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## THE SYNTHESIS OF FLUOROETHER-FLUOROSILICONE HYBRID POLYMERS

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### SUMMARY

The replacement of the fluorocarbon segment in the general class of hybrid fluorocarbon-fluorosilicones by fluoroether units was investigated in order to improve low temperature properties without sacrificing high temperature performance. The effects of the co-reactant halogens (bromine and iodine) and metallic fluorides (potassium fluoride and cesium fluoride) on the product yields in the syntheses of the requisite  $\alpha, \omega$ -dihalo-F-ether intermediates [1] from the corresponding acyl or diacyl fluorides were studied. While a better yield was obtained with bromine than with iodine, the iodoperfluoroethers produced superior yields in the subsequent ethylene addition reactions, as expected. Potassium fluoride was preferable to cesium fluoride in the synthesis of the iodo-F-ethers, since cesium fluoride effects decomposition of the ethers.

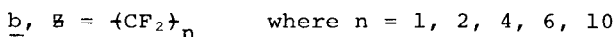
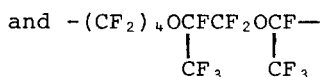
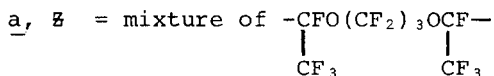
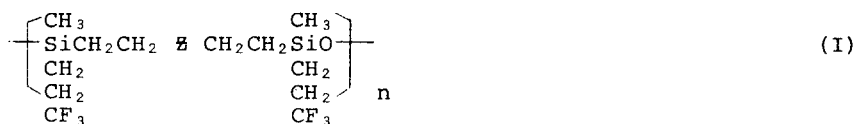
### INTRODUCTION

An earlier brief study [2] in the area of thermally stable reversion resistant hybrid fluoroether-fluorosilicone polymers showed that polymers having the general structure Ia possess

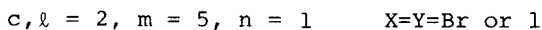
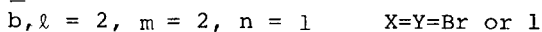
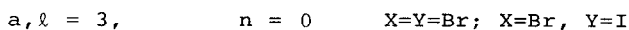
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thermal and oxidative stability which is comparable to that of the hybrid fluorocarbon-fluorosilicones Ib [3] while surpassing Ib in terms of low temperature flexibility.



It was of interest to demonstrate the generality of these results for other more synthetically accessible fluoroether precursors. In the course of this study we have synthesized a variety of  $\alpha, \omega$ -dihalo-F-ethers and -diethers (II) and converted them to hybrid fluoroether-fluorosilicone polymers.

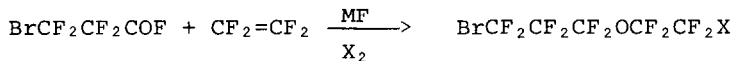


## RESULTS AND DISCUSSION

### Fluoroether Synthesis

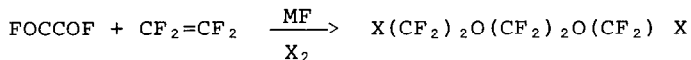
The first step of the synthesis, preparation of the  $\alpha, \omega$ -dihalo-F-ethers, was based on a method reported by Evans, *et al.* [4] which involves the reaction of a perhaloacyl fluoride with a metal fluoride, olefin, and a halogen to produce  $\alpha$ -halo-fluoroethers.

## SCHEME I



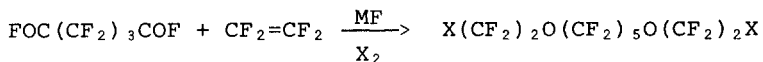
IIIa, X = Br

b, X = I



IVa, X = Br

b, X = I



We have shown that a similar reaction utilizing an  $\omega$ -halo-F-acyl fluoride or an  $\alpha,\omega$ -F-diacyl fluoride and tetrafluoroethylene leads to the formation (Scheme I) of  $\alpha,\omega$ -dihalo-F-ethers and -diethers, respectively, in moderate yields (Table I)<sup>†</sup>. A straight-forward synthesis of  $\omega$ -bromo-F-alkane carboxylic acids was already available [5]. Treatment of 3-bromo-F-propanoic acid with phosphorous pentachloride produced 1-bromo-F-propanoyl chloride in a 73% distilled yield. This material was readily converted by anhydrous potassium fluoride in diglyme to the corresponding acyl fluoride (95% yield). Two difunctional fluorocarbon acids were incorporated into the study as well, inasmuch as these are precursors to diethers. F-glutaryl chloride is commercially available, and readily converted (as described above) to F-glutaryl fluoride (>95% yield). Oxalyl chloride was of special interest because it is an inexpensive starting material.

The conversion of oxalyl chloride to oxalyl fluoride in 60% yield has been reported using sodium fluoride [6]. We have found that reaction with sodium fluoride slurried with acetonitrile resulted in a 66% isolated yield, but that potassium fluoride in acetonitrile or diglyme resulted in only about 10% yields. This is to be contrasted to the nearly quantitative yields obtained in the previously described exchange reactions involving 1-bromo-

<sup>†</sup> No attempt was made to recover unreacted starting material, or in the case of the diacyl fluorides, those products in which only one acyl fluoride was converted to an ether linkage.

TABLE 1

Synthesis of  $\alpha,\omega$ -Dihalo-F-Ethers

<u>Acyl Fluoride</u>	<u>MF</u>	<u>Halogen</u>	<u>Solvent</u>	<u>Ether</u>	<u>Isolated Yield (a)</u>
$\text{BrCF}_2\text{CF}_2\text{COF}$	CsF	$\text{Br}_2$	Diglyme <sup>b</sup>	$\text{BrCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{Br}$	72%
$\text{BrCF}_2\text{CF}_2\text{COF}$	CsF	$\text{I}_2$	Tetraglyme <sup>c</sup>	$\text{BrCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{I}$	58%
$\text{FCOCOF}$	CsF	$\text{Br}_2$	Diglyme <sup>b</sup>	$\text{Br}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{Br}$	59%
$\text{FCOCOF}$	KF	$\text{I}_2/\text{ICl}$	Diglyme <sup>b</sup>	$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}$	44%
$\text{FCO}(\text{CF}_2)_3\text{COF}$	CsF	$\text{Br}_2$	Diglyme <sup>b</sup>	$\text{Br}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{Br}$	59%
$\text{FCO}(\text{CF}_2)_3\text{COF}$	KF	$\text{I}_2$	Diglyme <sup>b</sup>	$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$	47%

a. Based on starting material

b. Ansul Ether 141, bis(2-methoxyethyl) ether

c. Ansul Ether 181, bis[2-(2-methoxyethoxy)ethyl] ether

F-propanoyl chloride and F-glutaryl chloride. Although no attempt was made to analyze the complete reaction mixture, fragmentation and/or further reaction of oxalyl fluoride with KF is probably contributing to the low yields obtained.

It was found, as expected on the basis of the previously cited work [4], that conversion of the acyl fluorides to  $\alpha,\omega$ -dihalo-F-ethers proceeded in better yield with bromine than with  $I_2$  as the co-reactant (Table I). Yields in the latter reaction could be increased slightly by the addition of iodine monochloride in conjunction with iodine. A Lewis acid, ferric bromide (generated *in situ*) was tested in a single reaction in order to evaluate the effect it could have upon the reaction course. It had been proposed previously [4] that a halogen-olefin  $\pi$  complex or halonium ion pair might be involved as an intermediate in the ether-forming step. The isolated yield of compound Va was virtually identical to that obtained in a similar reaction without ferric bromide (60.5% vs. 61%), but the relative amount of 1,2 dibromo-F-ethane produced increased by 19%, although it should be noted that the reagent ratios and reaction times were slightly different. Similarly, a mixture of aluminum and aluminum iodide in a reaction mixture of F-glutaryl fluoride/potassium fluoride/tetrafluoroethylene/iodine/diglyme resulted in a reduced yield of Va (ca. 12%), but a greatly increased conversion to 1,2-diiodo-F-ethane. Consequently, it appears that the Lewis acids which we studied do not favor formation of an "olefin-halogen" complex which is selectively reactive with the intermediate fluoroalkoxides.

Solvent effects were shown to be significant by conducting the reaction of IIIa with  $Br_2$  in three different solvents (Table II). Diglyme was found to be superior to either dimethylformamide or acetonitrile as a reaction medium in terms of isolated yield, although the time required for complete reaction as judged by discharge of the bromine color was longer than that required when dimethylformamide was employed.

Although cesium fluoride was found to be satisfactory for the synthesis of the  $\alpha,\omega$ -dibromo-F-ethers, IIIa, IVa, and Va, the low yields encountered when the reaction was extended to the corresponding iodoethers IIIb, IVb, and Vb were puzzling. The

TABLE II

Solvent Effects on the Reaction of  $\text{BrCF}_2\text{CF}_2\text{COF}/\text{CsF}/\text{CF}_2=\text{CF}_2/\text{Br}_2$ 

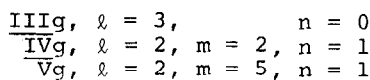
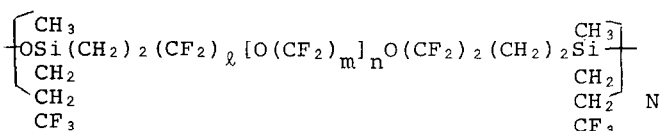
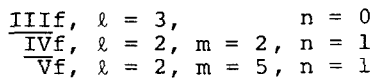
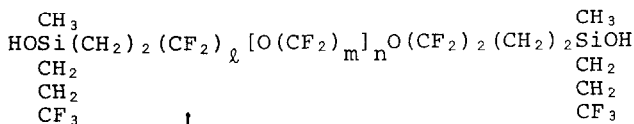
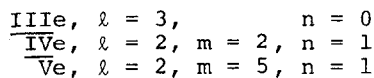
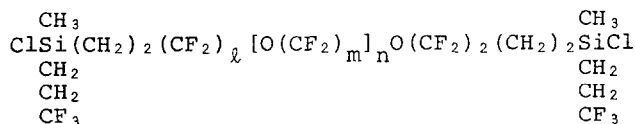
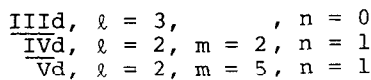
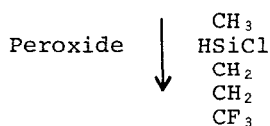
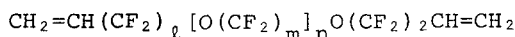
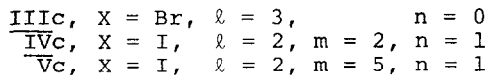
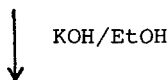
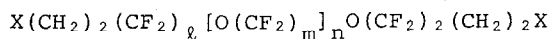
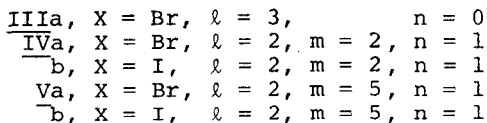
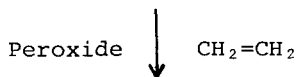
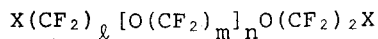
Rxn TIME (DAYS)	Solvent	Isolated Yield of <u>IV</u> , %	$\text{CsF}/$ $\text{BrCF}_2\text{CF}_2\text{COF}$	$\text{Br}_2/$ $\text{BrCF}_2\text{CF}_2\text{COF}$	TFE, (Psi)
9	Aceto- nitrile	33%	1.20/1	1.16/1	10
0.67	Dimethyl- formamide	44%	0.98/1	1.08/1	5
4	Diglyme	61%	1/1	1.22/1	16
4	Diglyme	72%	1.72/1	1.90/1	15

yield was found to decrease with elapsed reaction time after a certain minimum time, and the product mixture was found to contain 1,2-diiodo-F-ethane in addition to low molecular weight oligomers of tetrafluoroethylene and unidentified fluorocarbons. A separate reaction was conducted, in which Vb was treated with all the components of the original reaction mixture with the exception of iodine; after one week, no traces of the ether were detected by glc analysis, only 1,2-diiodo-F-ethane, tetrafluoroethylene oligomers, and unidentified fluorocarbons were found. The solid residue consisted of a mixture of iodide and fluoride salts. In contrast, a similar treatment of Vb with potassium fluoride caused no detectable decomposition, and the bulk of ether Vb was recovered. In addition, formation of the side reaction product F-ethyl iodide is reduced by about one-third when potassium fluoride is employed rather than cesium fluoride.

A mixture of sodium fluoride/iodine/tetrafluoroethylene was found to be totally ineffective in the conversion of oxalyl chloride to IVb either in diglyme, or in a diglyme/acetonitrile reaction medium. On the other hand, substitution of potassium fluoride for sodium fluoride did effect the desired reaction, although the yield was slightly lower than that achieved in a stepwise sequence, in which oxalyl fluoride was isolated before reaction with  $\text{KF}/\text{CF}_2=\text{CF}_2/\text{I}_2$  (20% vs. 26%, respectively). This may be due to the formation of a potassium chloride coating on the surface of the potassium fluoride in the direct synthesis.

It was demonstrated that in the synthesis of the iodoethers, IVb and Vb, screening the reaction mixture from light with aluminum foil is advantageous in that the formation of 1,2-diiodo-F-ethane is nearly eliminated. Although a slightly better yield (46% vs. 41%) of Vb could be obtained when a 3/1 iodine monochloride/iodine mixture was used as a reactant as opposed to iodine alone, a large amount of the iodine monochloride is consumed in the reaction with F-ethylene, a reaction which is of small consequence in a screened experiment in which iodine is the halogen source.

## SCHEME 2



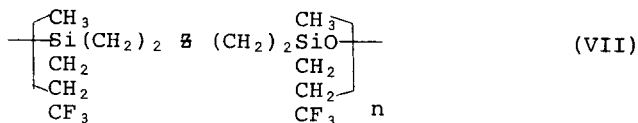


### Preparation of Polymers

The  $\alpha,\omega$ -dihalo-F-ethers were converted to polymers as shown in Scheme 2 [2]. The initial step in the sequence, ethylene insertion, proceeded in nearly quantitative yields for the  $\alpha,\omega$ -diiodo-F-ethers IVb and Vb. Reaction with the  $\alpha,\omega$ -dibromo-F-ether IIIa, on the other hand, was less clean-cut. Reaction at 130-135°C, 65 psig ethylene produced an unacceptably high level of high boiling products, presumably those in which multiple insertions of ethylene have occurred. Similar results were obtained at 45 psig, while reaction at 20 psig gave a reasonable conversion to the desired 1:1:1 ethylene:  $\alpha,\omega$ -dihalo-F-ether and -diether adducts. Intermediate products (1:1 adducts) were recycled. The dienes (IIIId, IVd, and Vd) were obtained in good yield (90, 91, and 88% ) via dehydrohalogenation in alcoholic potassium hydroxide. Peroxide-catalyzed silylation of the dienes proceeded satisfactorily. Careful distillation through a glass helices-packed column in an all glass apparatus was necessary to produce monomers of the required purity. In a monomer similar to that described previously [3] diethyl ether solutions of the chlorosilanes were hydrolyzed in aqueous sodium bicarbonate, and then polymerized by tetramethylguanidine-trifluoroacetic acid catalyzed bulk polymerization. Glass transition temperatures of the resulting polymers were determined by Differential Scanning Calorimetry (DSC, Table III). It is of interest to compare these results with those obtained earlier [2]. The lowest glass transition temperatures are exhibited by the polymers containing the most unsymmetrical fluoroether segments, even though the difluoromethylene to oxygen ratio is comparatively high in these molecules. Thermal gravimetric analysis provides a comparison of the oxidative and thermal stability of the raw polymers (Table IV) with that of the parent polymer. In general, the differences are quite small, indicating that it is possible to substitute a fluoroether segment for the fluorocarbon segment within the hybrid fluorocarbon-fluorosilicone polymer with substantially no loss of thermal and oxidative performance, while significantly extending low temperature capabilities.

TABLE III

Glass Transition Temperature (DSC Scan at 10°C/MIN)



POLYMER	B	Tg (DSC), °C	CF <sub>1,2</sub> /O
VIIa	-CF <sub>2</sub> CF <sub>2</sub> -	-26°	--
b	-(CF <sub>2</sub> ) <sub>3</sub> O(CF <sub>2</sub> ) <sub>2</sub> -	-39°	5/1
c	-(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> -	-40°	3/1
d	-(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub> -	-52°	4.5/1
e	mixture of $\begin{array}{c} \text{-CFO(CF}_2\text{)}_5\text{OCF-} \\   \quad   \\ \text{CF}_3 \quad \text{CF}_3 \end{array}$	-47°	4.5/1
	and $\begin{array}{c} \text{-(CF}_2\text{)}_4\text{OCF}_2\text{OCF-} \\   \quad   \\ \text{CF}_3 \quad \text{CF}_3 \end{array}$		

TABLE IV

Thermal Gravimetric Analysis (10°C/MIN)

POLYMER	Temperature At 10% wt. loss, °C		Temperature At 50% wt. loss, °C	
	AIR	NITROGEN	AIR	NITROGEN
IIIg	310°	--	355°	--
IVg	330°	412°	375°	497°
Vg	330°	450°	380°	502°
Ib (n=2)	324°	474°	442°	504°

## EXPERIMENTAL

All boiling points are uncorrected. Gas chromatography was carried out on a Hewlett-Packard Model 5750 instrument equipped with a 12' x 0.25" stainless steel column packed with 20% DOW CORNING® FS-1265 (10,000 cs.) on 100-120 mesh Chromosorb P AW (DMCS treated). The  $^1\text{H}$  resonance spectra were obtained on a Varian A-60 NMR spectrometer with tetramethylsilane as an internal standard ( $\delta=0\text{ppm}$ ). The  $^{19}\text{F}$  resonance spectra were measured on a Varian high resolution NMR spectrometer operating at 56.4 MHz. Chemical shifts were determined in parts per million with the use of  $\text{CCl}_3\text{F}$  as an internal standard ( $\delta=0\text{ppm}$ ). IR spectra were determined on a Perkin-Elmer Model 521 Grating Infrared Spectrophotometer. Glass transition temperatures and Thermal Gravimetric Analyses were obtained using a DuPont Differential Scanning Calorimeter Cell and a DuPont 950 Thermogravimetric Analyzer, respectively, each in combination with a DuPont 900 Differential Thermal Analyzer.

Those reactions which involved the use of water sensitive reagents were conducted in oven-dried glassware under an inert atmosphere. Solvents were dried by distillation from  $\text{P}_2\text{O}_5$  ( $\text{CH}_3\text{CN}$ ) or  $\text{LiAlH}_4$  (diglyme) or by passage through a column of activated Molecular Sieves (DMF, diglyme). Standard precautions were taken to avoid the introduction of moisture during manipulations.

Preparation of  $\text{CCl}_3\text{CF}_2\text{CF}_2\text{Br}$ 

Telomerization of  $\text{CF}_2=\text{CF}_2$  in the presence of  $\text{CCl}_3\text{Br}$  gave  $\text{CCl}_3\text{CF}_2\text{CF}_2\text{Br}$  in a yield greater than 75% [7].

Preparation of  $\text{BrCF}_2\text{CF}_2\text{COOCH}_3$ 

Following the reported method [4], the ester,  $\text{BrCF}_2\text{CF}_2\text{COOCH}_3$ , was prepared in an average of 75% yield from  $\text{BrCF}_2\text{CF}_2\text{CCl}_3$ .

TABLE V

## ELEMENTAL ANALYSES OF FLUOROETHERS

COMPOUND (all n.c.)	FORMULA	Calc'd %						Found %					
		C	H	F	Br	I	C	H	F	Br	I		
Br(CF <sub>2</sub> ) <sub>3</sub> O(CF <sub>2</sub> ) <sub>2</sub> Br	C <sub>5</sub> F <sub>10</sub> Br <sub>2</sub> O	14.1	-	44.7	36.6	-	14.1	-	46.7	34.8	-		
CH <sub>2</sub> =CH(CF <sub>2</sub> ) <sub>3</sub> O(CF <sub>2</sub> ) <sub>2</sub> CH=CH <sub>2</sub>	C <sub>9</sub> H <sub>6</sub> F <sub>10</sub> O	33.8	1.89	-	-	-	34.0	1.91	-	-	-		
Br(CF <sub>2</sub> ) <sub>3</sub> O(CF <sub>2</sub> ) <sub>2</sub> I	C <sub>5</sub> F <sub>10</sub> BrIO	12.7	-	40.2	16.9	26.8	13.2	-	40.1	14.9	26.1		
Br(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> Br	C <sub>6</sub> F <sub>12</sub> Br <sub>2</sub> O <sub>2</sub>	14.7	-	46.3	32.5	-	14.8	-	46.2	32.2	-		
I(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> I	C <sub>6</sub> F <sub>12</sub> I <sub>2</sub> O <sub>2</sub>	12.3	-	43.3	-	39.1	12.0	-	41.7	-	39.1		
I(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> - (CH <sub>2</sub> ) <sub>2</sub> I	C <sub>10</sub> H <sub>8</sub> F <sub>12</sub> I <sub>2</sub> O <sub>2</sub>	18.7	1.26	35.5	-	-	19.0	1.68	35.1	-	-		
CH <sub>2</sub> =CH(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> - CH=CH <sub>2</sub>	C <sub>10</sub> H <sub>6</sub> F <sub>12</sub> O <sub>2</sub>	31.1	1.57	59.1	-	-	31.1	1.60	59.0	-	-		
Br(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub> Br	C <sub>9</sub> F <sub>18</sub> Br <sub>2</sub> O <sub>2</sub>	16.8	-	53.3	24.9	-	16.9	-	54.0	25.0	-		
I(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub> I	C <sub>9</sub> F <sub>18</sub> I <sub>2</sub> O <sub>2</sub>	14.7	-	46.5	-	34.5	14.7	-	47.0	-	34.3		
CH <sub>2</sub> =CH(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub> - CH=CH <sub>2</sub>	C <sub>13</sub> H <sub>6</sub> F <sub>18</sub> O <sub>2</sub>	29.1	1.12	63.8	-	-	29.4	1.12	63.2	-	-		

Preparation of  $\text{BrCF}_2\text{CF}_2\text{COCl}$  (n.c.)a. From  $\text{BrCF}_2\text{CF}_2\text{COOMe}$ 

To a warm solution of 216 g (5.4 moles) of NaOH in one liter of water was added 863 g (3.6 moles) of  $\text{BrCF}_2\text{CF}_2\text{CO}_2\text{Me}$ , at room temperature overnight. Methanol was removed through a Vigreux column at minimum pressure and the aqueous residue was treated cautiously with 530 g (5.4 moles) of concentrated  $\text{H}_2\text{SO}_4$ . The heavy organic layer, 918 g, was separated and extracted with ether. The aqueous layer was extracted continuously with ether for three days. The combined ether extracts were dried (Drierite) and devolatilized to yield 830 g of a liquid product, which was added to 900 g (4.33 moles) of  $\text{PCl}_5$  contained in a three liter, three-necked flask. After standing at room temperature overnight, the reaction mixture was distilled through a Vigreux column to a pot temperature of  $100^\circ\text{C}$ . The distillate was fractionated through a 36" spinning band column to yield 634.7 g (2.61 moles = 72.5%) of  $\text{BrCF}_2\text{CF}_2\text{COCl}$ , b.p.  $66.5 - 69.5^\circ\text{C}$ . The IR spectrum is identical to that of an authentic sample with absorptions at  $1800\text{ cm}^{-1}$  (C=O) and  $1250-900\text{ cm}^{-1}$  (C-F). The mass spectrum of the material exhibits a molecular ion at  $m/e = 242$ ,  $m/e = 207$  ( $\text{M}^+-\text{Cl}$ ),  $m/e = 163$  ( $\text{M}^+-\text{Br}$ ), and  $m/e = 179$  ( $\text{M}^+-\text{COCl}$ ).

b. From  $\text{BrCF}_2\text{CF}_2\text{CCl}_3$  via  $\text{BrCF}_2\text{CF}_2\text{COOH}$ 

A three liter, three-neck flask fitted with a mechanical stirrer, one liter isobaric dropping funnel, and water-cooled condenser vented to a dry ice/acetone-cooled trap was heated thoroughly with a hot air gun and swept with dry nitrogen. After cooling, it was charged with 9 g of  $\text{Hg}_2\text{SO}_4$ , 45 g of  $\text{HgSO}_4$ , and 900 g (3 moles) of  $\text{Cl}_3\text{CCF}_2\text{CF}_2\text{Br}$ . About 900 ml. of 30% fuming sulfuric acid was added rapidly dropwise to the stirred solution, and the mixture was maintained at about  $115^\circ$  for 76 hours.

The dark reaction mixture was cooled to room temperature, and the salt was filtered off. The filtrate was added dropwise to ice water contained in a five liter flask fitted with a stirrer and cooled in an ice bath. About 400 g of a heavy

organic liquid separated and was dried over Drierite; the aqueous phase was continuously extracted with ether for four days. The ether extract was dried over Drierite, and the ether was stripped off. The residue was combined with the organic layer to give a total of 450 g of crude acid (67% yield). The crude acid was converted to  $\text{BrCF}_2\text{CF}_2\text{COCl}$  following the procedure described in Part (a).

Preparation of  $\text{BrCF}_2\text{CF}_2\text{COF}$  (n.c.)

A pre-dried flask was purged with dry  $\text{N}_2$  and loaded with anhydrous KF (300 g, 5.2 mole, dried at  $200^\circ\text{C}/0.08$  mm for 24 hrs.) and diglyme (200 ml, distilled from  $\text{LiAlH}_4$ ). The slurry was heated to a mantle temperature of  $155 \pm 5^\circ\text{C}$  while  $\text{BrCF}_2\text{CF}_2\text{COCl}$  (205 g, 0.84 mole) was added dropwise. A  $\text{N}_2$  sweep was employed to remove the product,  $\text{BrCF}_2\text{CF}_2\text{COF}$  (118.4 g, 0.80 mole), which collected in a cold trap in a 95% yield. The infrared spectrum contains absorptions at  $1870\text{ cm}^{-1}$  (C=O) and  $1280\text{--}900\text{ cm}^{-1}$  (C-F). The mass spectrum shows a molecular ion at  $m/e = 226$ ,  $m/e = 207$  ( $\text{M}^+-\text{F}$ ),  $m/e = 179$  ( $\text{M}^+-\text{COCl}$ ), and  $m/e = 163$  ( $\text{M}^+-\text{Br}$ ).

Preparation of  $\text{FOC}(\text{CF}_2)_3\text{COF}$

In a manner similar to that described above, the title compound was prepared in 95% yield. The infrared spectrum contains significant absorptions at  $1900\text{ cm}^{-1}$  (C=O) and  $1300\text{--}900\text{ cm}^{-1}$  (C-F). The mass spectrum exhibits a molecular ion at  $m/e = 225$  ( $\text{M}^+-\text{F}$ ),  $m/e = 197$  ( $\text{M}^+-\text{COF}$ ), and  $m/e = 169$  ( $\text{M}^+ - \text{C}_2\text{O}_2\text{F}$ ).

Preparation of  $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{Br}$ , IVa

A heavy wall ampoule was charged with CsF (163 g, 1.08 mole) which was dried for 60 hours at 0.02 mm Hg and a mantle temperature of  $200^\circ\text{C}$ . After cooling, the ampoule was loaded with diglyme (908 g), which had been distilled from  $\text{LiAlH}_4$ ,  $\text{Br}_2$  (140 g, 0.88 mole), and  $\text{BrCF}_2\text{CF}_2\text{COF}$  (140 g, 0.62 mole). The mixture was stirred with a magnetic stirrer and pressurized to 15 psi with  $\text{CF}_2=\text{CF}_2$  for 96 hours. The contents of the ampoule were poured into ice water (1000 ml), and the lower layer washed

with 5%  $\text{NaHCO}_3$  (500 ml). Distillation gave  $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{Br}$  (189 g, 72% yield), b.p. 111-112°C,  $n_D^{25} = 1.3288$ ; IR showed absorption at 1100 and 1250  $\text{cm}^{-1}$  (C-F),  $\text{F}^{19}$  nmr showed signals centered at 63.4 ppm and 69.1 ppm ( $A = 4.0$ ,  $\text{CF}_2\text{Br}$ ), 81.4 ppm and 86.0 ppm ( $A = 4.0$ ,  $\text{CF}_2\text{O}$ ) and 122 ppm ( $A = 2.0$ ,  $-\text{C}-\text{CF}_2-\text{C}-$ ).

#### Preparation of $\text{BrCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{Br}$ , Va

In a similar manner, reaction of FOCCOF,  $\text{Br}_2$ , CsF, and  $\text{CF}_2=\text{CF}_2$  in tetraglyme gave a 31% yield of Va.

The IR spectrum contained absorbing at: 1320-1100  $\text{cm}^{-1}$  ( $\text{CF}_2$ ) and 940  $\text{cm}^{-1}$  (C-O-C). The mass spectrum shows a molecular ion at  $M^+ = 490$  (2 Br atoms confirmed from isotope ratios) and a fragmentation pattern consistent with the suggested structure. The  $\text{F}^{19}$  nmr spectrum is comprised of three triplets,  $\delta = 69.5$  ( $A = 3.9$ ),  $\delta = 86.7$  ( $A = 4.1$ ), and  $\delta = 89.3$  ( $A = 4.1$ ).

#### Preparation of $\text{Br}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{Br}$ , VIA

A 600 ml. heavy wall ampoule was loaded with 23 g (151 mmole) of powdered CsF, which was dried in vacuo (180°C/0.02 mm). The vacuum was broken with dry nitrogen after the ampoule had cooled, and 250 ml. of dry diglyme was injected, followed by 18.3 g (75 mmole) of perfluoroglutaryl fluoride. The ampoule was shaken briefly, and then cooled in dry ice while 30.5 g (190.5 mmole) of  $\text{Br}_2$  was injected. After warming to room temperature the reaction vessel was pressurized to 15 psi with  $\text{CF}_2=\text{CF}_2$  and shaken for 2 days on a wrist action shaker.

The reaction mixture was poured into anhydrous methanol, and then hydrolyzed with ice water. Glc analysis of the organic products indicated the presence of  $\text{BrCF}_2\text{CF}_2\text{Br}$ ,  $\text{BrCF}_2\text{CF}_2\text{O}(\text{CF}_2)_4\text{CO}_2\text{CH}_3$  (19%), and  $\text{BrCF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{Br}$  (59%). About 20 g of pure  $\text{Br}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{Br}$  was isolated by fractional distillation (b.p. = 50°/4 mm).

The infrared spectrum features absorptions at 1350-1000  $\text{cm}^{-1}$  (C-F) and 940  $\text{cm}^{-1}$  (C-O), and the  $\text{F}^{19}$  nmr spectrum consists of five multiplets:  $\delta = 70$  ppm ( $\text{BrCF}_2-$ ,  $A = 3.9$ ); 84 ppm ( $-\text{OCF}_2\text{CF}_2\text{CF}_2-$ ,  $A = 4.1$ ); 87 ppm ( $\text{BrCF}_2\text{CF}_2\text{O}-$ ,  $A = 4.0$ ); 124 ppm ( $-\text{OCF}_2\text{CF}_2\text{CF}_2-$ ,  $A = 2.0$ ); 128 ppm ( $-\text{OCF}_2\text{CF}_2\text{CF}_2-$ ,  $A = 2.0$ ).

The mass spectrum is in agreement with the assigned structure:  $m/e = 640$  (isotope ratios confirm two Br atoms) ( $M^+$ ), 511 ( $M^+ - CF_2Br$ ), 445 ( $M^+ - OCF_2CF_2Br$ ), 179 ( $CF_2CF_2Br$ ), 125 ( $C_5F_{10}^{++}$ ).

Preparation of  $BrCF_2CF_2CF_2OCF_2CF_2I$ , IVb

About 30.4 g (200 mmole) of CsF was dried, in vacuo (200°/0.025 mm) in a 600 ml. heavy wall ampoule. After cooling, the ampoule was charged with 35.4 g (156 mmole) of  $BrCF_2CF_2COF$ , 70 g (276 mmole) of powdered iodine, and 300 ml. of dry tetraglyme. The reaction vessel was covered with aluminum foil and shaken for about 3 days under 15 psi of  $CF_2=CF_2$ . The mixture was poured into aqueous thiosulfate solution, yielding 87 g of a heavy oily yellow liquid which was dried ( $MgSO_4$ ) and strip-distilled in vacuo to give 43 g (58% yield) of  $BrCF_2CF_2CF_2OCF_2CF_2I$ . IR:  $1360-1060\text{ cm}^{-1}$  ( $CF_2$ ), 227 ( $M^+ = CF_2CF_2I$ ). The  $F^{19}$  nmr spectrum consists of a series of multiplets:  $\delta = 63.5$ , 64 ( $-CF_2Br$ ,  $-CF_2I$ ,  $A = 4.0$ ), 81.8, 85 ( $-CF_2OCF_2-$ ,  $A = 1.9$ , 2.1), and 122 ( $-C-CF_2-C-$ ,  $A = 2.0$ ).

Synthesis of  $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$ , Vb

a. A heavy wall ampoule was loaded with 130 g (2.24 mole) of KF and heated in vacuo (260°/0.25 mm) for 2 days. After cooling, 67.6 g of FOCCOF (0.72 mole) was transferred along with 1.21 mole of ICl in diglyme, followed by 308 g (1.21 mole) of crushed  $I_2$  in diglyme (total 907 g). The reaction vessel was covered with foil and stirred at 40 psi  $CF_2=CF_2$  for 123 hours, after which it was poured into an ice water solution of  $Na_2S_2O_3$ . The organic layer was distilled to give 184 g of pure  $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$  (44% yield), b.p. 58°/6 mm. The IR spectrum is nearly identical to that of  $Br(CF_2)_2O(CF_2)_2O(CF_2)_2Br$  ( $C-F = 1320-1100\text{ cm}^{-1}$ ,  $C-O-C = 920\text{ cm}^{-1}$ ) and the mass spectrum reveals a molecular ion at  $m/e = 586$  and fragment ions at  $m/e = 459$  ( $M^+ - I$ ), 293 ( $M^+ - CF_2OCF_2CF_2I$ ), and 227 ( $-CF_2CF_2I$ ).

The  $F^{19}$  nmr spectrum agrees with the assigned structure:  $\delta = 64.4$  (m,  $CF_2I$ ,  $A = 3.9$ );  $\delta = 86.5$ , 101 (m,  $OCF_2$ ,  $A = 4.1$ , 4.0).



b. Reaction of ClCOCOCl with KF/CF<sub>2</sub>=CF<sub>2</sub>/I<sub>2</sub>

A heavy-wall glass ampoule containing a magnetic stirring bar was loaded with 138 g (2.37 mole) of finely powdered anhydrous KF, and heated in vacuo (250-300°C/0.15 mm) for 4 days. After it had cooled, 59.4 g (0.47 mole) of oxalyl chloride was distilled (in vacuo) into the ampoule. A mixture of anhydrous diglyme (810 ml.), 307 g (1.21 mole) of finely powdered I<sub>2</sub>, and 15.8 g (0.1 mole) of ICl was introduced and the vessel was covered with aluminum foil and pressurized to 40 psi with CF<sub>2</sub>=CF<sub>2</sub>. After stirring for 126 hours the system was evacuated through a series of cold traps. Glc/mass spectral analysis of the products collected indicated the presence of the following components: (a) CF<sub>3</sub>CF<sub>2</sub>I, (b) ICF<sub>2</sub>CF<sub>2</sub>Cl and (c) a species of molecular weight 312 which contains a ICF<sub>2</sub>CF<sub>2</sub>- fragment.

Hydrolysis of the reaction mixture with cold sodium thiosulfate solution was followed by a wash with dilute sodium bicarbonate solution. The thick, dark organic layer was distilled, giving 130 g of C<sub>2</sub>F<sub>4</sub>ICl and C<sub>2</sub>F<sub>4</sub>I<sub>2</sub> and 54 g (20%) of I(CF<sub>2</sub>)<sub>2</sub>O-(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>I.

c. Reaction of ClCOCOCl with NaF/CF<sub>2</sub>=CF<sub>2</sub>/I<sub>2</sub>

A glass ampoule equipped with a magnetic stirring bar was loaded with 78 g of NaF (1.85 mole) and heated in vacuo (270°/0.4 mm) for 4 days. After it had cooled, 31.9 g (0.25 mole) of oxalyl chloride was distilled (in vacuo) into the ampoule. A mixture of dry diglyme (600 g) and powdered I<sub>2</sub> (150.2 g, 0.59 mole) was transferred into the reaction vessel, which was covered with aluminum foil and pressurized to 40 psi with TFE. After stirring for ca. 7 days, an aliquot was removed; glc analysis indicated that none of the desired product was present.

About 45 g (0.77 mole) of dry KF was added, and the reaction mixture was repressurized. Work up in the usual manner led to the isolation of only a small amount of I(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>O-(CF<sub>2</sub>)<sub>2</sub>I, but relatively large quantities of ICF<sub>2</sub>CF<sub>2</sub>Cl and ICF<sub>2</sub>CF<sub>2</sub>I.

Preparation of I(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>5</sub>O(CF<sub>2</sub>)<sub>2</sub>I

a. A heavy wall ampoule was charged with 26.5 g (455 mmole) of anhydrous KF and heated in vacuo (200°/.25 mm) for 5 days. After cooling, perfluoroglutaryl fluoride (40 g, 164 mmole) was distilled in vacuo into the reactor. Anhydrous diglyme (82 g) was added, and the mixture stirred for 3 hours before adding crushed I<sub>2</sub> (141 g, 554 mg-atom) and dry diglyme (255 g). The ampoule was covered with foil, pressurized to 40 psi, and stirred for 144 hours, after which it was poured into an ice water solution of sodium thiosulfate. The organic layer was washed with a dilute NaHCO<sub>3</sub> solution and distilled (43°/.55 mm) to give 49 g (41%) of pure I(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>5</sub>O(CF<sub>2</sub>)<sub>2</sub>I. The infrared spectrum contains absorptions at 1350-1100 cm<sup>-1</sup> (C-F) and 915 cm<sup>-1</sup> (C-O-C), and the F<sup>19</sup> nmr spectrum consists of five multiplets:  $\delta = 64.5$  (ICF<sub>2</sub>, A = 3.9),  $\delta = 83.5$  (OCF<sub>2</sub>, A = 4.1),  $\delta = 87.6$  (ICF<sub>2</sub>CF<sub>2</sub>O, A = 4.1),  $\delta = 123$  (CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>, (A = 2.2), and  $\delta = 126$  (CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>, A = 4.1).

The mass spectrum shows a molecular ion at m/e = 736, and significant fragment ions at m/e = 609 (M<sup>+</sup> - I), and CF<sub>2</sub>CF<sub>2</sub>I m/e = 227 (C<sub>2</sub>F<sub>4</sub>I).

b. Repeating the above experiment using 140 mmole I<sub>2</sub>/420 mmole ICl and a reaction time of 113 hours resulted in a distilled yield of 46%.

Preparation of Br(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>Br, IIIc

A mixture of about 282 g (0.75 mole) of Br(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>3</sub>Br, a solution of 330 g of Br(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>x</sub>O(CF<sub>2</sub>)<sub>y</sub>Br and Br(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>Br (>90% mono-ethylene adduct), and 16.5 g (8 mole %) di-t-butyl peroxide were loaded into a Paar autoclave equipped with a stirrer. The system was flushed five times with ethylene, pressurized with ethylene, and allowed to react at 125-130°C with stirring under a constant ethylene pressure of ca. 20 psi. The reaction was cooled at the end of 7 hours and allowed to stand for 2 days. An additional 10 g of di-t-butyl peroxide was added, and the mixture was heated for 24 hrs. Gas chromatographic analysis of the resulting mixture indicated ca.

85% conversion of starting ether, ca. 50% yield of 1:1 adducts,  $\text{Br}(\text{CH}_2)_2(\text{CF}_2)_X\text{O}(\text{CF}_2)_Y\text{Br}$ , and ca. 29% yield of 1:1:1 adducts,  $\text{Br}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_3(\text{CH}_2)_2\text{Br}$ . The 605 g reaction mixture was strip-distilled in vacuo to yield the following fractions:

a) dry ice trap - 75 g starting material, peroxide decomposition products; b) ice trap - 14 g starting material, small amount monoethylene adduct; c) air cooled receiver - 306 g of predominantly (86%) monoethylene adduct with a small amount of 1:1:1 adduct; d) pot - 205 g, 71% of which was found to be pure 1:1:1 adduct; the remainder is composed of higher boiling materials, presumably 1:1:2 and higher adducts.

Preparation of  $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{I}$ , IVc

A 300 ml. autoclave was loaded with 117 g (0.20 mole) of  $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}$  and ca. 540 psi (ca. 0.45 mole) of  $\text{CH}_2=\text{CH}_2$ . After being placed in a rocker, the autoclave was slowly heated to 200°C, and maintained at that temperature for 21 hours. The product, a solid, was dissolved in diethyl ether, boiled with activated carbon, filtered, and recrystallized, giving rise to 122 g of  $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{I}$  (95% yield).

An analytically pure sample was obtained by sublimation (m pt 46-47°C).

The IR spectrum is consistent with the suggested structure: 1440  $\text{cm}^{-1}$  ( $-\text{CH}_2$ ) and 1350-1110  $\text{cm}^{-1}$  ( $-\text{CF}_2$  and C-O-C). The mass spectrum shows a molecular ion at  $m/e = 642$ ,  $m/e = 515$  ( $\text{M}^+ - \text{I}$ )  $m/e = 495$  ( $\text{M}^+ - \text{HFI}$ ), and  $m/e = 141$  ( $-\text{CH}_2\text{I}$ ). The  $\text{H}^1$  nmr spectrum contains a complex multiplet at  $\tau = 7.2$ ; the  $\text{F}^{19}$  nmr spectrum shows  $-\text{CF}_2\text{O}-$  ( $A = 2.0, 2.0$ ),  $\phi = 87.8, 89.3$ ; and  $-\text{CF}_2\text{CH}_2-$  ( $A = 2.0$ ),  $\phi = 119$ .

Preparation of  $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{I}$ , Vc

A 300 ml. autoclave was loaded with 55 g (.075 mole) of  $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$  which was then pressurized with  $\text{CH}_2=\text{CH}_2$  (ca. .164 mole). The autoclave was placed in a rocker and slowly heated to 200°C. After 23 hours, it was cooled and opened, yielding 56.4 g (95%) of crude  $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{I}$ , a dark liquid. The product was used without purification.

Preparation of  $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_3\text{CH}=\text{CH}_2$ , IIIId

About 145 g (0.30 mole) of  $\text{Br}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_3(\text{CH}_2)_2\text{Br}$  was added dropwise to a solution of 43 g (0.767 mole) of KOH in 330 ml. of ethanol. External cooling was employed so that the temperature of the reaction mixture never rose above  $38^\circ\text{C}$ . The mixture was stirred overnight and then poured into ice water to give 90 g of the crude title compound. The aqueous layer extracted three times with 40 ml. portions of  $\text{CH}_2\text{Cl}_2$  and these were combined with the washed organic layer. The combination was dried over  $\text{MgSO}_4$ , filtered, and distilled ( $139\text{--}140^\circ\text{C}$ ) to yield 77 g (80% yield) of  $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_3\text{CH}=\text{CH}_2$ . The mass spectrum exhibits a molecular ion at  $m/e = 320$ ,  $m/e = 301$  ( $\text{M}^+ - \text{F}$ ), and fragments ions at  $m/e = 177$  ( $\text{M}^+ = \text{C}_3\text{H}_7\text{C}_3\text{F}_6$ ) and at  $m/e = 127$  ( $\text{M}^+ = \text{C}_3\text{H}_7\text{C}_2\text{F}_4$ ).

Preparation of  $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$ , IVd

In a similar manner, a 68% yield (91% including intercuts) of  $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$  (b.p.  $68^\circ\text{C}/38$  mm) was obtained.

The IR spectrum is consistent with the expected structure containing absorptions at 1652, 1420, 977, and  $965\text{ cm}^{-1}$  ( $-\text{CH}=\text{CH}_2$ ) and  $1100\text{--}1350\text{ cm}^{-1}$  ( $\text{CF}_2$ ,  $-\text{COC}-$ ). The mass spectrum exhibits a molecular ion at  $m/e$  386, and fragment ions at  $m/e$  243 ( $\text{M}^+ - \text{C}_4\text{H}_3\text{F}_4\text{O}$ ), 127 ( $\text{C}_4\text{F}_4\text{H}_3$ ) and 77 ( $\text{C}_3\text{F}_2\text{H}_3$ ). The  $\text{F}^{19}$  and  $\text{H}^1$  nmr spectra are also in agreement with the assigned structure:  $\delta = 87.4$ , 88.3 ( $-\text{OCF}_2-$ , m, A = 8.0);  $\delta = 117$  ( $-\text{CF}_2\text{CH}-$ , m, A = 4.0);  $\tau \sim 4.1$  ( $\text{CH}=\text{CH}-$ , m).

Preparation of  $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$

About 89 g (0.11 mole)  $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{I}$  was added dropwise to 25 g (0.45 mole) KOH in 110 ml. of ethanol. After stirring overnight at room temperature, water was added, the organic layer was separated, washed with saturated NaCl solution and distilled on a 36" spinning band distillation column. About 53 g (88% yield) of pure  $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$  were obtained (b.p. =  $29^\circ\text{C}/0.2$  mm).

The  $F^{19}$  nmr spectrum is in agreement with the assigned structure:  $\delta = 83.5$  ( $-OCF_2-$ , m, A = 3.9);  $\delta = 87.8$  ( $-OCF_2-$ , m, A = 4.0);  $\delta = 122$  ( $-CH_2CF_2-$ , m, A = 4.1);  $\delta = 127$  ( $CF_2CF_2CF_2-$ , m, A = 2.1);  $\delta = 130$  ( $-OCF_2CF_2-$ , m, A = 4.0). The  $H^1$  nmr spectrum exhibits an olefinic multiplet at  $\tau = 4.1$ .

The infrared spectrum contains the following absorptions: C=C,  $1653\text{ cm}^{-1}$ ;  $CH_2=C$ ,  $1420\text{ cm}^{-1}$ ;  $-CF_2-$ , C-O-C,  $1100-1250\text{ cm}^{-1}$ . The mass spectrum shows a molecular ion at  $m/e = 536$  and fragment peaks at  $m/e 517$  ( $M^+ - F$ ),  $516$  ( $M^+ - HF$ ), and  $243$  ( $M^+ - C_2H_3C_5F_{10}O$ ).

$$\begin{array}{c} CH_3 \\ \text{Preparation of } ClSi(CH_2CH_2CF_3)CH_2CH_2(CF_2)_3O(CF_2)_2CH_2CH_2Si- \\ (CH_2CH_2CF_3)Cl, IIIe \text{ (n.c.)} \end{array}$$

A dry 2 liter flask containing a magnetic stirring bar was charged with 155 g (0.48 mole) of  $CH_2=CH(CF_2)_3O(CF_2)_2CH=CH_2$ , 17.7 g (0.12 mole) of di-t-butylperoxide, and 854 g (4.84 mole)

H  
Cl

of  $CH_3SiCH_2CH_2CF_2$  under an atmosphere of dry nitrogen. The mixture was heated to  $110^\circ$  (gentle reflux) with stirring overnight. Glc analysis of the reaction mixture indicated complete consumption of the diene.

The reaction mixture was stripped under vacuum through a short Vigreux column, leaving a residue of 372 g which appeared to be about 88% pure according to glc analysis. This was distilled in vacuo ( $120^\circ/0.45\text{ mm}$ ) through a 36" spinning band column to yield 234 g (72%) of pure product  $n_D^{27^\circ} = 1.3805$ .

The infrared spectrum contains the following absorptions: C-H ( $2900-3000\text{ cm}^{-1}$ ), C-F ( $950-1450\text{ cm}^{-1}$ ) and C-O-C ( $900\text{ cm}^{-1}$ ). The  $H^1$  nmr spectrum consists of two multiplets,  $\tau = 7.3-8.5$  ( $CF_2-CH_2-$ , A = 4.0) and  $\tau = 8.7-9.1$  ( $Si-CH_2$ , A = 4.0), and a singlet,  $\tau = 9.5$  ( $SiCH_3$ , A = 3.1). The  $F^{19}$  nmr spectrum exhibits the following absorptions:  $\delta = 68.9$  ( $CF_2$ , triplet, A = 6.1);  $\delta = 83.5, 87.8$  ( $OCF_2$ , m, A = 2.0, 2.0);  $\delta = 116, 119$  ( $CH_2CF_2$ , m, A = 2.0, 2.0);  $\delta = 127$  ( $CF_2-CF_2-CF_2$ , m, A = 1.9).

Anal. calcd. for  $C_{17}H_{22}Cl_2F_{16}OSi_2$ : C, 30.3, H, 3.3, F, 45.1. Found: C, 30.4, H, 3.5; F, 45.7.

Preparation of  $(CF_3CH_2CH_2)(CH_3)(Cl)Si(CH_2)_2(CF_2)_2O-$   
 $(CF_2)_2O(CF_2)_2(CH_2)_2Si(Cl)(CH_3)(CH_2CH_2CF_3)$ , IVe (n.c.)

A dry 250 ml. round bottom flask equipped with a magnetic stirrer, condenser, and gas inlet was charged with 56.1 g (0.145 mole) of  $CH_2=CH(CF_2)_2O(CF_2)_2O(CF_2)_2CH=CH_2$ , 173.1 g (0.980 mole) of (3,3,3-trifluoropropyl)methylchlorosilane, and 2.1 g (0.014 mole) of di-t-butylperoxide. The system was slowly purged with dry nitrogen while being heated to 60° overnight. An additional 3.5 g of di-t-butylperoxide was added and the reaction mixture was heated to reflux (ca. 105°) for a day. Glc analysis indicated incomplete reaction.

About 5 g more of peroxide was added in two portions over a two day period, while maintaining a heavy reflux. Starting material was still present, so the low boiling materials (including  $CH_2=CH(CF_2)_2O(CF_2)_2O(CF_2)_2CH_2CH_2Si^{PrF}Cl$ ) were stripped

out of the reaction mixture and retreated with (3,3,3-trifluoropropyl)methylchlorosilane and di-t-butylperoxide. The combined reaction mixtures were distilled in vacuo to yield 22.6 g (25%)

of pure  $ClSi^{PrF}(CH_2)_2(CF_2)_2O(CF_2)_2O(CF_2)_2(CH_2)_2Si^{PrF}Cl$ , (A) as well

as ca. 20 g of somewhat impure (A).

Significant IR absorptions appear at  $3000\text{ cm}^{-1}$ ,  $1450-1100\text{ cm}^{-1}$ ,  $990\text{ cm}^{-1}$ ,  $850\text{ cm}^{-1}$ , and  $800\text{ cm}^{-1}$ . The  $F^{19}$  nmr spectrum contains absorptions at  $\delta = 69.0$  ( $CF_3-$ , A = 3.5),  $\delta = 88.0$  and  $89.0$  ( $OCF_2-$ , A = 3.4, 4.1) and  $\delta = 118$  and  $120$  ( $CF_2-CH_2$ , A = 2.0, 2.0). The  $H^1$  nmr spectrum contains absorptions at  $\tau = 7.8$  ( $-CF_2CH_2-$ ) and  $\tau = 8.93$  ( $-SiCH_2CH_2CF_2$ , A = 8.4) and  $\tau = 9.51$  ( $-SiCH_3$ , A = 3.0) as well as peaks attributable to hydrolyzed products.

Preparation of  $(CF_3CH_2CH_2)(CF_3)(Cl)Si(CH_2)_2(CF_2)_2-$   
 $O(CF_2)_5O(CF_2)_2(CH_2)_2Si(Cl)(CH_3)(CH_2CH_2CF_3)$ , Vc (n.c.)

A dry flask equipped with a mechanical stirrer and a reflux condenser was charged with 51.5 g (0.096 mole) of  $CH_2=CH(CF_2)_2O-(CF_2)_5O(CF_2)_2CH=CH_2$ , 171 g (0.097 mole) of 3,3,3-trifluoropropylmethylchlorosilane, and 3.6 g (0.024 mole) of di-t-butylperoxide. The system was kept under a slight positive nitrogen pressure as it was heated to 105-110°C. After 24 hours, an additional 3.6 g of the peroxide was added and the heating was continued for an additional day. Three distillations of the reaction mixture produced 42 g (96% pure by glc) of the desired chlorosilane (49% yield).

The  $F^{19}$  and  $H^1$  nmr spectra are consistent with the assigned structure:  $\delta = 68.9$  ( $CF_3^-$ , m, A = 5.7);  $\delta = 83.0$  ( $-OCF_2^-$ , m, A = 4.3);  $\delta = 87.0$  ( $-OCF_2^-$ , m, A = 3.9);  $\delta = 120$  ( $-CH_2CF_2^-$ , m, A = 4.0);  $\delta = 123$  ( $-CF_2CF_2^*CF_2^-$ , m, A = 2.1);  $\delta = 126$  ( $-OCF_2CF_2^*-$ , m, A = 4.0);  $\tau = \sim 7.8$  ( $-CF_2CH_2^-$ , m, A = 4.0);  $\tau = \sim 8.9$  ( $-SiCH_2^-$ , m, A = 4.0);  $\tau = 9.50$  ( $-SiCH_3$ , s, A = 3.0).

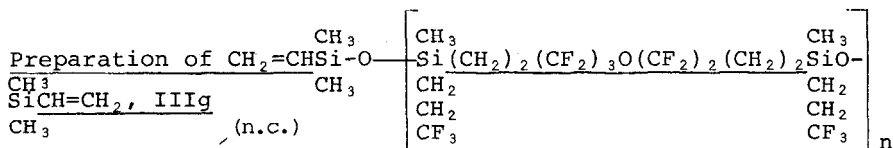
Anal. calc'd. for  $C_{21}H_{22}F_{24}Cl_2O_2Si_2$ : C, 28.3; H, 2.47; Cl, 7.97. Found: C, 28.7; H, 2.50; Cl, 8.25.

Preparation of  $HOSi(CH_2)_2(CF_2)_3O(CF_2)_2(CH_2)_2SiOH$ , IIIIf (n.c.)

$CH_3$	$CH_3$
$CH_2$	$CH_2$
$CH_2$	$CH_2$
$CF_3$	$CF_3$

A suspension of 162 g of  $NaHCO_3$  in 1500 ml. of water/300 ml. of diethyl ether was stirred vigorously while 234 g of  $Cl(CH_3)(CF_3CH_2CH_2)Si(CH_2)_2(CF_2)_3O(CF_2)_2(CH_2)_2Si(CH_2CH_2CF_3)-(CH_3)(Cl)$  dissolved in 300 ml. of diethyl ether was added dropwise over a period of 3 1/2 hours. The mixture was stirred for an additional 19 hours, after which the phases were separated, and the organic layer was washed three times with saturated sodium chloride solution until neutral, and then dried over  $CaSO_4$ .

After filtering, the solvent was removed by rotary evaporative and the residue was evacuated overnight. The infrared spectrum of the product shows the presence of a hydrogen-bonded SiOH absorption centered at  $3350\text{ cm}^{-1}$  (broad) and a free SiOH absorption at  $3750\text{ cm}^{-1}$  (sharp).



About 201 g of  $\text{HO}(\text{CH}_3)(\text{CF}_3\text{CH}_2\text{CH}_2)\text{Si}(\text{CH}_2)_2(\text{CF}_2)_3\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{Si}(\text{CH}_2\text{CH}_2\text{CF}_3)(\text{CH}_3)\text{OH}$  was stirred rapidly under a dry nitrogen atmosphere while 5.06 g (0.042 mole) of  $(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiCl}$  was added slowly. The mixture was gradually heated to  $80^\circ$  under a slow stream of nitrogen after mixing was complete, and maintained at that temperature for 4 hours. After cooling, the reaction mixture was dissolved in diethyl ether, and shaken three times with saturated sodium bicarbonate solution.

The separated organic layer was dried, filtered, and stripped of solvent; 5 drops of tetramethylguanidine-trifluoroacetic acid were added, and the flask was swept with nitrogen while being slowly heated to  $100^\circ$ , at which point it was evacuated for several hours.

The viscous residue was dissolved in diethyl ether and shaken with two 300 ml. portions of sodium bicarbonate solution. The organic layer was dried, stripped of solvent and heated to  $100^\circ/1\text{ mm}$  for 2 hrs., and then to  $150^\circ/0.9\text{ mm}$  for 2 1/2 hours. The resulting polymer cured using conventional techniques [4].

The  $\text{F}^{19}$  nmr spectrum is in agreement with the assigned structure:  $\delta = 69$  (m,  $\text{CF}_3^-$ , A = 5.8);  $\delta = 82.7, 86.8$  (m,  $-\text{OCF}_2-$ , A = 2.2, 2.0);  $\delta = 117, 120$  (m,  $-\text{CH}_2\text{CF}_2-$ , A = 2.2, 2.1);  $\delta = 128$  (m,  $-\text{C}-\text{CF}_2-\text{C}-$ , A = 2.0).

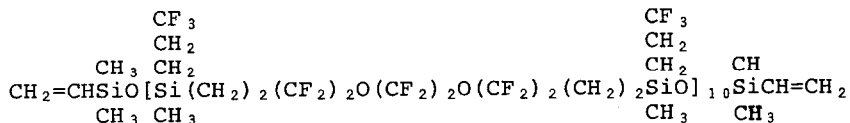
Anal. calc'd. for  $\text{C}_{17}\text{H}_{22}\text{F}_{16}\text{O}_2\text{Si}_2$ : C, 33.01; H, 3.58.  
Found: C, 33.64; H, 3.85.



Hydrolysis and Polymerization of (CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>)(CH<sub>3</sub>)(Cl)-  
Si(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Si(Cl)(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>)

In a manner similar to that described for IIIif and IIIg, the title chlorosilane was hydrolyzed to IVf and IVg.

The H<sup>1</sup> nmr of the uncured polymer indicates a DP of 10, and a spectrum consistent with the following structure:



H<sup>1</sup> nmr: τ = 8.0 (-CH<sub>2</sub>CF<sub>2</sub>, m, A = 6.5); τ = 9.2 (-SiCH<sub>2</sub>-, m, A = 5.4); τ = 9.8 (-SiCH<sub>3</sub>-, m, A = 5.1). F<sup>19</sup> nmr: Ø = 88.4 (CF<sub>3</sub>O, m, A = 1.7); Ø = 90.0 (CF<sub>2</sub>O, m, A = 2.1); Ø = 119.8 (CF<sub>2</sub>CH<sub>2</sub>, m, A = 2.0).

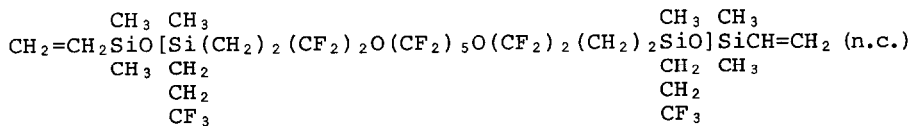
Anal. Calc'd. for C<sub>18</sub>H<sub>22</sub>F<sub>12</sub>Si<sub>2</sub>O: C, 31.6; H, 3.22.

Found: C, 31.9 ± 0.2; H, 3.51 ± 0.10.

The polymer was found to cure satisfactorily by an RTV method.

Hydrolysis and Polymerization of (CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>)(CH<sub>3</sub>)-  
(Cl)Si(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>5</sub>O(CF<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Si(Cl)(CH<sub>3</sub>)-  
(CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>)

In a manner similar to that described for IIIif and IIIg, the title chlorosilane was hydrolyzed to Vf and Vg. Both H<sup>1</sup> and F<sup>19</sup> nmr spectra are consistent with the structure:



and a DP of 16.4 is indicated.

Anal. calc'd. for C<sub>21</sub>H<sub>22</sub>F<sub>24</sub>O<sub>3</sub>Si<sub>2</sub>: C, 30.2; H, 2.63; Si, 6.71. Found: C, 30.6; H, 2.91; Si, 6.86.

The polymer was found to cure by an RTV method.

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