyl or fluorocycloalkyl group on the $\alpha$-carbon, in good yields. In the addition of diethyl ether,[1–3] the 1 : 2 adduct with symmetrical structure has been produced along with the 1 : 1 adduct.

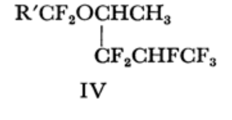
In order to investigate the scope and limitation of these addition reactions for the syntheses of fluorine-containing ethers, the reaction of various fluoroalkyl ethyl ethers and perfluoropropene was undertaken. The effects of the substitution of fluorine for hydrogen in the ethers on their reactivity in the addition reaction were also investigated by a competitive reaction.

The two types of fluoroakyl ethyl ethers with general formulas of $RCH_2OCH_2CH_3$ ($R=CH_2F$, $CHF_2$, $CF_3$, $CH_2Cl$, $CHF_2CF_2$) and $R'CF_2OCH_2CH_3$ ($R'=CHF_2$, $CHFCl$, $CHCl_2$) were prepared and used as addends. A mixture of perfluoropropene and an ether in an autoclave was irradiated by $\gamma$-ray ($5—20\times 10^7$ R). The products were separated by distillation or by preparative gas chromatography. Their structures were established by elemental analyses, and by IR and NMR (proton and fluorine) spectra.

While the addition of ethers of the type $R'CF_2OCH_2CH_3$ gave only the 1 : 1 adduct **IV**, the addition of ethers of the type $RCH_2OCH_2CH_3$ resulted in a mixture of products composed of the 1 : 1 adducts, **I** and **II**, and the 1 : 2 adduct **III**.



$$RCH_2OCH_2CH_3 + CF_3CF{=}CF_2 \longrightarrow \underset{\text{I}}{RCH_2O\underset{\substack{|\\ CF_2CHFCF_3}}{C}HCH_3} + \underset{\text{II}}{R\underset{\substack{|\\ CF_2CHFCF_3}}{C}HOCH_2CH_3} + \underset{\text{III}}{R\underset{\substack{|\\ CF_2CHFCF_3}}{C}H{-}O{-}\underset{\substack{|\\ CF_2CHFCF_3}}{C}HCH_3}$$



$$R'CF_2OCH_2CH_3 + CF_3CF{=}CF_2 \longrightarrow \underset{\text{IV}}{R'CF_2O\underset{\substack{|\\ CF_2CHFCF_3}}{C}HCH_3}$$

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[1] H. Muramatsu, K. Inukai and T. Ueda, *J. Org. Chem.*, **29**, 2220 (1964); *ibid.*, **30**, 544 (1965).

[2] H. Muramatsu, S. Moriguchi and K. Inukai, *ibid.*, **31**, 1306 (1966).

[3] H. Muramatsu, K. Inukai and T. Ueda, This Bulletin, **40**, 903 (1967).

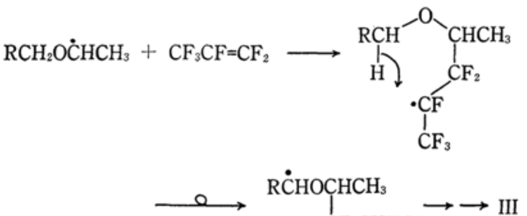
[4] W. E. Hanford, U. S. Pat. 2433844 (1948).

The reaction conditions and yields of the adducts are shown in Table 1. It is apparent that, in the case of the type $RCH_2OCH_2CH_3$, the ratio of III/I decreases with the number of fluorine on the $\beta$-carbon and that perfluoropropene adds preferentially on the $\alpha$-methylene with a less electronegative group. The addition of ethers of the type $RCF_2OCH_2CH_3$ was much more difficult than that of ethers of the type $RCH_2OCH_2CH_3$.

TABLE 1. REACTION CONDITIONS AND YIELDS OF ADDUCTS

| Ether R | Molar ratio of propene/ether | Total dose MR | Yield, % | | | |
|---|---|---|---|---|---|---|
| | | | I | II | III | IV |
| | | $RCH_2OCH_2CH_3$ | | | | |
| $CF_3$ | 2.2 | 113 | 67 | 0.3 | 5.3 | |
| $CHF_2$ | 2.7 | 60 | 64 | 1.3 | 19.3 | |
| $CH_2F$ | 2.2 | 60 | 37 | 7.1 | 39 | |
| $CH_3$[3] | 0.3 | 11 | 43.5 | | 56.5 | |
| $CH_2Cl$ | 2.3 | 63 | 7.6 | | | |
| $CHF_2CF_2$ | 0.9 | 46 | 35 | | | |
| | | $RCF_2OCH_2CH_3$ | | | | |
| $CHF_2$ | 0.7 | 143 | | | | 8 |
| CHFCl | 0.8 | 145 | | | | 10 |
| $CHCl_2$ | 0.7 | 218 | | | | 22 |

The 1 : 2 adduct III could be formed by two pathways. One pathway is a successive addition of two perfluoropropenes and another is an addition involving an intramolecular rearrangement.



To clarify this point, we studied the addition reaction of diethyl ether to perfluoropropene under various reaction conditions. As shown in Table 2, the ratio of III/I in products was almost constant if the ratio of olefin/ether was kept constant, showing no dependence on irradiation time. Besides, the ratio of III/I increased with increasing the ratio of olefin/ether (Table 3).

The fact that the reaction of I with perfluoropropene produced only a small amount of III and that the addition reaction of a cyclic ether such as tetrahydrofuran to perfluoropropene did not give any 1 : 2 adduct,[3] also support the latter pathway involving the radical rearrangement. The rigid structure of tetrahydrofuran would prohibit the formation of six-membered cyclic structure of the intermediate radical.

TABLE 2. RELATIONS BETWEEN IRRADIATION TIME AND RATIO OF III TO I

| Propene/diethyl ether | Irradiation time, hr | Yield, % | | Ratio of III/I |
|---|---|---|---|---|
| | | I | III | |
| 1.0 | 22.9 | 8.0 | 12.2 | 1.52 |
| 1.0 | 45.6 | 10.8 | 14.7 | 1.36 |
| 1.0 | 68.6 | 13.2 | 19.1 | 1.44 |
| 1.0 | 112.0 | 15.3 | 23.2 | 1.52 |
| 2.0 | 45.6 | 10.9 | 22.8 | 2.08 |
| 2.0 | 112.0 | 16.2 | 33.6 | 2.08 |

TABLE 3. RELATIONS BETWEEN RATIO OF PERFLUOROPROPENE TO DIETHYL ETHER AND RATIO OF III TO I

| Propene/diethyl ether | Concentration of ether, mol % | Yield, % | | Ratio of III/I |
|---|---|---|---|---|
| | | I | III | |
| 0.25 | 0.80 | 6.47 | 5.67 | 0.88 |
| 0.50 | 0.67 | 7.03 | 7.13 | 1.01 |
| 1.00 | 0.50 | 7.00 | 10.1 | 1.44 |
| 2.00 | 0.33 | 8.40 | 17.6 | 2.10 |

The relative reactivities of fluoroalkyl ethyl ethers in the addition reaction to perfluoropropene were determined by a competitive reaction. A one-to-one mixture of two substrates was irradiated with olefin in a glass ampoule. The amount of each adduct was determined by gas chromatography. The relative reactivities of the ethers are listed in Table 4, taking the reactivity of diethyl ether as 1000.

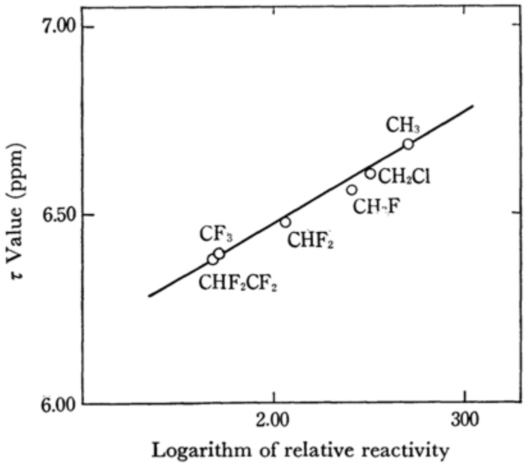


Fig. 1. Plots of the chemical shifts (τ values) of hydrogens in the methylene of $RCH_2O\underline{CH_2}CH_3$ *vs.* logarithms of its relative reactivity.

Table 4. Relative reactivity of the fluoroalkyl ethyl ethers

| Ether R or R′ | $RCH_2OCH_2CH_2$ | | | | | | $R'CF_2OCH_2CH_3$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $CH_3$ | $CH_2F$ | $CHF_2$ | $CF_3$ | $CH_2Cl$ | $CHF_2CF_2$ | $CHF_2$ | $CHFCl$ | $CHCl_2$ |
| Relative reactivity | 1000 | 260 | 110 | 56 | 320 | 46 | 0.8 | 1.0 | 0.1> |

Table 5. Physical properties of the 1 : 1 adducts and 1 : 2 adducts

| R | Bp °C | $n_D^{20}$ | $d_4^{20}$ | $MR_D$ Found | $MR_D$ Calcd | C, % Found | C, % Calcd | H, % Found | H, % Calcd |
|---|---|---|---|---|---|---|---|---|---|
| 1 : 1 Adduct, $CF_3CHFCF_2R$ | | | | | | | | | |
| $CF_3CH_2O\overset{|}{C}HCH_3$ | 118 | 1.3086 | 1.469 | 35.9 | 36.9 | 30.7 | 30.6 | 2.71 | 2.56 |
| $CHF_2CH_2O\overset{|}{C}HCH_3$ | 132 | 1.3233 | 1.441 | 36.1 | 36.8 | 31.7 | 32.3 | 2.92 | 3.10 |
| $CH_2FCH_2O\overset{|}{C}HCH_3$ | 147 | 1.3328 | 1.377 | 36.2 | 36.7 | 34.2 | 34.7 | 3.82 | 3.75 |
| $CH_2ClCH_2O\overset{|}{C}HCH_3$ | 165 | 1.3621 | 1.378 | 41.6 | 41.5 | 32.8 | 32.5 | 3.65 | 3.51 |
| $CHF_2CF_2CH_2O\overset{|}{C}HCH_3$ | 152 | 1.3207 | 1.498 | 41.2 | 41.6 | 30.7 | 31.0 | 2.61 | 2.60 |
| $CH_2F\overset{|}{C}HOCH_2CH_3$ | 116 | 1.3293 | 1.367 | 36.1 | 36.7 | 34.5 | 34.7 | 3.59 | 3.75 |
| $CHF_2CF_2O\overset{|}{C}HCH_3$ | 123 | 1.3048 | 1.534 | 36.6 | 37.0 | 27.9 | 28.4 | 1.91 | 2.04 |
| $CHFClCF_2O\overset{|}{C}HCH_3$ | 138 | 1.3307 | 1.532 | 41.7 | 41.8 | 27.3 | 26.9 | 2.01 | 1.93 |
| $CHCl_2CF_2O\overset{|}{C}HCH_3$ | 163 | 1.3569 | 1.552 | 46.4 | 46.6 | 25.5 | 25.6 | 1.91 | 1.84 |
| 1 : 2 Adduct, $(CF_3CHFCF_2)_2R$ | | | | | | | | | |
| $CF_3\overset{|}{C}HO\overset{|}{C}HCH_3$ | 164 | 1.3130 | 1.630 | 51.1 | 51.2 | 27.5 | 28.1 | 1.79 | 1.65 |
| $CHF_2\overset{|}{C}HO\overset{|}{C}HCH_3$ | 168 | 1.3218 | 1.595 | 51.3 | 51.5 | 29.1 | 29.3 | 1.68 | 1.97 |
| $CH_2F\overset{|}{C}HO\overset{|}{C}HCH_3$ | 176 | 1.3270 | 1.560 | 50.9 | 51.1 | 30.6 | 30.6 | 1.95 | 2.31 |

In the ethers of the type $RCH_2OCH_2CH_3$ ($R=CH_3$, $CH_2F$, $CHF_2$, $CF_3$), the logarithm of reactivity was found to be inversely proportional to the number of substituted fluorines in the β-methyl group, indicating that the Hammett relationship holds in the radiation-induced addition reaction. As expected, it was also observed that τ values of chemical shift of hydrogen in α-methylene of the fluoroalkyl ethyl ethers have a linear relation with the logarithms of their reactivity as shown in Fig. 1. All these facts indicate that the substituted fluorines exerted their electron-withdrawing effect remarkably through oxygen upon the α-methylene group and that the hydrogen abstraction on the α-methylene was a rate-determining step in the radiation-induced addition reaction of ethers to fluoroolefins.

The physical properties of the 1 : 1 adduct and 1 : 2 adduct are shown in Table 5. In the adducts of the type $RCH_2OCH_2CH_3$, the substitution of fluorine for hydrogen of β-methyl group of diethyl ether decreases the boiling point and refractive index of both the 1 : 1 adduct and 1 : 2 adduct, but increases their density. Similar trends were known[5] for $RCOCH_3$, $RCH_2OC_2H_5$, $RCOOC_2H_5$, and $RCOCl$ where R is $CH_2F$, $CHF_2$ or $CF_3$.

## Experimental[6]

**Preparation of Ethers of the Type $RCH_2OCH_2CH_3$.** *(1) β-Fluoroethyl Ethyl Ether.* Ethylene chlorohydrin was fluorinated with potassium fluoride in ethylene glycol - diethylenel gycol solvent at 150°C to give β-fluoroethanol (60% yield). Upon heating at 130°C with ethanol in the presence of sulfuric acid, β-fluoroethanol gave β-fluoroethyl etheyl ether (30% yield). bp 75—76°C( lit.[7] 74.5—75.5°C).

*(2) β,β-Difluoroethyl Ethyl Ether.* α,α,β,β,-Tetrafluoroethyl ethyl ether prepared from tetrafluoroethylene and ethanol was hydrolyzed in the presence of sulfuric acid at 0°C to produce ethyl difluoroacetate (45% yield). The difluoroacetate was converted into difluoroethanol by reduction with lithium aluminum hydride in ether (65% yield). A mixture of the difluoroethanol and ethanol was heated at 130°C with sulfuric acid to give β,β-difluoroethyl ethyl ether (55% yeild). bp 66—67°C (lit.[8] 66.3—66.7°C).

*(3) β,β,β-Trifluoroethyl Ethyl Ether.* Reduction of trifluoroacetic acid with lithium aluminum hydride

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[5] M. Hudlicky, "Chemistry of Organic Fluorine Compound," The Macmillan Co., New York (1962), p. 298.

[6] All temperature readings are uncorrected. NMR spectra were taken on a JNM-C-60 NMR high resolution spectrometer with tetramethylsilane as an internal standard for $^1H$ and with trifluoroacetic acid as an external standard for $^{19}F$.

[7] E. Gryszkiewicz-Trochimowski, A. Sporzynski and J. Wnuk, *Rec. Trav. Chim.*, **66**, 413 (1947).

[8] F. Swarts, *Bull. Acad. Roy. Belg.*, **1901**, 383.

was carried out in ether at 35°C to yield $\beta,\beta,\beta$-trifluoroethanol (50% yield). The trifluoroethanol was refluxed with ethanol in the presence of sulfuric acid to give trifluoroethyl ethyl ether (18% yield). bp 50—51°C (lit.[9] 49.9°C).

*(4) β-Chloroethyl Ethyl Ether.* β-Chloroethyl ethyl ether was prepared from ethylene chlorohydrin and ethanol as mentioned above (65% yield). bp 107—108°C (lit.[10] 108—109°C).

*(5) β,β,γ,γ-Tetrafluoropropyl Ethyl Ether.* A mixture of sodium $\beta,\beta,\gamma,\gamma$-tetrafluoropropoxide, ethyl bromide, and dioxane in a stainless steel autoclave was heated at about 190°C for 54 hr to give $\beta,\beta,\gamma,\gamma$-tetrafluoropropyl ethyl ether (34% yield). bp 86—88°C, $n_D^{20}$ 1.3252, $d_4^{20}$ 1.184.

Found: F, 47.2%; $MR_D$ 27.2 Calcd for $C_5H_8OF_4$: F, 47.5%; $MR_D$ 27.3.

**Preparation of Ethers of the Type $RCF_2OCH_2$-$CH_3$.** $\alpha,\alpha,\beta,\beta$-Tetrafluoroethyl-, $\alpha,\alpha,\beta$-trifluoro-$\beta$-chloroethyl- and $\alpha,\alpha$-difluoro-$\beta,\beta$-dichloroethyl ethyl ether were prepared by the nucleophilic addition reaction[11] of ethanol to tetrafluoroethylene, trifluorochloroethylene, and 1,1-dichloro-2,2-difluoroethylene, respectively.

**Addition Reaction of Ethers to Perfluoropropene.** A mixture of 37 g (0.34 mol) of $\beta,\beta$-difluoroethyl ethyl ether and 137 g (0.91 mol) of perfluoropropene was placed in an autoclave (capacity, 200 m*l*) and received $\gamma$-irradiation at room temperature to a total dose 60 MR for a period of 1030 hr. After recovery of unchanged perfluoropropene (72.5 g), the content in the autoclave was distilled to give dimers of perfluoropropene (0.8 g), a mixture of 1 : 1 adducts (58.3 g), a 1 : 2 adduct (27 g, 0.066 mol, 19.3% yield) and viscous residues (8 g). From its gas chromatogram and NMR spectrum, the mixture of 1 : 1 adducts was found to consist of $\beta,\beta$-difluoroethyl $\alpha$-methyl-$\beta,\beta,\gamma,\delta,\delta,\delta$-hexafluorobutyl ether (57 g, 0.22 mol, 64% yield) and ethyl $\alpha$-fluoromethyl-$\beta,\beta,\gamma,\delta,\delta,\delta$-hexafluorobutyl ether (1.3 g, 0.0051 mol, 1.5% yield).

Addition reactions of other ethers were carried out under similar conditions, which are summarized in Table 1 together with the yields. Though products were mainly separated by distillation, some products were isolated by a preparative gas chromatograph. Physical properties of the 1 : 1 adducts and 1 : 2 adducts are shown in Table 5.

The authors wish to express their thanks to the Daikin Kogyo Co. for supplying perfluopropene.

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[9] A. L. Henne and M. A. Smook, *J. Am. Chem. Soc.*, **72**, 4378 (1950).

[10] L. C. Swallen and C. E. Boord, *ibid.*, **52**, 651 (1930).

[11] R. D. Chambers, "Ionic Reactions of Fluoroolefins" in "Advances in Fluorine Chemistry," Vol. 4, Butterworth & Co. (1965), p. 50.