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OCTAFLUOROISOBUTYLENE EPOXIDE DERIVATIVES

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SUMMARY

Octafluoroisobutylene epoxide (OFIBO) reacts with alkoxides in a manner similar to hexafluoropropylene epoxide (HFPO). Higher oligomers of OFIBO than previously reported have been prepared, but no difunctional polymers with molecular weights as high as obtained with HFPO could be made.

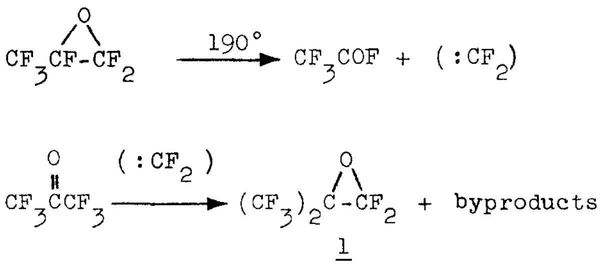
Unsaturated ethers derived from OFIBO dimer and from a potassium pentafluorophenoxide-OFIBO adduct have been incorporated into perfluorinated polymers. The unsaturated ether, perfluoro(2-phenoxypropene), affords a crosslinking site for the nucleophilic vulcanization of a tetrafluoroethylene-perfluoro(methyl vinyl ether) perfluoroelastomer.

INTRODUCTION

Syntheses of OFIBO and some of the chemical reactions of this compound have been reviewed by Tarrant [1]. In the course of our work on the polymerization of perfluorinated epoxides [2] we have studied several new reactions of OFIBO and its derivatives.

RESULTS AND DISCUSSION

OFIBO, 1, was prepared by reaction of hexafluoroacetone with HFPO at 190°C [3]. Unreacted hexafluoroacetone and trifluoroacetyl fluoride were removed from the crude reaction mixture by passing the gases through aqueous sodium fluoride. Low-temperature distillation was effective in separating pure OFIBO from byproducts (Eq. 1).



$$CF_3\overset{O}{\overbrace{CF-CF_2}} \xrightarrow{190°} CF_3COF + (:CF_2)$$

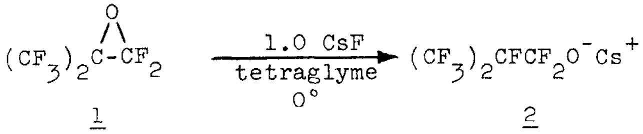
$$CF_3\overset{\overset{O}{\|}}{C}CF_3 \xrightarrow{(:CF_2)} (CF_3)_2\overset{O}{\overbrace{C-CF_2}} + \text{byproducts} \qquad (1)$$

1

OFIBO reactions with fluoride ion

(a) With one equivalent of fluoride ion

OFIBO reacts quantitatively with one equivalent of dry cesium fluoride in tetraethyleneglycol dimethyl ether (tetraglyme) at 0° to yield the cesium alkoxide 2 resulting from fluoride ion attack at the tertiary carbon atom of 1 (Eq. 2). This very same alkoxide can be made by reacting perfluoroisobutyryl fluoride 3 with cesium fluoride under the same conditions (Eq. 3).



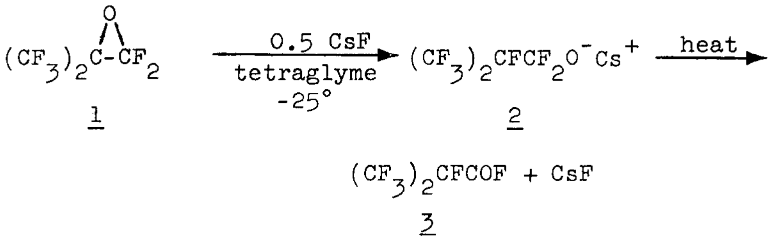
$$(CF_3)_2\overset{O}{\overbrace{C-CF_2}} \xrightarrow[\text{tetraglyme}\ 0°]{1.0\ CsF} (CF_3)_2CFCF_2O^-Cs^+ \qquad (2)$$

1 2

$$\underset{\underline{3}}{(CF_3)_2CFCOF} \xrightarrow[\text{tetraglyme, } 0^\circ]{1.0\ CsF} \underset{\underline{2}}{(CF_3)_2CFCF_2O^-Cs^+} \qquad (3)$$

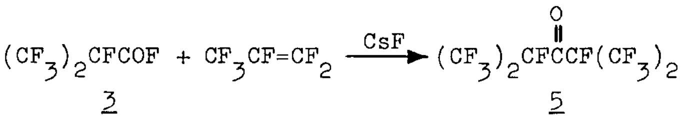
(b) <u>With less than one equivalent of fluoride ion</u>

The reaction of OFIBO with less than one equivalent of fluoride ion first yields alkoxide $\underline{2}$. Additional products may be formed depending on reaction conditions. If, for example, 2.0 moles of OFIBO react with 1.0 mole of dry cesium fluoride in tetraglyme at -25° and the mixture is heated directly to 180° to distill volatile materials, several products are produced. Various analytical techniques show the five major products to be perfluoroisobutyryl fluoride $\underline{3}$, a dimer of hexafluoropropene $\underline{4}$, ketone $\underline{5}$, OFIBO dimer $\underline{6}$, and unsaturated ether $\underline{7}$. Reasonable reaction routes to these products are given in Equations 4-8.

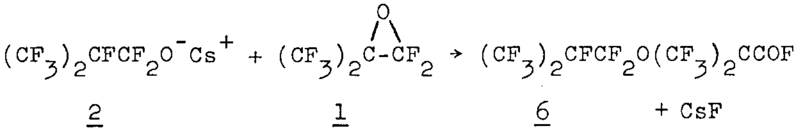


(4)

$$\underset{\underline{3}}{(CF_3)_2CFCOF} \xrightarrow{\text{heat}} CF_3CF{=}CF_2 \xrightarrow{CsF} \underset{\underline{4}}{(CF_3)_2CFCF{=}CFCF_3} \qquad (5)$$



$$\underset{\underline{3}}{(CF_3)_2CFCOF} + CF_3CF{=}CF_2 \xrightarrow{CsF} \underset{\underline{5}}{(CF_3)_2CF\overset{O}{\overset{\|}{C}}CF(CF_3)_2} \qquad (6)$$



(7)

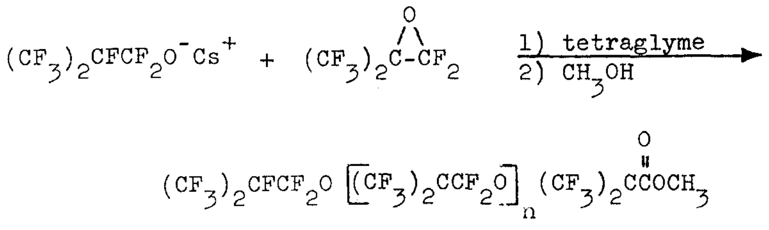
$$\underset{\underline{6}}{(CF_3)_2CFCF_2O(CF_3)_2CCOF} \xrightarrow{heat} \underset{\underline{7}}{(CF_3)_2CFCF_2O(CF_3)C{=}CF_2} \qquad (8)$$

Knunyants et al. [4] obtained OFIBO dimer $\underline{6}$ by the room temperature reaction of refluxing OFIBO with the reaction product of perfluoroisobutyryl fluoride and cesium fluoride in diethyleneglycol dimethyl ether (diglyme).

OFIBO reactions with alkoxides

(a) With OFIBO cesium alkoxide

Three moles of OFIBO react with one mole of previously prepared cesium alkoxide $\underline{2}$ (Eq. 2 or 3) in tetraglyme at -25° to afford oligomers of OFIBO. These oligomers were isolated as their corresponding methyl esters in order to avoid any fluoride ion catalyzed reactions such as those shown in Equations 4-8. Distillation and preparative vapor phase chromatography afforded pure samples of OFIBO dimer $\underline{8}$, trimer $\underline{9}$, tetramer $\underline{10}$, and pentamer $\underline{11}$ methyl esters (Eq. 9).

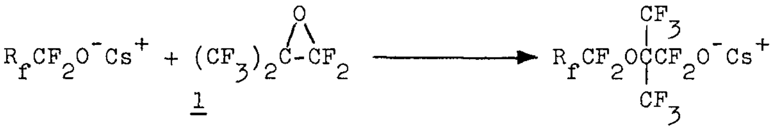


$$(CF_3)_2CFCF_2O^-Cs^+ + (CF_3)_2\overset{O}{\overbrace{C-CF_2}} \xrightarrow[2)\ CH_3OH]{1)\ tetraglyme}$$

$$(CF_3)_2CFCF_2O\left[(CF_3)_2CCF_2O\right]_n(CF_3)_2\overset{O}{\overset{\Vert}{C}}OCH_3 \qquad (9)$$

$\underline{8}$, $\underline{9}$, $\underline{10}$, $\underline{11}$ (for n = 0,1,2,3)

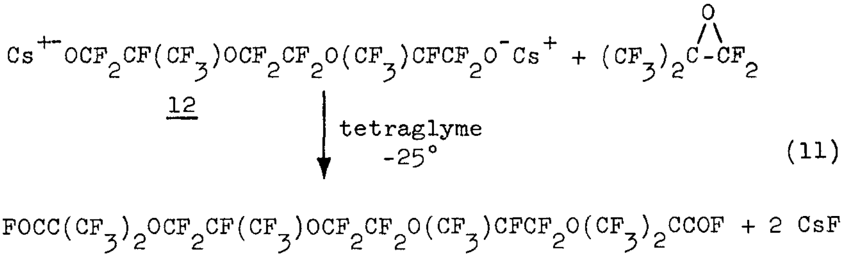
Mass spectra for dimer 8 and fluorine nmr spectra for 8, 9, 10, and 11 clearly establish their identity and are definitive in showing that oligomerization proceeds by alkoxide attack only at the tertiary carbon atom of OFIBO (see Experimental Section). It was carefully determined that all of the OFIBO was consumed and that no traces of other products were formed under these reaction conditions (Eq. 10).



$$R_fCF_2O^-Cs^+ + \underset{\underline{1}}{(CF_3)_2\overset{O}{C\text{—}CF_2}} \longrightarrow R_fCF_2O\underset{CF_3}{\overset{CF_3}{C}}CF_2O^-Cs^+ \qquad (10)$$

(b) With a bis-alkoxide

The preparation of a tetraglyme solution of bis-alkoxide 12 and its utility for preparing difunctional polymers of HFPO have been described [5]. Addition of OFIBO to 12 at either -10° or -25° yielded oils with molecular weights of about 1000 (Eq. 11).

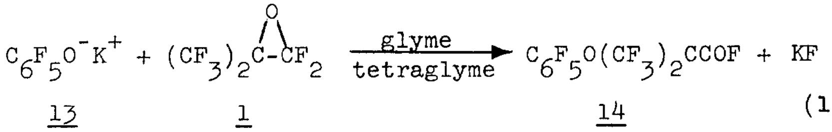


$$\underset{\underline{12}}{Cs^{+-}OCF_2CF(CF_3)OCF_2CF_2O(CF_3)CFCF_2O^-Cs^+} + (CF_3)_2\overset{O}{C\text{—}CF_2}$$
$$\Big\downarrow \text{tetraglyme, } -25° \qquad (11)$$
$$FOCC(CF_3)_2OCF_2CF(CF_3)OCF_2CF_2O(CF_3)CFCF_2O(CF_3)_2CCOF + 2\ CsF$$

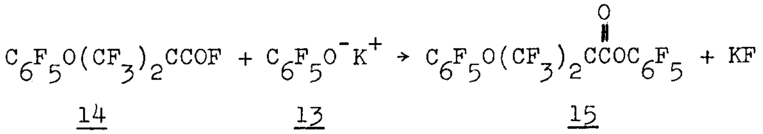
Under the same general reaction conditions, difunctional HFPO polymers of molecular weight 6000 have been prepared. It is surmised that increased steric hindrance toward nucleophilic epoxide ring cleavage and increased inductive stabilization of negative charge of the propagating alkoxide are responsible for the reduced anionic polymerization tendency of OFIBO relative to HFPO.

(c) With potassium pentafluorophenoxide

In preliminary experiments it was shown that OFIBO reacts with potassium pentafluorophenoxide 13 in ethylene glycol dimethyl ether (glyme) and tetraglyme solutions at low temperatures to give the expected oligomer adducts. By careful control of reaction conditions the desired mono-adduct 14 could be obtained in good yield (Eq. 12), but a byproduct was the unexpected ester 15 (Eq. 13).

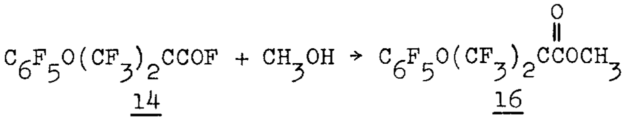


$$\underset{\underline{13}}{C_6F_5O^-K^+} + \underset{\underline{1}}{(CF_3)_2\overset{O}{C-CF_2}} \xrightarrow[\text{tetraglyme}]{\text{glyme}} \underset{\underline{14}}{C_6F_5O(CF_3)_2CCOF} + KF \qquad (12)$$

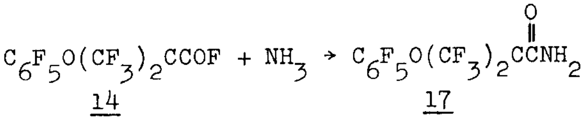


$$\underset{\underline{14}}{C_6F_5O(CF_3)_2CCOF} + \underset{\underline{13}}{C_6F_5O^-K^+} \rightarrow \underset{\underline{15}}{C_6F_5O(CF_3)_2C\overset{O}{\overset{\|}{C}}OC_6F_5} + KF \qquad (13)$$

Acid fluoride 14 can be obtained in pure form from the crude reaction mixture by vacuum distillation. The structures of acid fluoride 14 and ester 15 are clear from the spectral information presented in the Experimental Section. Infrared and fluorine nmr spectra of methyl ester 16 (Eq. 14) and amide 17 (Eq. 15) are also conclusive with regard to the structure of 14.



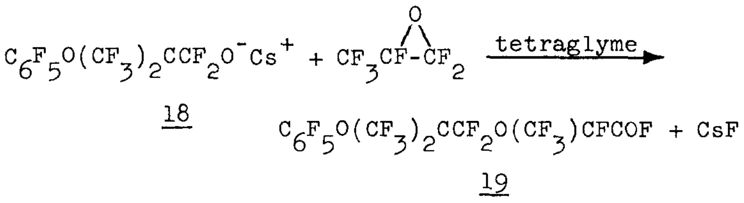
$$\underset{\underline{14}}{C_6F_5O(CF_3)_2CCOF} + CH_3OH \rightarrow \underset{\underline{16}}{C_6F_5O(CF_3)_2C\overset{O}{\overset{\|}{C}}OCH_3} \qquad (14)$$



$$\underset{\underline{14}}{C_6F_5O(CF_3)_2CCOF} + NH_3 \rightarrow \underset{\underline{17}}{C_6F_5O(CF_3)_2C\overset{O}{\overset{\|}{C}}NH_2} \qquad (15)$$

Acid fluoride 14 reacts with dry cesium fluoride in tetraglyme to yield alkoxide 18 (Eq. 16) which can be used to initiate the polymerization of HFPO (Eq. 17). Only the HFPO adduct 19 was isolated and characterized.

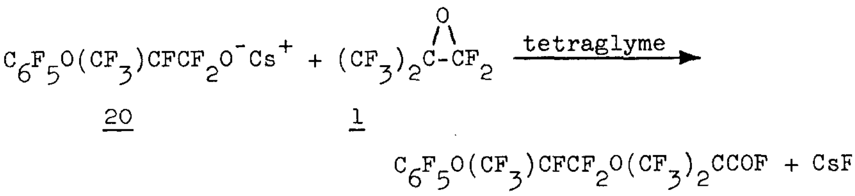
$$\underset{\underline{14}}{C_6F_5O(CF_3)_2CCOF} \xrightarrow[\text{tetraglyme}]{\text{CsF}} \underset{\underline{18}}{C_6F_5O(CF_3)_2CCF_2O^-Cs^+} \qquad (16)$$



$$\underset{\underline{18}}{C_6F_5O(CF_3)_2CCF_2O^-Cs^+} + CF_3\overset{O}{\overbrace{CF-CF_2}} \xrightarrow{\text{tetraglyme}} \underset{\underline{19}}{C_6F_5O(CF_3)_2CCF_2O(CF_3)CFCOF} + CsF \qquad (17)$$

and
higher adducts

Cesium alkoxide 20 can be made by reacting cesium pentafluorophenoxide with HFPO. Alkoxide 20 is effective in oligomerizing OFIBO, as shown in Eq. 18.



$$\underset{\underline{20}}{C_6F_5O(CF_3)CFCF_2O^-Cs^+} + \underset{\underline{1}}{(CF_3)_2\overset{O}{\overbrace{C-CF_2}}} \xrightarrow{\text{tetraglyme}} C_6F_5O(CF_3)CFCF_2O(CF_3)_2CCOF + CsF$$

and (18)
higher adducts

Reactions according to Equations 17 and 18 suggest that OFIBO and HFPO should copolymerize under suitable conditions.

Unsaturated ethers derived from OFIBO

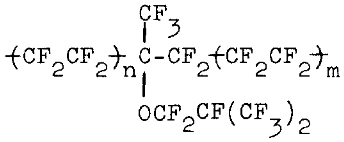
(a) From OFIBO dimer

Unsaturated ether 7 was prepared in good yield by passing OFIBO dimer 6 through a hot fluidized sodium carbonate column (Eq. 19).

$$\underset{\underline{6}}{(CF_3)_2CFCF_2O(CF_3)_2CCOF} \xrightarrow[Na_2CO_3]{270°} \underset{\underline{7}}{(CF_3)_2CFCF_2O(CF_3)C{=}CF_2} \qquad (19)$$

Emulsion polymerization of 7 with tetrafluoroethylene yielded a white, powdery plastic copolymer similar in appearance to polytetrafluoroethylene except for an infrared absorption at 995 cm^{-1} (Eq. 20). This absorption is characteristic for fluorinated ethers and could not be diminished by solvent extractions of copolymer 21. Incorporation of 7 must take place by radical attack at the double bond.

$$\underset{\underline{7}}{(CF_3)_2CFCF_2O(CF_3)C{=}CF_2} + (n + m)\ CF_2{=}CF_2 \xrightarrow{R\cdot} \qquad (20)$$



$$\left(CF_2CF_2\right)_n\underset{OCF_2CF(CF_3)_2}{\overset{CF_3}{\underset{|}{\overset{|}{C}}}}-CF_2\left(CF_2CF_2\right)_m$$

21

(b) From acid fluoride 14

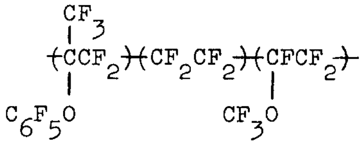
Perfluoro(2-phenoxypropene) (22) was prepared by pyrolysis of acid fluoride 14 over sodium carbonate (Eq. 21) as described in the Experimental Section. This new compound is well characterized by elemental analysis and spectral data.

$$\underset{\underline{14}}{C_6F_5O(CF_3)_2CCOF} \xrightarrow[Na_2CO_3]{265^\circ} \underset{\underline{22}}{C_6F_5O(CF_3)C{=}CF_2} \qquad (21)$$

Terpolymer from perfluoro(2-phenoxypropene)

Emulsion polymerization of a mixture of perfluoro(2-phenoxypropene)(22), tetrafluoroethylene, and perfluoro(methyl vinyl ether) gave a low yield of a tough perfluoroelastomer (23) with a 997 cm^{-1} infrared absorption (Eq. 22).

$$\underset{\underline{22}}{C_6F_5O(CF_3)C{=}CF_2} + CF_2{=}CF_2 + CF_3OCF{=}CF_2 \xrightarrow{R\cdot} \qquad (22)$$



$$-\!\!(\underset{\displaystyle C_6F_5O}{\overset{\displaystyle CF_3}{C}}CF_2)\!\!-\!\!(CF_2CF_2)\!\!-\!\!(\underset{\displaystyle CF_3O}{CF}CF_2)\!\!-$$

23

Perfluoroelastomer 23 could be vulcanized in the manner described by Arnold, Barney and Thompson [6], while a copolymer of tetrafluoroethylene and perfluoro(methyl vinyl ether) could not be vulcanized under the same conditions. Perfluoro(2-phenoxypropene) 22 thus provides a cure site for this perfluoroelastomer.

EXPERIMENTAL

OFIBO was handled as if it were as toxic as perfluoroisobutylene. All fluorine nmr values are based on external $CFCl_3$ reference and absorptions are multiplets unless otherwise indicated.

(a) Preparation of OFIBO

Hexafluoropropylene oxide (415 g) and hexafluoroacetone (415 g) were condensed in a clean, dry, evacuated 1 liter Hastelloy C bomb. This mixture was heated to 190° for 8 h under autogenous pressure. The products from five runs were combined and passed through saturated aqueous sodium fluoride scrubbing columns to yield a mixture containing 85% of OFIBO and 15% of perfluorocyclopropane (C_3F_6, m/e 150). Distillation afforded pure OFIBO in about 50% yield from hexafluoroacetone.

OFIBO (1): C_4F_8O, m/e 216; ir (gas), 1494, 1332, 1265, 1220, 1096, 1030, 985, 862, 717 cm^{-1}; ^{19}F nmr, 69.9 (2 CF_3, triplet), 109.8 ppm (CF_2).

(b) Reaction of OFIBO with cesium fluoride

OFIBO (17.9 g) was added to anhydrous cesium fluoride (12.6 g) and anhydrous tetraglyme (37.2 g) at 0° to -20°, in a flask equipped with a cold reflux condenser, to yield alkoxide 2.

Similarly, perfluoroisobutyryl fluoride (16.8 g), cesium fluoride (13.0 g), and tetraglyme (57.5 g) afforded alkoxide 2.

Alkoxide 2: Ir, 1690 cm^{-1}; cesium by atomic absorption, found 0.933 meq/g, theory 0.905 meq/g; ^{19}F nmr, 19.4 (CF_2), 73.1 (2 CF_3), 180.3 ppm (CF).

(c) Reaction of OFIBO with less than one equivalent of cesium fluoride

OFIBO (35.9 g), cesium fluoride (12.6 g) and tetraglyme (37.2 g), stirred at -25° and heated to 180°, gave five major distillation products 3, 4, 5, 6, and 7.

Product 3: Identical to authentic perfluoroisobutyryl fluoride. C_4F_8O, m/e 216; ir (gas), 1880, 1318, 1278, 1194, 1156, 995 cm^{-1}; ^{19}F nmr, -32.3 (CF), 73.0 (2 CF_3, triplet), 179.9 ppm (CF).

Product 4: Identical to an authentic dimer of hexafluoropropylene. C_6F_{12}, m/e 300; ir, 1690 cm^{-1}; ^{19}F nmr, 57.3 (CF_3), 59.9 (CF_3), 83.0 (CF_3), 97.6 (CF), 116.4 ppm (CF_2).

Product 5: $C_7F_{14}O$, m/e 366; ir, 1760 cm^{-1}.

Product 6: Ir, 1860 cm^{-1}. Methyl ester identical to OFIBO dimer methyl ester 8.

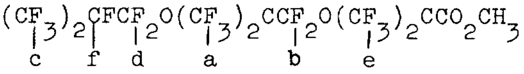
Product 7: Ir, 1670 cm^{-1}. Identical to product of Eq. 19, nc.

Reaction of OFIBO with alkoxide 2

Alkoxide 2 was prepared from perfluoroisobutyryl fluoride (26.9 g), cesium fluoride (17.5 g), and tetraglyme (52.3 g). OFIBO (64.4 g) was added in 1 h at -25° to 74.5 g of the alkoxide 2 solution. After stirring for 1 h, the mixture was diluted with $CF_2ClCFCl_2$ (100 ml) and esterified with methyl alcohol (16 ml) in the presence of suspended sodium fluoride. The bottom layer of this centrifuged mixture contained only four ester products. Fractional distillation and preparative vapor phase chromatography afforded 8 (14%), 9 (36%), 10 (40%), and 11 (10%); all showing a 1780 cm^{-1} infrared absorption.

Dimer ester 8: $C_9H_3F_{15}O_3$, m/e 429 ($C_9H_3F_{15}O_3$ minus CH_3); ^{19}F nmr, 73.4 (2 CF_3), 75.1 (2 CF_3, CF_2), 186.7 ppm (CF), nc.

Trimer ester 9: $C_{13}H_3F_{23}O_4$; ^{19}F nmr, 70.6 (a, $2CF_3$), 71.3 (b, CF_2), 73.0 (c, 2 CF_3), 74.2 (d, CF_2), 75.1 (e, 2 CF_3), 186.3 ppm (f, CF), nc:



$$\underset{c}{(CF_3)_2}\underset{f}{C}F\underset{d}{CF_2}O\underset{a}{(CF_3)_2}C\underset{b}{CF_2}O\underset{e}{(CF_3)_2}CCO_2CH_3$$

Tetramer ester 10: $C_{17}H_3F_{31}O_5$; ^{19}F nmr, 70.5 (16 F), 72.9 (8 F), 75.1 (6 F), 186.2 ppm (1 F), nc.

Pentamer ester 11: $C_{21}H_3F_{39}O_6$; ^{19}F nmr, 69.1 (23 F), 71.6 (8 F), 73.8 (7 F), 185.9 ppm (1 F), nc.

Reaction of OFIBO with potassium pentafluorophenoxide

Under anhydrous conditions pentafluorophenol (100 g) in acetonitrile (400 ml) was added slowly to potassium carbonate (112 g) in acetonitrile (1000 ml), refluxed for 4 h, cooled, and centrifuged. The solid residue was washed with dry acetonitrile, filtered, and dried to yield potassium pentafluorophenoxide (114.9 g, 95%).

OFIBO (89.9 g) was added in 1 h to potassium pentafluorophenoxide (66.6 g) dissolved in a mixture of glyme (115 ml) and tetraglyme (230 ml) stirred at -44°. This mixture was fractionally vacuum distilled to give acid fluoride 14 (32.8 g) and ester 15 (22.6 g).

Acid fluoride 14: Ir, 1850, 1510, 1240, 1085, 1010, 997, 975 cm^{-1}; ^{19}F nmr, -39.0 (CF), 71.6 (2 CF_3), 151.0 (2 aromatic CF), 157.4 (1 aromatic CF, triplet), 163.2 ppm (2 aromatic CF), nc.

Ester 15: Ir, 1780 cm^{-1}; ^{19}F nmr, 71.8 (2 CF_3), 151.6 (2 aromatic CF), 153.4 (2 aromatic CF), 155.8 (1 aromatic CF, triplet), 157.7 (1 aromatic CF, triplet), 162.1 (2 aromatic CF), 163.5 ppm (2 aromatic CF), nc.

Methyl ester of 14: Ir, 1770, 1505, 1460, 1435, 1300, 1270, 1230, 1160, 1090, 1050, 997, 812 cm^{-1}, nc.

Amide of 14: Ir, 1720, 1595, 1510, 1475, 1380, 1320, 1285, 1260, 1240, 1170, 1085, 1020, 1000, 980, 900, 805 cm^{-1}, nc.

Alkoxide 18 and HFPO Adducts

Acid fluoride 14 (25.8 g), cesium fluoride (11.0 g), and tetraglyme were ball milled in a glass bottle and centrifuged to yield alkoxide 18 (ir, 1670 cm^{-1}). This stirred liquid catalyst was cooled to -36°, and HFPO (13 ml at -78°) was added in 2 h under anhydrous conditions. Vacuum distillation afforded a fraction (bp 106°/0.6 mm Hg) consisting mainly of acid fluoride 19 and small amounts of the next two higher HFPO oligomers as determined by vapor phase chromatography.

Acid fluoride 19: Ir, 1860, 1510, 1250 (broad), 1160, 1125, 1090, 998, 980 cm^{-1}, nc.

Alkoxide 20 and OFIBO Adducts

Cesium pentafluorophenoxide was prepared in the same manner as the potassium salt. HFPO (35 ml at -78°) was added in 1 h to cesium pentafluorophenoxide (37.8 g) dissolved in a mixture of glyme (40 ml) and tetraglyme (80 ml) stirred at -42°. Vacuum distillation afforded the expected adduct which was converted to alkoxide 20 (ir, 1690 cm^{-1}) by mixing the adduct (68 g), cesium fluoride (34 g), and tetraglyme (90 ml). Centrifugation gave a clear catalyst solution to which OFIBO (62.1 g) was added in 1 h at -20° reaction temperature.

Fractional distillation gave one cut (bp 72°/11 mm Hg) composed of the reaction product of Equation 18 as determined by vapor phase chromatography. The infrared spectrum of this cut showed absorptions at 1870, 1510, 1250 (broad), 1160, 1135, 1070, 1010, 980, and 965 cm^{-1}, nc.

Unsaturated ether from OFIBO dimer

OFIBO dimer and trimer acid fluorides were isolated from reactions of OFIBO with alkoxide 2 by low temperature vacuum distillation. Mixtures of these acid fluorides were pyrolyzed at 270° in a fluidized sodium carbonate bed using nitrogen carrier gas to sweep reactants from a heated flask through the column. The condensed products were fractionally distilled to yield unsaturated ether 7 (bp 82-83°).

Unsaturated ether 7: $C_7F_{14}O$, m/e 366; ir, 1670 cm^{-1}; elemental analysis, theory 22.9% C and 72.8% F, found 22.3% C and 73.0% F; ^{19}F nmr, 66.7 (CF_3), 74.5 (2 CF_3), 78.7 (CF_2), 81.1 (CF), 88.9 (CF, pentuplet), 187.8 ppm (CF), nc.

Polymerization of unsaturated ether 7

Unsaturated ether 7 (1.0 g), tetrafluoroethylene (17.0 g), demineralized water (100 g) and catalysts were shaken in a bomb for 8 h at 50° to give a fine powdery polymer (14.4 g) having an infrared absorption at 995 cm^{-1} not present in polytetrafluoroethylene prepared in the same manner.

Perfluoro(2-phenoxypropene) 22

Pyrolysis of the adduct 14 from potassium pentafluorophenoxide and OFIBO at 265° in a sodium carbonate fluidized bed afforded perfluoro(2-phenoxypropene)(22), which was obtained in pure form (bp 120°/90 mm Hg) by preparative vapor phase chromatography.

Perfluoro(2-phenoxypropene) 22: $C_9F_{10}O$; ir, 1760 cm^{-1}; elemental analysis, theory 34.4% C and 60.5% F, found 34.5% C and 61.2% F; ^{19}F nmr, 67.5 (CF_3), 85.8 (CF), 95.4 (CF), 159.3 (2 aromatic CF), 162.6 (1 aromatic CF, triplet), 165.0 ppm (2 aromatic CF), nc.

Polymerization of perfluoro(2-phenoxypropene)

Perfluoro(2-phenoxypropene) (2.0 g), tetrafluoroethylene (17.0 g), and perfluoro(methyl vinyl ether) (38.0 g) were polymerized under conditions identical to those given for unsaturated ether 7. The resulting latex was coagulated and the wet crumb (11.5 g) was washed repeatedly with ethyl alcohol and water, but the 997 cm^{-1} infrared absorption band was not reduced. This absorption was absent in a copolymer of tetrafluoroethylene and perfluoro(methyl vinyl ether).

Perfluoroelastomer 23 containing no vulcanizing agents exhibited a tensile strength at break of 14.3 MPa and an elongation at break of 260%. The same sample containing crosslinking agents, press and postcured, showed a tensile strength at break of 20.8 MPa and an elongation at break of 220%. A copolymer of tetrafluoroethylene and perfluoro(methyl vinyl ether) showed no change in tensile strength and elongation values before and after attempted vulcanization.

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