# Polyfluoroalkyl Ethers of Alicyclic Fluoroolefins

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**The base-catalyzed addition of polyfluoroalkanols to perhalo-alicyclic olefins yields stable polyfluoroalicyclic ethers. Two series of di- and triethers are obtained, depending on the identity of the vinylic halogens in the four-, five-, and six-membered ring alicyclic olefins. Evidence is cited for the presence of double bond isomers only in the five- and six-membered ring diethers. All of the diethers (but not the triethers) readily undergo chlorine addition to yield stable $\alpha$-chloroethers. The fluid characteristics of these two types of ethers are compared, including the effects of ring size.**

NUCLEOPHILIC displacement of halogens in alicyclic perhalo-olefins by alkoxide ions yields two types of ethers, depending upon the nature of the vinylic halogen in the olefin. Most of the reported work (*6, 7, 8, 10, 11, 12, 14, 15*) relates to the reactions of the perhalocyclobutene ring system with methoxide ion to yield methyl ethers. Two recent papers have shown that octafluorocyclopentene (*16*) and decafluorocyclohexene (*3*) react similarly with methoxide ion to yield the methyl ethers. This paper summarizes the results obtained from reactions of the four-, five-, and six-membered ring systems having either fluoro or chloro atoms at the vinylic position. Comparable yield data and product characteristics based on ring size are shown for this reaction, which has general applicability for the three ring sizes.

## EXPERIMENTAL

Infrared spectra were obtained on the neat liquids between sodium chloride plates using a Beckman IR-5 spectrometer. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratories.

The general synthesis of Type III and IV ethers is illustrated below by one example for each type. Minor modification of such conditions as reaction time, temperature, and solvent composition would be applicable to the other ethers.

**1-Chloro-3,3,4,4-tetrafluoro-2,5,5-tri(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyloxy)-1-cyclopentene (XI).** To a solution of 2.0 grams (0.05 mole) of sodium hydroxide, 16.6 grams (0.05 mole) of 1H,1H,7H-dodecafluoro-1-heptanol, 20 ml. of water, and 20 ml. of tetrahydrofuran was added 4.1 grams (0.017 mole) of 1,2-dichloro-3,3,4,4,5,5-hexafluoro-1-cyclopentene. After an initial exothermic reaction, the stirred mixture was refluxed 24 hours.

The cooled mixture was poured into water and extracted with two 100-ml. portions of carbon tetrachloride. The organic layer was washed with water, then dried over $MgSO_4$ and fractionated, yielding 14.1 grams (54.9% yield) of near colorless oil, b.p. 168° to 178° C./0.08 mm., $n_D^{25}$ 1.3421.

**1,2, - Di(2,2,3,3,4,4,5,5,6,6,7,7 - dodecafluoroheptyloxy) - 3,3,4,4-tetrafluoro-1-cyclobutene (V).** A prepared solution of 116 grams (0.35 mole) of 1H,1H,7H-dodecafluoro-1-heptanol, 14.4 grams (0.36 mole) of sodium hydroxide, 30 ml. of water and 100 ml. of tetrahydrofuran was added to a solution of 25 grams (0.154 mole) of perfluorocyclobutene in 40 ml. of tetrahydrofuran at −10° C. The stirred solution was allowed to warm slowly to ambient temperature, then refluxed for 3 hours. The product was isolated as above and fractionated to obtain 64.2 grams of colorless oil, b.p. 105° C./0.1 mm., $n_D^{25}$ 1.3322, $d^{20°\,C.}$ 1.8011.

**Chlorination of 1,2-Di(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyloxy)-3,3,4,4-tetrafluoro-1-cyclobutene (V).** Chlorine was bubbled slowly through 41.2 grams (52.4 mmoles) of the cyclobutene (V) at 110° to 115° C. Reaction progress was monitored by vapor phase chromatography through a 12-foot, 5% silicone (DC200) on 30- to 60-mesh Chromosorb-P column operated at 175° C. with a helium flow of 80 ml. per minute. After 8 hours, only a trace of starting material remained (37.5 mm.), with a major product peak at 68-mm. retention. Fractionation yielded 35.9 grams (80%) of colorless oil, b.p. 105° to 107° C./0.07 mm., $n_D^{25}$ 1.3439, $d^{100°\,F.}$ 1.7874.

Infrared analysis showed no absorption in the double bond region, confirming product identity as 1,2-dichloro-1,2-di(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyloxy)-3,3,4,4-tetrafluorocyclobutane (XVII).

Anal. Calcd. for $C_{18}H_6Cl_2F_{28}O_2$: C, 25.22; H, 0.71; Cl, 8.27; F, 62.07. Found: C, 25.28; H, 0.81; Cl, 8.27; F, 62.33.

**3-[2-(heptafluorocyclobutyl) - hexafluorocyclobutyl]-1,2,3-tri-[2,2,3,3,4,4,4 - heptafluorobutoxy] - 4,4 - difluorocyclobutene (XVI).** A solution of 18.4 grams (0.092 mole) of 1H,1H-heptafluorobutanol-1 and 3.7 grams (0.092 mole) of sodium hydroxide in 7 ml. of water and 35 ml. of tetrahydrofuran (THF) was added to a stirred solution of trimer (XV) in 30 ml. of THF at 20° C. The solution was warmed to reflux for 6 hours, then poured into water. The crude product was isolated by extraction with dichloromethane. Two fractionations gave 4.3 grams of product, b.p. 91° to 92° C./0.1 mm.

Anal. Calcd. for $C_{24}H_6F_{36}O_3$ (1026.29): C, 28.08; H, 0.59; F, 66.64. Found: C, 28.32; H, 0.69; F, 66.58.

## DISCUSSION

The synthetic importance of this reaction for obtaining singularly pure fluids in the intermediate molecular weight range of 500 to 2000 was demonstrated by the use of higher alcohols, particularly the finding that the polyfluoroalkanols can be used as nucleophiles in this reaction. Reported procedures for obtaining high fluorine content (>60%) fluids in this range usually yield oligomers requiring fractionation techniques to obtain the desired fluid properties, whereas the combination of properly selected cyclic olefin and polyfluoroalkanol can be used for specific fluid design.

Stable di- and tri(polyfluoroalkyl)alicyclic ethers (Types III and IV) were obtained in high yield by direct displacement of a polyfluoroalkoxide ion on the perhalogenated four-, five-, and six-membered ring olefinic systems, I and II.

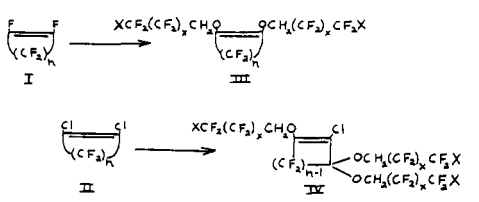
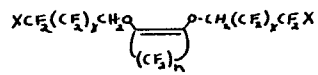
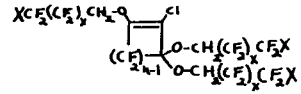


Table I. Diethers of General Structure III



| Compound | X | x | n | Empirical Formula | Yield, % | B.P., ° F./ 760 mm.[a] | Mol. Wt., Calcd./Found[b] | $n_D^{25}$ | Analysis, % C Calcd. | C Found | H Calcd. | H Found | F Calcd. | F Found | Infrared Absorption > C=C <, Cm.[-1] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| V | H | 5 | 2 | $C_{18}H_6F_{28}O_2$ | 53 | 543 | 786/822 | 1.3322 | 27.49 | 27.62 | 0.77 | 0.79 | 67.66 | 67.51 | 1750 |
| VI | H | 5 | 3 | $C_{19}H_6F_{30}O_2$ | 40 | 536 | 836/837 | 1.3331 | 27.29 | 27.13 | 0.72 | 0.71 | 68.16 | 68.02 | 1728, 1707 |
| VII | H | 5 | 4 | $C_{20}H_6F_{32}O_2$ | 53 | 561 | 886/863 | 1.3317 | 27.10 | 26.95 | 0.68 | 0.58 | 68.60 | 68.98 | 1711, 1679 |
| VIII | H | 9 | 2 | $C_{26}H_6F_{44}O_2$ | 86 | 642 (m.p. 75° to 77° C.) | 1186/1130 | ... | 26.32 | 26.76 | 0.51 | 0.48 | 70.47 | 70.61 | ... |

Triethers of General Structure IV



| Compound | X | x | n | Empirical Formula | Yield, %[c] | B.P., ° F./ 760 mm.[a] | Mol. Wt., Calcd./Found[b] | $n_D^{25}$ | Analysis, % C Calcd. | C Found | H Calcd. | H Found | F Calcd. | F Found | Cl Calcd. | Cl Found | Infrared Absorption > C=C <, Cm.[-1] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IX | F | 2 | 3 | $C_{17}H_6ClF_{25}O_3$ | 83 | 474 | 769/736 | 1.3325 | 26.56 | 26.97 | 0.79 | 0.96 | 61.79 | 62.26 | 4.61 | 4.72 | 1673 |
| X | H | 3 | 3 | $C_{20}H_9ClF_{28}O_3$ | 74 | 586 | 864/821 | 1.3502 | 27.78 | 27.63 | 1.05 | 1.28 | 61.52 | 61.56 | 4.10 | 3.70 | 1670 |
| XI | H | 5 | 3 | $C_{26}H_9ClF_{40}O_3$ | 72 | 618 | 1165/1234 | 1.3421 | 26.81 | 26.99 | 0.78 | 1.51 | 65.25 | 65.22 | 3.04 | 2.92 | 1660 |
| XII | H | 7 | 3 | $C_{32}H_9ClF_{52}O_3$ | 74 | 676 | 1465/1473 | 1.3386 | 26.24 | 26.44 | 0.62 | 0.60 | 67.45 | 67.58 | 2.42 | 2.48 | 1665 |
| XIII | H | 5 | 2 | $C_{25}H_9ClF_{38}O_3$ | 55 | 561 | 1115/1078 | 1.3429 | 26.93 | 27.09 | 0.81 | 0.73 | 64.77 | 63.79 | 3.18 | 3.19 | 1697 |
| XIV | H | 5 | 4 | $C_{27}H_9ClF_{42}O_3$ | 68 | 629 | 1215/1200 | 1.3440 | 26.69 | 26.83 | 0.75 | 1.01 | 65.69 | 65.36 | 2.92 | 3.01 | 1649 |

[a] Extrapolated boiling points from vapor pressure data. [b] Molecular weights determined by Mechrolab Vapor Pressure Osmometer ($CHCl_3$ solvent). The values are within 6%, which is considered within the accuracy limits for this molecular weight range. [c] This procedure is also more effective with the lower, non-halogen containing alcohols. An 87% yield of 1-chloro-3,3-difluoro-2,4,4-trimethoxy-1-cyclobutene was obtained in an aqueous system and none of the tetraether was detected (*17*).

The earlier published work described reactions of the lower alcohols, principally with perfluorocyclobutene, using dissolved base in excess alcohol as solvent. An aqueous system was used in the present synthesis in conjunction with a water-miscible, nonreactive solvent to obtain higher yields and quality of product ethers. The weakly nucleophilic fluoroalkoxide ions readily undergo this displacement reaction, although the polyfluoroalkanols are considerably more acidic ($K_a \sim 4 \times 10^{-12}$) than their hydrogen analogs. The benzoate anion and the perfluorobutyryl anion were completely unreactive toward these alicyclic olefins. Other reactive anions included the phenoxide anion and polyols such as 2,2,3,3,4,4-hexafluoropentane-1,5-diol, which yielded a colorless polyfluorocarbon polymer. The series of new polyfluoroalkyl alicyclic diethers obtained from the reaction of four- to six-membered ring perfluoroolefins (I) with polyfluoroalkanols and the triethers obtained from the four- to six-membered ring alicyclic olefins (II) with displaceable vinylic chloro groups are listed in Table I.

The infrared spectra of the triether structures (IV) in the double bond region (Table I) show a single absorption for each ether, suggesting that these compounds are pure isomers. The three-step, anion addition-elimination sequence must involve, in each step, specific addition to yield the most stable carbanion at carbon atom number two of the three-carbon system.

$$>\mathrm{C}-\underset{\displaystyle -}{\overset{\displaystyle \mathrm{Cl}}{\overset{|}{\mathrm{C}}}}-\mathrm{C}<$$

1 2 3

Elimination of chloride or fluoride ion from carbon one or three—but not alkoxide—yields the single isomer found in this type of ether. Apparently, ring size has no effect on direction of the over-all reaction, and the yields of the triethers are generally better than the diethers. Addition of a fourth alkoxide ion to a Type IV triether would yield a carbanion which can either abstract a solvent proton (*17*) or, more favorably, regenerate starting material by trans-elimination from either contiguous carbon atom. This suggests that Type IV ethers should undergo exchange with dissimilar alkoxide ions.

The observation of two double-bond isomers in the five- and six-membered ring diethers (VI and VII, Table I) must result from partial fluoride ion elimination at a

$$>\mathrm{C}<\overset{\mathrm{F}}{\underset{\mathrm{F}}{}}$$

position, rather than the more favored

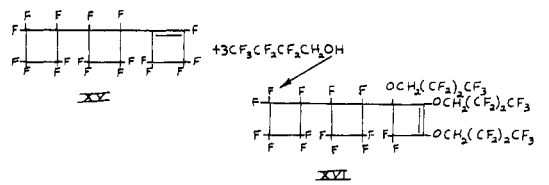
$$>\mathrm{C}<\overset{\mathrm{F}}{\underset{\mathrm{OR}}{}}$$

position (*9*). Clayton *et al.* (*3*) recently reported similar results on two isomers of dimethoxyperfluorocyclohexene with infrared absorptions at 1675 and 1700 cm.$^{-1}$, in agreement with the absorptions reported for the cyclohexene structure VII in Table I. The octafluorocyclopentene system must react similarly to yield the two isomers as reported in Table I; however, the anomalous fluoride elimination apparently did not occur in the hexafluorocyclobutene system, where only a single isomer was detected (V).

The positions of the carbon-to-carbon double bond infrared absorptions reflect ring size in both types of ethers ranging from 1697 to 1649 cm.$^{-1}$ for the four- to six-membered triethers, and in the same order but at shorter wavelengths for the diethers.

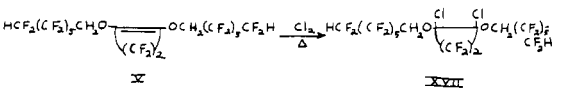
The fluorine NMR spectra of these polyfluoro ethers were extremely complex compared to the characteristics of some simpler alicyclic fluorocarbons reported previously (*5*), and adequate resolution was not obtained. The interaction of spatially close fluorine nuclei observed in the multiplicity of such simple compounds as perfluorocyclobutene was notable in these compounds, particularly the trimer (XV).

An interesting extension of the alkoxide displacement was the reaction of 2,2,3,3,4,4,4-heptafluorobutanol-1 with 1-[2-(heptafluorocyclobutyl)-hexafluorocyclobutyl]-2,3,3,4,4-pentafluorocyclobutene (XV) (*13*) to obtain a triether, tentatively of structure XVI, based on the carbanion addition-elimination mechanism (*9*) and earlier work (*13*), with a triethyl ether derivative. A procedural modification gave up to 65% yields of the trimer (XV) with correct elemental analysis and a single, strong double bond absorption at 1660 cm.$^{-1}$ in the Raman spectrum.




XV XVI

The diethers of Type III were readily chlorinated with thermal or light catalysis to the saturated ethers (V to XVII) in high yield. The chlorination of Type IV ethers gave complex mixtures, with no positive evidence of similar addition products.




X XVII

## PHYSICAL PROPERTIES

The synthesis of these ethers having low volatility and high (60 to 70%) fluorine content prompted interest in their fluid characteristics, which are briefly summarized in Table II. The contribution of ether functionality to molecular flexibility (*2*) is evident in the low-temperature viscosities and pour points of these fluids—five have pour points below −40° F.

The effect of omega hydrogen is clearly evident in comparison of IX (no omega hydrogen) and X (with omega hydrogen), which differ by only 97 molecular weight units. The viscosity of X is a factor of 9.4 higher than IX at 0° F. This marked effect of omega hydrogen in esters was noted earlier (*4*), and in this case must be ascribed to hydrogen bonding between the terminal hydrogen and fluorine in other molecules.

Table II. Physical Properties of Polyfluoroalkyl Alicyclic Ethers

| Compound | Viscosity (Cs., ° F.)[a] | | | ASTM Slope, 100° to 210° F. | Density, 100° F. | $T_D$,[b] ° F. |
|---|---|---|---|---|---|---|
| | −40 | 0 | 100 | | | |
| IX | 7,800 | 392 | 8.0 | 1.21 | 1.6996 | 518 |
| X[c] | 79,000 | 3,700 | 42.4 | 0.98 | 1.7460 | 523 |
| XI | 40,500(-20) | 8,800 | 68.6 | 0.91 | | 489 |
| XII[c] | | 4,700(32) | 162.0 | 0.86 | 1.8423 | 504 |
| XIII | | 13,181 | 87.9 | 0.91 | 1.7891 | 390 |
| XIV | | 33,915 | 132.9 | 0.89 | 1.8231 | 480 |
| V[c] | 5,770 | 461 | 12.6 | 1.02 | 1.7676 | >550[d] |
| VI | 5,390 | 429 | 12.0 | 1.02 | 1.7891 | 482 |
| VII | 18,094 | 1,053 | 18.5 | 1.01 | 1.8010 | >550[d] |

[a] Kinematic viscosity was determined by the ASTM D445-T 1960 procedure, using Cannon-Manning semimicro viscometers. [b] Thermal stability was measured by the isoteniscope method (*1*). [c] Compounds X, XII, and V had AIT's of 700° to 750°, 950° to 1000°, and 1000° to 1050° F., respectively, nor did they flash or burn spontaneously on molten metal at 1250° F. [d] The exact $T_D$ could not be measured in the atmospheric isoteniscope.

A correlation of molecular flexibility with ring size is also possible in both types of ethers III and IV. Compounds V, VI, and VII, which differ only in number of ring difluoromethylene groups (from four- to six-membered rings), vary in order of 0° F. viscosity in ring-size order of 6 ≫ 4 > 5. The same relationship in the Type IV ethers establishes the better fluid properties of perfluorinated cyclopentane and cyclobutane systems over cyclohexane systems.

The thermal stabilities of most of these ethers averaged about 500° F., although V and VII ethers had stabilities above 550° F., with the high fluorine content of both ether types resulting in good fire resistance properties. The perfluorocyclobutene trimer, XV, was an extremely mobile fluid with a viscosity of 117 cs. at −65° F., compared to the acyclic $n$-$C_{12}F_{26}$, which is a solid at 167° F. The thermal stability of XV was above 900° F., as measured by a pressure isoteniscope.

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# Copper Chromite Reduction of Ethyl Pinonate


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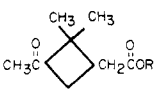
**The effect of copper chromite catalyst on the hydrogenation of ethyl pinonate, ethyl 3-acetyl-2,2-dimethylcyclobutaneacetate was to reduce the carbonyl at 140° C., giving ethyl pinolate, some of which pyrolyzed and gave 3-vinyl- and 3-ethylidienecyclobutane derivatives before the carboxyl function was reduced to alcohol. The result was a mixture of 2,2-dimethyl-3-ethylcyclobutaneethanol and 2,2-dimethyl-3-(2-hydroxyethyl)-cyclobutaneethanol. Because the yield of mono alcohol was about 38% and of glycol only 34%, copper chromite reduction of ethyl pinonate is considered impractical.**


A NUMBER of papers have emanated from this laboratory on the chemistry of *dl*-pinonic acid ($I_A$) and *dl*-pinolic acid ($II_A$). This report is closely related to some of the earlier work and was prompted by a request for a large sample of the glycol, 2,2-dimethyl-3-(2-hydroxyethyl)-cyclobutaneethanol (III) for evaluation as an intermediate for polyurethanes. Accordingly, a study of the copper chromite reduction of ethyl pinonate ($I_B$) was made as a preparative method for this glycol. When $I_B$ was reduced, the reduction product was a mixture of $III_A$ and 2,2-dimethyl-3-ethylcyclobutaneethanol (IV). The composition of each was obtained by comparing $III_A$ and $IV_A$ with materials made by alternate syntheses, $III_B$, $III_C$, and $IV_B$.

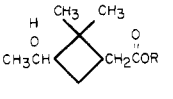
## EXPERIMENTAL

Boiling points, °C., are uncorrected. The carbon and hydrogen analyses were made by Galbraith Laboratories, Inc., Knoxville, Tenn. The GLPC data were obtained from (A) a column ⅛ inch by 15 feet, packed with 30% Carbowax 20M on Chromosorb W, or (B) a column 3/16 inch by 12 feet, packed with 20% Carbowax 20M on Gas Chrom Q.

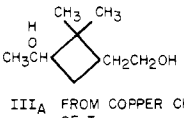
**2,2-Dimethyl-3-(2-hydroxyethyl)cyclobutaneethanol (III). A.** Ethyl pinonate, $I_B$, 360 grams (1.65 mole) $\eta_D^{20}$ 1.4526 [lit. 1.4526 (*4*)], prepared by the esterification of *cis-dl*-pinonic acid with ethanol in toluene using *p*-toluenesulfonic acid as a catalyst, was reduced with lithium aluminum hydride



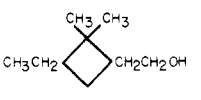
$I_A$ R=H
$I_B$ R=$C_2H_5$



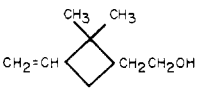
$II_A$ R=H
$II_B$ R=$C_2H_5$



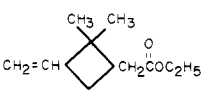
$III_A$ FROM COPPER CHROMITE REDUCTION OF $I_B$
$III_B$ FROM THE LAH REDUCTION OF $I_B$
$III_C$ FROM THE LAH REDUCTION OF $II_A$



$IV_A$ COPPER CHROMITE REDUCTION OF $I_B$
$IV_B$ HYDROGENATION OF V



V



VI