

air-dried to yield 10.5 grams (83%) of yellow powder, m.p. 236–8° C. (decomposed).

***N,N'*-Vinylene bis(aryl or alkyl carboxylic acid carbamic acid anhydrides).** *N,N'*-Vinylene bis(*p*-toluic acid carbamic acid anhydride). To a solution of *p*-toluic acid (0.20 mole) in dry benzene (25 ml.) was added rapidly a filtered solution of *trans*-vinylene diisocyanate (0.098 mole) in dry benzene (150 ml.). A white solid precipitated almost immediately. The mixture was allowed to stand for one hour at room temperature and then filtered; the collected solid was washed with benzene and dried in vacuo at 50° C. to yield 34 grams (19%) of white solid, m.p. 149.5–50.5° C.

ACKNOWLEDGMENT

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Polyhaloethers from the Reaction of Fluoroalcohols and Haloolefins

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The base-induced addition of several fluorinated alcohols to a variety of cyclic and acyclic polyhaloolefins is described. The general reaction scheme is: $RCF_2CH(R')OH + CF_2=CXY \rightarrow RCF_2CH_2(R')OCF_2CXYH$, where *R* is F or fluoroalkyl, *R'* is H, alkyl, or fluoroalkyl, *X* is F, Cl, Br, or H, and *Y* is F, Cl, fluoroalkyl, or H. With perfluorocycloolefins, an addition-elimination mechanism gave rise to unsaturated products containing one, two, or three fluoroalkoxy groups, depending on the reaction conditions. Twenty novel fluorinated ethers were thus prepared. NMR spectroscopy was used in many instances to confirm product structure. All new data thus acquired are presented.

THE NUCLEOPHILIC addition of aliphatic nonfluorinated alcohols to acyclic fluorinated olefins is well known (2), although analogous reactions of fluorinated alcohols have been little studied. The addition of 2,2,2-trifluoroethanol to tetrafluoroethylene was reported by Henne and Smook (5), and the reaction of fluoroalkylmethanols with perfluoropropylene was described briefly (4).

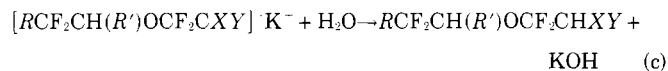
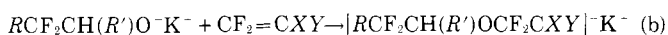
Fluorinated alcohols react readily with a variety of fluorinated olefins, in the presence of potassium hydroxide, to produce highly fluorinated aliphatic ethers.

$RCF_2CH(R')OH + CF_2=CXY \rightarrow RCF_2CH(R')OCF_2CXYH$. *R*, *R'*, *X*, and *Y* are defined in Table I.

First attempts to prepare these ethers were based on earlier work (4), which indicated that only a catalytic amount of base was necessary. This proved true only for the more reactive olefins, such as perfluoropropylene. Other olefins gave little or no product under these conditions. In the present study, optimum results were obtained when equimolar amounts of base and olefin were used. It was convenient to have excess alcohol present as a reaction medium. In some cases, the reaction vessel was heated to accelerate the reaction, although no detailed study was made of the relative reactivities of the olefins. Generally, the reactants were combined in a 300-ml. stainless steel pressure vessel, and the consumption of olefin was followed by a decline in pressure within the reactor. Alternately,

the ethers were prepared by bubbling the olefin through a solution of potassium hydroxide in the appropriate alcohol. Water was present in all reactions, since the potassium hydroxide employed was the standard 85% material.

The probable reaction mechanism may be represented by (2):



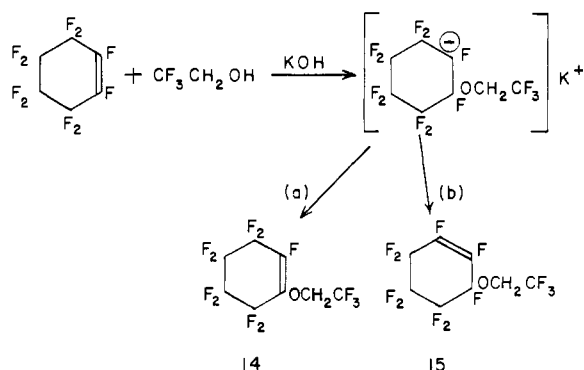
In the presence of excess alcohol, the last step may be written with water replaced by alcohol; the by-product would then be the corresponding alkoxide. A small amount of olefin by-product was observed in the ethers prepared from perfluoropropylene. This may arise either from collapse of the anion of step (b) or by a base-induced dehydrofluorination of the saturated ether of step (c). By analogy with prior work (2, 4), the former route is preferred. The resulting olefin was removed from the reaction mixture by bromination. The direction of elimination was not determined, but it is more probable that the fluoride was eliminated from the difluoromethylene group adjacent to the oxygen atom, since similar eliminations occurred in the

Table I. Physical Properties of New Linear Ethers $\text{RCF}_2\text{CH}(R')\text{OCF}_2\text{CHXY}$

Compd.	R	R'	X	Y	B.P., °C.	Refractive Index, n_D^{25}	Analytical Data		
							Calcd., %	Found, %	
1	F	H	Cl	F	82	1.3066	C	22.19	22.02
							H	1.40	1.51
							Cl	16.37	16.28
2	F	H	Br	F	97	1.3306	C	18.40	18.59
							H	1.16	1.24
							Br	30.62	30.41
3	F	H	Cl	Cl	109	1.3439	C	20.69	20.40
							H	1.30	1.06
							Cl	30.54	30.47
4	F	H	H	Cl	87	1.3119	C	24.20	24.41
							H	2.03	2.00
							Cl	17.86	18.05
5	F	H	H	F	64.5	<1.3	C	26.38	26.56
							H	2.22	2.41
							C	29.28	29.66
6	F	H	H	H	39	<1.3	H	3.07	3.00
							C	22.65	22.87
							H	0.63	0.84
7	F	CF_3	F	CF_3	77	<1.3	C	18.25	18.54
							H	0.61	0.68
							Br	24.29	24.22
8	F	CF_3	Br	F	97	1.3110	C	26.02	26.29
							H	2.12	2.14
							Cl	15.38	15.21
9	F	CH_3	Cl	F	96	1.3175	C	20.49	20.85
							H	1.38	1.65
							Br	27.28	27.66
10	CHF_2	H	Br	F	130.5	1.3425	C	19.31	19.14
							H	0.97	0.82
							Br	25.70	25.17
11	CF_3	H	Br	F	108	1.3210	C	22.53	22.96
							H	1.14	1.38
							C	22.77	22.87
12	CF_3	H	Cl	F	93.5	1.3015	H	0.96	0.99
							C	11.20	10.68
							Cl		
13	C_2F_5	H	Cl	F	112.5	1.3024			

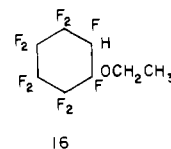
preparation of ethers from 1,1-difluoroethylene and 1,1-difluoro-2-chloroethylene.

The reaction of fluorinated alcohols with cyclic perfluoroolefins was examined briefly. In the case of trifluoroethanol and perfluorocyclohexene, the reaction apparently follows a course similar to that noted for the linear olefins, except that addition of alkoxide to the double bond is followed by elimination of fluoride.



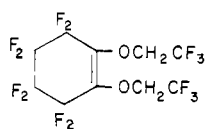
This pathway was proposed recently for this particular reaction (3). The mixture of olefins produced cannot be separated by distillation, but is resolved readily by means of preparative-scale gas-liquid chromatography. In addition to confirming the results reported by Tatlow and coworkers (3), it was observed that the distillate obtained from the

reaction mixture, before gas chromatographic separation, contained a third component accompanying the two olefinic ethers. This component had no characteristic infrared absorption bands due to OH, C=C, or C=O groups, and was removed by refluxing with aqueous potassium hydroxide. This component was probably the saturated ether

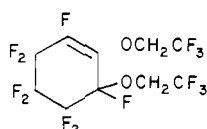


which was converted to the olefinic ethers on treatment with KOH. If this is correct, it is further support for the addition-elimination theory cited above. From the same reaction, a higher-boiling fraction which consisted of olefinic diethers was isolated. Infrared and NMR examination indicated that these were formed by addition of a further molecule of alkoxide, followed by spontaneous fluoride elimination.

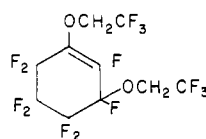
Clarification of this point was sought by carrying out an experiment using 2 moles of potassium hydroxide to each mole of perfluorocyclohexene, so that an enhanced yield of diethers could be realized. Preliminary distillation yielded a fraction rich in diethers, which, by GLC examination, contained four components. The compounds were separated by preparative-scale gas chromatography and examined by infrared and NMR spectroscopy. This showed conclusively that the compounds were



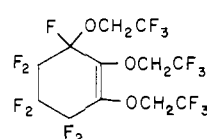
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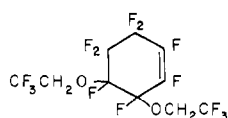


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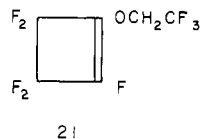
Mechanistically, the diethers are derived readily from the monoalkoxyolefins by further addition-elimination reactions. The infrared C=C stretching frequencies of the diethers are exactly those to be expected from the environment of each bond (1). These figures are reported in the experimental section, together with the NMR data. A fourth possible diether



was not present. From electronic considerations, the formation of this isomer is very unlikely, since it would involve addition of alkoxide ion to the less positive carbon of a fluorine-bearing double bond. Apart from the equivalent CF₃ groups, 17 shows only two kinds of —CF₂— in its ¹⁹F NMR spectrum. In 18, the CF₃ groups are not equivalent, and the vinyl fluorine atom appears in a characteristic downfield location. The vinyl fluorine in 19 has a slightly smaller chemical shift, since it is now adjacent to a single fluorine, rather than a difluoromethylene group. No vinyl fluorine signal is apparent in 20, although a tertiary fluorine is present.

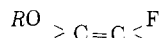
The triether 20 may be derived by further reaction of 18 and 19 with excess alkoxide. Although alternate structures are possible, these were not detected by infrared or NMR spectroscopy.

Perfluorocyclobutene reacted differently. With trifluoroethanol, one monoalkoxy olefin was formed predominantly; no isomer was isolated having a fluorine atom attached to each end of the double bond. The infrared spectrum of product 21 showed a C=C stretching frequency at 1773 cm.⁻¹, indicative of a —CF=C(OR)— structure (1). NMR examination confirmed the structure of 21 as

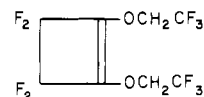


21

A minor amount of the product consisted of a dialkoxy olefinic ether. When the experimental conditions were varied suitably, this product could be made to predominate. Examination by GLC confirmed that a single dialkoxy product was formed, and infrared spectroscopy showed it to have C=C absorption at 1761 cm.⁻¹. The only review on the subject (1) would indicate this to be of the type



However, ¹⁹F NMR showed only equivalent CF₃ and CF₂ groups, with an integrated ratio of 6 to 4 for the fluorine atoms, indicating that the structure can be only

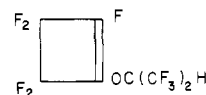


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Further examination of the literature shows that the observed C=C stretching frequency is not particularly anomalous, since 1,2-dimethoxytetrafluorocyclobutene has a C=C stretching frequency of 1750 cm.⁻¹ (6).

The diether 22 must arise through a further addition-elimination reaction of the monoalkoxy product. A concerted mechanism would result in a product containing a vinyl fluorine atom. This is clearly not the case here.

The reaction of hexafluoroisopropanol with perfluorocyclobutene resulted in a complex mixture of products, from which a monoalkoxy olefin was isolated. This was



23.

No other products were characterized.

The structures of the ether products were determined by elemental analysis (Table I and Table II), infrared, and NMR spectroscopy. The last method was of particular value, since little useful information could be deduced from the infrared spectra, other than the absence of starting materials, because the characteristic ether absorption region coincides with the strong bands produced by the polyfluoroalkyl groups. In many cases, both ¹H and ¹⁹F NMR spectra were obtained, and the results are given in the experimental section.

Proton spectra generally were not complex, but in the fluorine spectra, resolution was often limited by the complex overlapping of first-order multiplet lines. The main points to notice are that for the —OCF₂— group, the chemical shift is in the CF₃ range, chemical shifts for —CF— groups depend greatly on the other atoms or groups attached to the carbon, and the chemical shifts for most CF₃— and —CF₂— groups vary only slightly with the nature of the adjacent groups.

EXPERIMENTAL

Analytical gas chromatography was carried out in stainless steel columns (10-foot × ¼-inch) packed with 20% silicone gum rubber SE-30 on Chromosorb-W and run at 65°C. with a helium flow rate of 50 ml. per minute. Preparative scale work was done with 20-foot × ¾-inch aluminum columns packed with 30% Carbowax 20M supported on 40- to 60-mesh Chromosorb-W, run at 100°C. with a helium flow rate of 55 ml. per minute. NMR spectra were recorded using an A-60 instrument for ¹H measurements and a DP-56 spectrometer for ¹⁹F resonance. Chemical shifts are reported in δ units—i.e., parts per million from tetramethylsilane and trichlorofluoromethane, respectively, as internal standards. All elemental analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

1,1,2-Trifluoro-2-chloroethyl-2',2',2'-trifluoroethyl ether: CF₃CH₂OCF₂CHFCI 1. A solution of potassium hydroxide (20 grams; 0.3 mole, based on 85% purity) was prepared in 100 grams of 2,2,2-trifluoroethanol and placed in a 300-ml. stainless steel pressure reactor. The reactor was closed, cooled to -78°C., and the enclosed air was evacuated. Chlorotrifluoroethylene (35 grams, 0.3 mole) was introduced into the reactor through a vacuum-manifold system, after which the reactor was allowed to stand for 65 hours at ambient temperatures (23-5°C.). The internal pressure rose

Table II. Physical Properties of New Ethers Derived from Cyclic Olefins

Compd.	Structure	B.P., °C.	Refractive Index, n_D^{25}	Analytical Data	
				Calcd., %	Found, %
21		95	1.3120	C 29.76 H 0.83	29.99 0.92
22		144-145	...	C 29.83 H 1.25	29.82 1.18
23		81	<1.3	C 27.11 H 0.33	27.29 0.32

to 65 p.s.i.g. and gradually fell to <10 p.s.i.g. The excess pressure was released and the contents of the reactor were poured into an excess of water. The organic layer was removed, dried over CaSO_4 , and distilled to give 1,1,2-trifluoro-2-chloroethyl-2',2',2'-trifluoroethyl ether, 40.1 grams, b.p. 82°C ., n_D^{25} 1.3066, 61.2% of theoretical yield. ^1H NMR showed: δCH_2 4.33 (quartet); δCHF 6.18 (doublet of triplets); $J_{\text{F,CCH}_2}$ 8.5Hz; $J_{\text{F,CCH}}$ 6.5Hz; J_{HCF} 48Hz.

The following ethers were prepared in a similar manner from the appropriate alcohols and olefins in the presence of potassium hydroxide. Reaction times and yields are recorded in parentheses, followed by NMR details. Physical constants were given earlier.

1,1,2-Trifluoro-2-bromoethyl-2',2',2'-trifluoroethyl ether: $\text{CF}_3\text{CH}_2\text{OCF}_2\text{CHBr}$ **2** (40 hours) (81%) δCH_2 4.33 (quartet); δCH 6.39 (doublet of triplets); $J_{\text{F,CCH}}$ 8.5Hz; $J_{\text{F,CCH}}$ 5.5Hz; J_{HCF} 48Hz.

1,1-Difluoro-2-chloroethyl-2',2',2'-trifluoroethyl ether: $\text{CF}_3\text{-CH}_2\text{OCF}_2\text{CH}_2\text{Cl}$ **4** (72 hours) (47%) δCH_2 4.21 (quartet); δCH 3.74 (triplet); $J_{\text{F,CCH}_2}$ 8.0Hz; $J_{\text{F,CCH}}$ 9.0Hz. The lower yield is partly accounted for by the concomitant production of $\text{CH}_3\text{CH}_2\text{OCF}=\text{CHCl}$, which was recovered as $\text{CF}_3\text{CH}_2\text{OCFBr-CHClBr}$; b.p., 76°C . (26 mm. of Hg); n_D^{25} 1.4052; δCH_2 4.32 (quartet); δCH 5.94 (doublet); $J_{\text{F,CCH}_2}$ 8.0Hz; $J_{\text{F,CCH(erythro)}}$ 4.0Hz; $J_{\text{F,CCH(threo)}}$ 7.5Hz.

1,1,2-Trifluoroethyl-2',2',2'-trifluoroethyl ether: $\text{CF}_3\text{CH}_2\text{-OCF}_2\text{CH}_2\text{F}$ **5** (3 hours at 87°C .) (61%) δCF_3 76.5 (quartet of triplets); δOCF_2 87.0 (complex); δCF not recorded; δCH_2 4.20 (quartet); δCH_2 4.47 (doublet of triplets); $J_{\text{F,CCH}_2}$ 8.0Hz; $J_{\text{F,CCOCF}_2}$ 2.0Hz; $J_{\text{F,CCH}_2}$ 8.5 Hz; J_{HCF} 46.0Hz.

1,1-Difluoroethyl-2',2',2'-trifluoroethyl ether: $\text{CF}_3\text{CH}_2\text{OCF}_2\text{CH}_3$ **6** (10½ hours at 87°C .) (41%) δCF_3 77.3 (triplet of triplets); δOCF_2 72.9 (quartet of quartets); δCH_2 4.10 (quartet); δCH_3 1.75 (triplet); $J_{\text{F,CCH}_2}$ 8.0Hz; $J_{\text{F,CCOCF}_2}$ 2.0Hz; $J_{\text{F,CCH}}$ 13.0Hz. $\text{CF}_3\text{CH}_2\text{OCF}=\text{CH}_2$ was formed in the reaction mixture and was brominated to $\text{CF}_3\text{CH}_2\text{OCFBrCH}_2\text{Br}$, b.p. $145-6^\circ\text{C}$., n_D^{25} 1.4034; δCF_3 76.0 (triplet of doublets); δCF 56.9 (triplet of quartets); δCH_2 4.26 (quartet); δCH_2 4.00 (doublet); $J_{\text{F,CCH}_2}$ 8.0Hz; $J_{\text{F,CCOCF}_2}$ 2.0Hz; $J_{\text{F,CCH}_2}$ 14.0Hz.

1,1,2,3,3,3-Hexafluoropropyl-1',1',1',3',3',3'-hexafluoro-2-propyl ether: $\text{HC}(\text{CF}_3)_2\text{OCF}_2\text{CHFCF}_3$ **7** (72 hours) (76.5%) δCF_3 (i-pr) 74.9 (complex, partially resolved); δCF_3 77.0 (complex, partially resolved); δOCF_2 82.0 (complex, partially resolved); δCF 222 (complex, partially resolved); δCH (i-pr) 4.88 (septet); δCH 4.82 (complex, partially resolved). $J_{\text{F,CCH}}$ 5.5Hz; J_{FCF} 150Hz; J_{HCF} 44Hz; $J_{\text{F,CCF}}$ 10.5Hz; J_{FCCF_3} 10.5Hz; J_{FCCH} 6.5Hz; J_{FCCH} 5.5Hz.

1,1,2-Trifluoro-2-bromoethyl-1',1',1',3',3',3'-hexafluoro-2-propyl ether: $\text{HC}(\text{CF}_3)_2\text{OCF}_2\text{CHBr}$ **8** (2 hours at 90°C .) (42.5%) δCH (i-pr) 4.96 (septet); δCH 6.55 (doublet of triplets); $J_{\text{F,CCH}}$ 5.5Hz; $J_{\text{F,CCH}}$ 5.5Hz; J_{HCF} 48Hz. Some unsaturated

by-product was removed by bromination, but was not characterized further.

1,1,2-Trifluoro-2-chloroethyl-1'-trifluoromethylethyl ether: $\text{HC}(\text{CF}_3)(\text{CH}_3)\text{OCF}_2\text{CHFCI}$ **9** (20 hours) (42%) δCF_3 78.0 (complex, partially resolved); δOCF_2 84.7 (complex, partially resolved); δCF 150 (complex, partially resolved); δCH_3 1.48 (doublet); δCH (i-pr) 4.70 (complex, partially resolved septet); δCH 6.05 (complex, partially resolved doublet); $J_{\text{F,CCH}}$ 6.0Hz; $J_{\text{H,CCH}}$ 7.0Hz; J_{FCF} 100Hz; J_{HCF} 48.5Hz; $J_{\text{F,CCF}}$ 10.0Hz.

1,1,2-Trifluoro-2-bromoethyl-2',2',3',3'-tetrafluoropropyl ether: $\text{HC}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHBr}$ **10** (4½ hours) (85%) $\delta\text{CF}_2(\text{H})$ 145 (complex, partially resolved doublet); δCF_2 127 (complex, partially resolved); δOCF_2 88.9 (complex, partially resolved doublet); δCF 160 (complex, partially resolved); δCH_2 4.29 (triplet of triplets); δCHF_2 5.87 (triplet of triplets); δCH 6.34 (doublet of triplets); J_{HCF} 54Hz; J_{HCCF_2} 4.5Hz; J_{FCCCH_2} 1.5Hz; $J_{\text{F,CCH}}$ 5.0Hz; J_{HCF} 48Hz.

1,1,2-Trifluoro-2-bromoethyl-2',2',3',3',3'-pentafluoropropyl ether: $\text{CF}_3\text{CH}_2\text{CH}_2\text{OCF}_2\text{CHBr}$ **11** (28 hours) (52.5%) δCF_3 85.5 (complex, partially resolved triplet); δCF_2 126 (complex, partially resolved); δOCF_2 89.0 (complex, partially resolved); δCF 160 (doublet of triplets); δCH_2 4.34 (triplet); δCH 6.36 (doublet of triplets); $J_{\text{F,CCF}_2}$ 2.0Hz; $J_{\text{F,CCH}_2}$ 11.5Hz; $J_{\text{F,CCF}}$ 13.5Hz; $J_{\text{F,CCH}}$ 5.0Hz; J_{HCF} 47.5Hz.

1,1,2-Trifluoro-2-chloroethyl-2',2',3',3',3'-pentafluoropropyl ether: $\text{CF}_3\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHFCI}$ **12** (16 hours) (65.5%) δCF_3 85.2 (complex, partially resolved); δCF_2 126 (complex, partially resolved); δOCF_2 90.4 (complex, partially resolved doublet); δCF 156 (doublet of triplets); δCH_2 4.33 (triplet); δCH 6.07 (doublet of triplets); $J_{\text{F,CCH}_2}$ 12.0Hz; $J_{\text{F,CCF}}$ 11.5Hz; $J_{\text{F,CCH}}$ 4.0Hz; J_{HCF} 48Hz.

1,1,2-Trifluoro-2-chloroethyl-2',2',3',3',4',4'-heptafluorobutyl ether: $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHFCI}$ **13** (1½ hours at 50°C .) (66.5%) δCF_3 82.4 (complex, partially resolved triplet); $\delta\text{CF}_2(\text{CF}_3)$ 129 (complex, partially resolved); δCF_2 123 (complex, partially resolved); δOCF_2 90.3 (complex, partially resolved doublet); δCF 156 (doublet of triplets); δCH_2 4.37 (triplet of triplets); δCH 6.07 (doublet of triplets); $J_{\text{F,CCF}_2}$ 1.0Hz; $J_{\text{F,CCCF}_2}$ 9.5Hz; $J_{\text{F,CCCH}_2}$ 1.0Hz; $J_{\text{F,CCH}_2}$ 12.5Hz; $J_{\text{F,CCF}}$ 12.0Hz; $J_{\text{F,CCH}}$ 4.0Hz; J_{HCF} 48.0Hz.

2,2,2-Trifluoroethyl-pentafluorocyclobut-1-enyl ether: **21** (16 hours) (82%) $\text{C}=\text{C}$ Str 1779 cm^{-1} , δCF_3 76.5 (triplet); δCF_2 120 (complex, partially resolved); δCF 139 (complex, partially resolved); $J_{\text{F,CCH}_2}$ 8Hz; other coupling constants not measured. A 5% yield of dialkoxy cyclobutene was recovered from the reaction mixture, but was not characterized until a second experiment was performed, using 2 moles of KOH per mole of perfluorocyclobutene. This reaction was continued for 16 hours at 25°C . and gave a 60% yield of 1,2-bis(2',2',2'-trifluoroethoxy)-tetrafluoro-

cyclobut-1-ene. $\delta C=C$ Str 1761 cm^{-1} , δCF_3 76.1 (triplet); δCF_2 114.6 (singlet); $J_{F,CCH}$ 8Hz.

1,1,1,3,3,3-Hexafluoro-2-propyl-pentafluorocyclobut-1-enyl ether: 23 (20 hours) (35.5%) $C=C$ Str 1779 cm^{-1} , δCF_3 76.1 (triplet); δCF_2 121 (complex, partially resolved); δCF 136 (complex, partially resolved); δCH 4.81 (septet); $J_{F,CCH}$ 5.0Hz; no other coupling constants could be measured. Other products of the reaction were not identified.

1,1,2,2-Tetrafluoroethyl-2',2',2'-trifluoroethyl ether: $CF_3CH_2OCF_2CHF_2$ [previously prepared by Henne and Smook (5)]: δCF_3 76.4 (complex, partially resolved, triplet of triplets); δOCF_2 94.2 (complex, partially resolved); δCF_2 139 (doublet of triplets); δCH_2 4.23 (quartet); δCH 5.70 (triplet of triplets); J_{F,CCH_2} 8Hz; J_{F,CCF_2} 5.5Hz; $J_{F,CCH}$ 3Hz; J_{HCF} 53Hz.

1,1,2,3,3,3-Hexafluoropropyl-2',2',2'-trifluoroethyl ether: $CF_3CH_2OCF_2CHFCF_3$ [Previously prepared by Gubanov *et al.* (4)]: δCF_3 71.9 (triplet of triplets); δCF_3 (propyl) 77.2 (complex, partially resolved, triplet of doublets of doublets); δOCF_2 84.6 (complex, partially resolved); δCF 214 (doublet); δCH_2 4.27 (quartet); δCH 4.81 (complex, partially resolved, doublet of quartets of triplets); J_{F,CCH_2} 8Hz; $J_{F,CCOFCF_2}$ 2Hz; J_{FCF} 170Hz; $J_{F,CCH}$ 5.5Hz; J_{HCF} 43Hz; J_{HCCF_3} 5.5Hz.

1,1-Difluoro-2,2-dichloroethyl-2',2',2'-trifluoroethyl ether: $CF_3CH_2OCF_2CHCl_2$ **3.** Potassium hydroxide (40 grams, 0.6 mole, based on 85% purity) was dissolved in 250 ml. of trifluoroethanol in a 500-ml. three-necked flask. The flask was equipped with a magnetic stirring bar, cold water reflux condenser, and a sintered glass inlet tube dipping below the liquid surface. The solution was stirred, and, from a cylinder, dichlorodifluoroethylene (80 grams, 0.6 mole) was introduced. An exothermic reaction occurred. The crude reaction mixture was stirred for 12 hours at 25°C. and then poured into 2 liters of water. Separation of the heavy, organic layer, followed by drying and distillation, afforded 1,1-difluoro-2,2-dichloroethyl-2',2',2'-trifluoroethyl ether, b.p. 109°C., n_D^{25} 1.3439; 56.7 grams (40.5% of theoretical yield). A run carried out with the same quantities of reactants in a pressure vessel at 50°C. for 2 hours gave a 74% yield of the ether. δCH_2 4.33 (quartet); δCH 5.87 (triplet); J_{F,CCH_2} 8.0Hz; $J_{F,CCH}$ 5.0Hz. From the residue of the pressure reaction, a higher-boiling material was isolated in low yield. This was $(CF_3CH_2O)_2CFCHCl_2$, b.p. 155°C., n_D^{25} 1.3511; δCH_2 4.25 (quartet); δCH 5.76 (doublet); J_{F,CCH_2} 8.0Hz; J_{FCCH} 4.5Hz.

Reaction of Decafluorocyclohexene with 2,2,2-Trifluoroethanol: Decafluorocyclohexene (52.4 grams, 0.2 mole) was mixed in a 250-ml. three-necked flask with 2,2,2-trifluoroethanol (20 grams, 0.2 mole). No reaction occurred in the absence of potassium hydroxide. A solution of potassium hydroxide (11.2 grams, 0.17 mole) in 40 grams of trifluoroethanol was added slowly to the reaction flask. The temperature in the flask rose to 35°C. and declined gradually over a 3-hour period to 22°C. The mixture was stirred under nitrogen overnight, then poured into 75 ml. of water. The lower layer was separated and dried. Distillation gave a forerun of 8.9 grams of unreacted olefin, a fraction (i) boiling at 115–9°C. (40.6 grams) and a fraction (ii) boiling at 156–61°C. (4.0 grams). Gas chromatography showed (i) to consist of three components: the two unsaturated isomers, 14 and 15, together with 16, present in 65, 28, and 7% (area) concentrations, respectively. The last compound was removed by refluxing the mixture with aqueous potassium hydroxide for 3 hours. Redistillation

of this fraction gave 36.5 grams (65% of theoretical yield) of a mixture boiling at 117–8°C., containing about 63% 14 and 37% 15. These were separated by preparative scale gas chromatography. The first to elute was the 3-cyclohexene isomer 15 ($C=C$ Str 1742 cm^{-1}), followed by the 1-isomer 14 ($C=C$ Str 1718 cm^{-1}).

2,2,2-Trifluoroethyl-nonafluorocyclohex-1-enyl ether 14 δCF_3 77 (triplet); δCF_2 118 (C-3); δCF_2 120 (C-6); δCF_2 135 (C-4, C-5); δCF 155; δCH_2 4.53 (quartet); $J_{F,CCH}$ 7.5Hz; a coupling J_{HCOCCF} 1.5Hz was also noted.

2,2,2-Trifluoroethyl-nonafluorocyclohex-2-enyl ether 15 δCF_3 77 (triplet); δCF_2 118 (C-4); δCF_2CF 131 (C-1; C-6); δCF 134 (C-5); δCF 150 (C-2); δCF 157 (C-3); δCH_2 4.30 (quartet); $J_{F,CCH}$ 8.0Hz.

A third fraction, accounting for approximately 5% of the starting olefin, was obtained. When 2 moles of KOH were used with one equivalent of decafluorocyclohexene in trifluoroethanol, a substantial amount of dialkoxylefin could be obtained. GLC examination showed four components present in relative area amounts of 39, 35, 15 and 11%. These were separated by preparative scale gas chromatography, and each component eluted in the order in which it is characterized below.

1,2-Bis(2',2',2'-trifluoroethoxy)-octafluorocyclohex-1-ene 17 $C=C$ Str 1669 cm^{-1} , δCF_3 75.8 (triplet); δCF_2 114.8 (C-3; C-6); ΔCF_2 134.3 (C-4; C-5); δCH_2 4.48 (quartet); J_{FCCH} 7.5Hz.

1,6-Bis(2',2',2'-trifluoroethoxy)-octafluorocyclohex-1-ene 18 $C=C$ Str 1712 cm^{-1} , δCF_3 75.8 (triplet, with further splitting); δCF_2 117.5; 118.3; (two peaks) (C-3); δCF 128.3 (C-6); δCF_2 130.1 (C-4); δCF_2 132.0; 133.8 (two peaks) (C-5); δCF 154.7 (C-2); δCH_2 —two overlapping quartets at 4.32 and 4.52, with the downfield quartet further split by the tertiary fluorine. J_{FCCH} 8.0Hz.

1,3-Bis(2',2',2'-trifluoroethoxy)-octafluorocyclohex-1-ene 19 $C=C$ Str 1706 cm^{-1} , δCF_3 75.8 (two superimposed triplets, with further splitting); δCF_2 115.5; 117.8 (two peaks) (C-6); δCF 128.5 (C-3); δCF_2 130.1 (C-5); δCF_2 132.8; 134.0 (two peaks) (C-4); δCF 147.1 (C-2); δCH_2 —two overlapping quartets at 4.32 and 4.52, with the downfield quartet further split by the tertiary fluorine. $J_{FCCH} \cong 8.0$ Hz.

1,2,3-Tris(2',2',2'-trifluoroethoxy)-heptafluorocyclohex-1-ene 20 $C=C$ Str 1675 cm^{-1} , δCF_3 76.0 (complex, partially resolved); δCF_2 114.5; 117 (two peaks) (C-6); δCF 126.2 (C-3); δCF_2 130.2 (C-5); δCF_2 133; 135 (two peaks) (C-4); δCH_2 —complex structure of overlapping quartets.

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