

New polyfluoroalkoxysulfonyl fluorides. Part VIII. Alcoholic and polymeric derivatives

N.N. Hamel and G.L. Gard*

Department of Chemistry, Portland State University, Portland, OR 97207-0751 (USA)

Abstract

The epoxide $\overline{\text{OCH}_2\text{CHCH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}}$ (1) has been used in the preparation of new fluorocarbon sulfonyl fluorides containing aromatic primary and secondary alcohols, chlorohydrin and diol groups: $\text{HOCH}_2\text{CH}(\text{OCH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (2); $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (3); $\text{ClCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (4); and $\text{HOCH}_2\text{CH}(\text{OH})\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (5). A new polyester, $[\text{C}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})\text{O}]_n$ (6) and a derived urethane polymer 7 were also prepared. The composition of the urethane polymer indicated that per mol of diol 5, 6 mol of 1,6-diisocyanohexane were needed. Infrared, NMR and mass spectra data support the assigned structures.

Introduction

The utilization of fluorocarbon sulfonyl fluorides as ion-exchange resins, surface-active agents and in the preparation of strong sulfonic acids continues to make them a subject of considerable interest [1–4]. Solid polymer electrolyte (S.P.E.) fuel cells using Nafion or other fluorinated ionomeric materials have promise for use in electric vehicles [5].

In a previous paper we reported the synthesis of the epoxide $\overline{\text{OCH}_2\text{CHCH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}}$ (1) which contains a fluorinated alkyl sulfonyl fluoride group [6]. In this paper we wish to report our success in utilizing the reactivity of this epoxide to yield fluorocarbon derivatives containing not only the sulfonyl fluoride group but aromatic primary and secondary alcohols, chlorohydrin and diol groups as well. New polyester and urethane polymers are also reported. The results of this study along with homo- and co-polymerization studies are summarized in Fig. 1.

Experimental

Materials

The sulfonyl fluoride epoxide $\overline{\text{OCH}_2\text{CHCH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}}$ (1) was prepared according to the literature method [6]. Nafion NR50 beads 10–35 mesh (Aldrich Chemical Company) were converted to the acidic form as reported [7]. Benzyl alcohol (Matheson Coleman &

Bell) was distilled to use. Perfluoroglutaric anhydride (PCR Research Chemicals), 1,6-diisocyanohexane (Aldrich) and other chemicals obtained from commercial sources were used as received.

General procedures

Infrared spectra were obtained as capillary films on sodium chloride windows for liquid samples and as thin films for solid samples using a Nicolet 20DX spectrometer. NMR spectra were recorded with a Varian EM390 spectrometer operating at 90 MHz for proton and 84.7 MHz for fluorine resonances or with a Bruker AMX400 spectrometer operating at 400, 376.5 and 100.6 MHz for proton, fluorine and carbon resonances; $(\text{CH}_3)_4\text{Si}$, CFCl_3 , CD_3Cl and CD_3CN were used as internal standards. In ^{19}F spectra, chemical shifts upfield from CFCl_3 are assigned negative values. ^{13}C NMR data are for proton-decoupled spectra, except where noted. Mass spectra were obtained using a Hewlett Packard HP5890 series II gas chromatograph with a 5970 mass selective detector utilizing a 15 m DB-5 column.

Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, Germany.

Synthesis of aromatic primary and secondary alcohols $\text{HOCH}_2\text{CH}(\text{OCH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (2) and $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (3)

To a 15 ml round-bottom flask, equipped with a Teflon-coated stirring bar, reflux condenser and a calcium chloride drying tube, was added 1.97 g (7.70 mmol)

*Author to whom correspondence should be addressed.

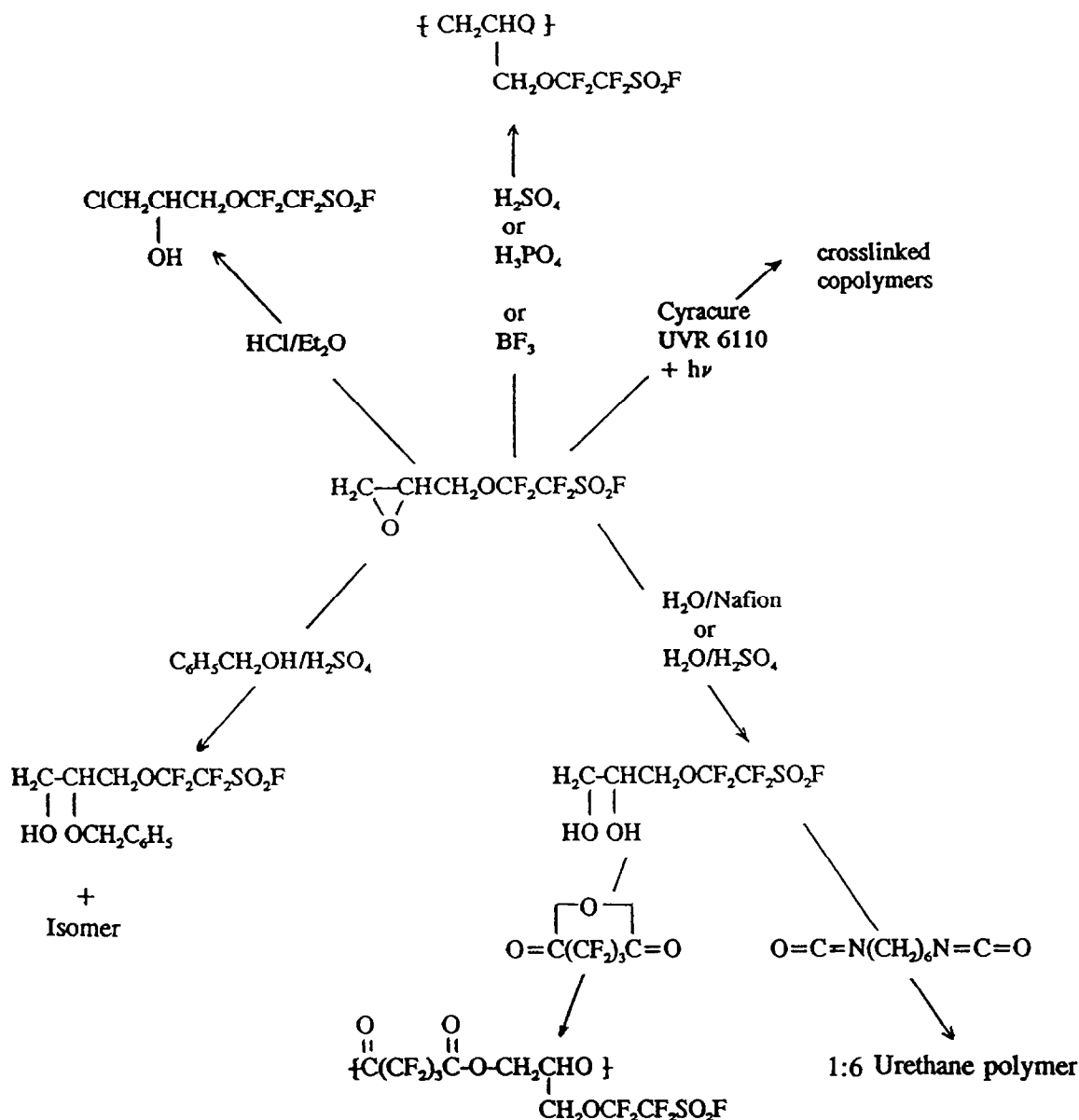


Fig. 1. Reactions of epoxide $\text{OCH}_2\text{CHCH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (**1**).

of epoxide **1**, 1.67 g (15.5 mmol) of freshly distilled benzyl alcohol, 8 ml of diethyl ether and three drops of concentrated sulfuric acid. After heating to reflux with vigorous stirring for 20 h, the diethyl ether was removed by distillation at atmospheric pressure. The pot residue was washed five times with 25 ml of water then dried over sodium sulfate. Distillation gave 1.06 g (2.95 mmol) of product, 38% yield, b.p. 138–140 °C/0.5 mmHg, which was a mixture consisting of 55% of **2** and 45% of **3** as determined by GC-MS and ^1H NMR analysis. No further attempts were made to separate the two components. MS (m/z) (EI) $^+$: 364 (molecular ion) $^+$; 243 ($\text{M}-\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2$) $^+$; 151 ($\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{CHOH}$) $^+$; 133 ($\text{CF}_2\text{SO}_2\text{F}$) $^+$; 107 ($\text{C}_6\text{H}_5\text{CH}_2\text{O}$) $^+$; 83 (SO_2F) $^+$; 77 (C_6H_5) $^+$; 65 (C_5H_5) $^+$;

51 (C_4H_3) $^+$; 39 (C_3H_3) $^+$; 31 (CH_2OH) $^+$. Analysis: Calc. for $\text{C}_{12}\text{H}_{13}\text{F}_5\text{SO}_4$: C, 39.57; H, 3.60; F, 26.1; S, 8.80%. Found: C, 42.64; H, 4.16; F, 24.1; S, 8.20%.

Synthesis of chlorohydrin

$\text{ClCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (**4**)

To a 10 ml round-bottom flask containing a Teflon-coated stirring bar and fitted with a reflux condenser and calcium chloride drying tube was added 1.45 g (5.66 mmol) of epoxide **1**, 1.10 g of 12 M hydrochloric acid and 5 ml of diethyl ether. The contents were heated to reflux with vigorous stirring for 24 h. After the addition of 5 ml of water, the resulting oily lower phase was separated, washed with water, dried over sodium sulfate and filtered. Distillation resulted in 1.32

g (4.52 mmol) of product, 80% yield, b.p. 84–86 °C/8 mmHg.

The infrared spectrum of **4** exhibited the following bands (cm^{-1}): 3585 (w); 3423 (m); 2973 (s); 2910 (w); 1455 (s); 1401 (w); 1336 (m); 1242 (s); 1202 (s); 1142 (s); 1118 (s); 1078 (shldr); 1043 (m); 1006 (s); 981 (w); 951 (w); 909 (w); 817 (s); 792 (s); 710 (w); 656 (s); 609 (s). MS (m/z) (EI)⁺: 243 (M – CH₂Cl)⁺; 133 (CF₂SO₂F)⁺; 83 (SO₂F)⁺; 81/79 (ClCH₂CHOH)⁺; 51/49 (CH₂Cl)⁺. Analysis: Calc. for C₅H₆F₅SClO₄: C, 20.52; H, 2.07; S, 10.69; Cl, 12.12%. Found: C, 20.49; H, 2.11; S, 10.89; Cl, 12.19%.

Synthesis of diol HOCH₂CH(OH)CH₂OCF₂CF₂SO₂F (**5**)

With H₂SO₄

Into a 25 ml round-bottom flask containing a Teflon-coated stirring bar and fitted with a reflux condenser and a calcium chloride drying tube was added 2.60 g (10.2 mmol) of epoxide **1**, 2.50 ml of water containing 0.1 g of 95% sulfuric acid and 15 ml of tetrahydrofuran. After refluxing for 5 h, the flask was cooled and 25 ml of water were added. The lower organic phase was removed and washed five times with 10 ml portions of water, dried over sodium sulfate and filtered. Distillation gave 1.00 g (3.65 mmol) of product, 36% yield, b.p. 100–101 °C/0.5 mmHg.

With Nafion

Using a similar apparatus, 20 ml of tetrahydrofuran containing 3.50 g (13.7 mmol) of epoxide **1**, 2 g of 10–35 mesh Nafion NR50 beads in the acidic form and 2 ml of water was stirred at room temperature for 24 h. The solution was filtered and the solvent removed by distillation at atmospheric pressure. The product (2.14 g, 7.81 mmol; 57% yield) was isolated by distillation, b.p. 100–101 °C/0.5 mmHg.

The infrared spectrum of **5** exhibited the following bands (cm^{-1}): 3381 (m); 2966 (w); 2946 (w); 2896 (w); 1456 (s); 1404 (w); 1335 (m); 1244 (s); 1202 (s); 1145 (s); 1117 (s); 1047 (m); 1005 (m); 944 (w); 933 (w); 881 (w); 814 (m); 791 (m); 657 (m); 609 (s); 523 (s). MS (m/z) (EI)⁺: 243 (M – CH₂OH)⁺; 133 (CF₂SO₂F)⁺; 100 (CF₂CF₂)⁺; 97 (C₂F₃O)⁺; 83 (SO₂F)⁺; 61 (CH₂(OH)CH(OH))⁺; 31 (CH₂OH)⁺. Analysis: Calc. for C₅H₇F₅SO₅: C, 21.91; H, 2.56; F, 34.6; S, 11.69%. Found: C, 22.21; H, 2.70; F, 34.2; S, 11.42%.

Synthesis of polyester

[C(O)CF₂CF₂CF₂C(O)OCH₂CH(CH₂OCF₂CF₂SO₂F)O]_n (**6**)

Into a thick-walled polymerization tube was placed 0.43 g (1.6 mmol) of diol **5** and 0.35 g (1.6 mmol) of hexafluoroglutaric anhydride. The contents of the tube were frozen at liquid nitrogen temperature, evacuated

and then sealed. After heating to 100 °C for 2 h, the tube was opened and heated to 100 °C under dynamic vacuum for 12 h. The resulting light brown, extremely viscous, product weighed 0.68 g (87% yield) and had a refractive index of 1.3818 at 21 °C.

The infrared spectrum of **6** exhibited the following bands (cm^{-1}): 2973 (vw); 1792 (s); 1455 (s); 1335 (m); 1313 (m); 1242 (s); 1201 (s); 1146 (s); 1051 (m); 1015 (w); 993 (w); 946 (w); 925 (w); 810 (m); 747 (w); 717 (w); 657 (m); 608 (m). Analysis: Calc. for C₁₀H₅F₁₁SO₇: C, 25.12; H, 1.05; F, 43.7%. Found: C, 24.87; H, 1.05; F, 43.6%.

Synthesis of urethane polymer **7**

Bulk method

To a thick-walled polymerization tube containing a Teflon-coated stirring bar was added 0.56 g (2.0 mmol) of diol **5**, 0.34 g (2.0 mmol) of 1,6-diisocyanohexane and 2 ml of chlorobenzene. The contents of the vial were frozen at liquid nitrogen temperature and the tube sealed. Vigorous stirring for 12 h at 100 °C resulted in the formation of a slightly yellow polymeric sponge-like product. The product was removed, cut into small pieces, washed 10 times with 5 ml of diethyl ether and dried under vacuum to give 0.60 g of light yellow product in 67% yield.

Film method

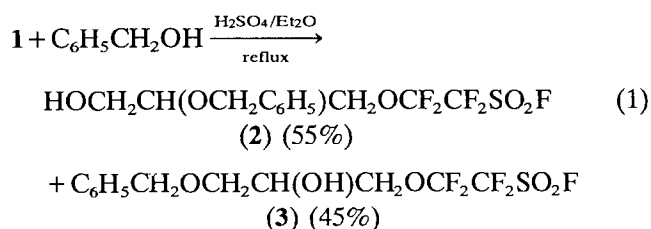
A portion of a mixture of 0.40 g (1.4 mmol) of diol **5** and 0.24 g (1.4 mmol) of 1,6-diisocyanohexane was spread on a clean glass plate and heated to 95 °C for 30 min under a nitrogen atmosphere. The tough flexible film was removed from the plate and washed by continuous extraction with acetone to remove unreacted monomer.

The infrared spectrum of **6** exhibited the following bands (cm^{-1}): 3339 (w); 2938 (m); 2681 (m); 1750 (s); 1714 (s); 1532 (m); 1455 (s); 1250 (s); 1145 (s); 1068 (s); 997 (m with sh. at 811); 765 (m); 653 (m); 610 (w). Analysis: Calc. for 1:6 polymer C₅₃H₇₉F₅SN₁₂O₁₇: C, 49.60; H, 6.20; F, 7.4%. Found: C, 46.72; H, 6.90; F, 7.4%.

Results and discussion

In a previous paper we presented the first report of a fluorocarbon molecular system containing both a sulfonyl chloride and an alcohol group [8]. We have also reported on the homo- and co-polymerization of compound **1** (Fig. 1) [9]. By using the synthon OCH₂CHCH₂OCF₂CF₂SO₂F (**1**), a number of new alcoholic systems containing the OCF₂CF₂SO₂F grouping were prepared.

We have found that the addition of benzyl alcohol to $\overline{\text{OCH}_2\text{CHCH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}}$ (**1**) appears to be equally favorable at either the terminal or more hindered internal site, as shown by the product composition:



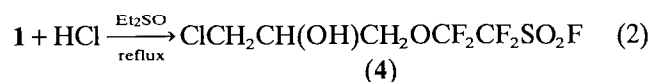
The GC-MS data of the distilled product gave molecular ion peaks for both alcohol products. For one product fraction, the molecular ion had a relative intensity of 27% and a fragment ion, $(m/z)^+$ of 31 $(\text{CH}_2\text{OH})^+$, which was assigned to product **2**. The second product fraction had a smaller molecular ion intensity of 2.5% and had a fragment ion, $(m/z)^+$ of 243 $(\text{CH}(\text{OH})\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})^+$, which was assigned to product **3**.

The ratio of alcoholic products **2** and **3** in the mixture was also revealed in the ^1H NMR spectrum; at 400 MHz two distinct pentets at 4.01 and 3.87 ppm for the methine protons with relative integration values of one proton each were found (Table 1). The ^{13}C NMR spectrum revealed separate signals for **2** and **3** for all but the fluorinated alkyl and aromatic carbons (Table 3). The ^{19}F NMR spectrum did not show any differences for the two components in the mixture (Table 2).

The infrared spectrum of the mixture contained a broad hydroxyl band at 3416 cm^{-1} , and weak C-H

stretches at 3093 and 3064 cm^{-1} , overtone bands at 1955 , 1836 , 1810 and 1724 cm^{-1} and out-of-plane bending motions at 745 and 700 cm^{-1} for the aromatic group.

The addition of HCl to **1** led to the isolation of a single alcoholic product. The orientation was as observed in the addition of HCl to other propylene oxide derivatives with electron-withdrawing substituents [10].



The second-order effects exhibited in the ^1H NMR spectrum of **4** were analyzed by computer-aided simulation [11] as an ABMX system (Table 1). Analysis of the mass spectrum and infrared data provides further support for this structure. The $(m/z)^+$ fragments of 243 and 51 can be unambiguously assigned to $(\text{M}-\text{ClCH}_2)^+$ and ClCH_2^+ peaks by the lack of and the presence of a Cl isotope peak, respectively. The infrared spectrum of **4**, as a neat film, showed a broad hydroxyl band at 3423 cm^{-1} while the C-Cl stretch was found at 710 cm^{-1} and was in the region expected for a primary chloride [12].

The synthesis of the diol $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (**5**) was achieved by the following routes:

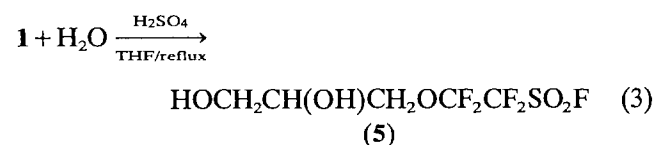


TABLE 1. ^1H NMR spectral data for $\text{R}^1\text{CH}_2\text{CH}(\text{R}^2)\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}^a$

Compound	R ¹	R ²	-CH ₂ -	-CH-	-CH ₂ O-
2 ^b			3.54 (m)	4.01 (p)	4.22 (m)
3 ^b			3.53 (m)	3.87 (p)	4.16 (m)
4	Cl	HO ^c	X 3.68 (d,d) Y 3.66 (d,d) $J_{X-Y} = 11.2$	C 4.15 (d,d,d,d) $J_{A-C} = 7.5$ $J_{B-C} = 3.6$ $J_{C-X} = 0.7$ $J_{C-Y} = 5.7$	A 4.23 (d,d) B 4.21 (d,d) $J_{A-B} = 9.9$
5	HO	HO ^d	A 4.19 (d,d) B 4.11 (d,d) $J_{A-B} = 10.2$	M 3.86 (d,d,d,d) $J_{A-M} = 4.4$ $J_{B-M} = 6.0$ $J_{M-X} = 4.9$ $J_{M-Y} = 5.7$	X 3.55 (d,d) Y 3.51 $J_{X-Y} = 11.4$
6 ^e					

^aChemical shifts in ppm; coupling constants in Hz.

^bFrom unseparated mixture of **2** and **3**; aromatic protons observed at δ 7.35 (m) ppm, benzylic protons at δ 4.53–4.55 ppm and hydroxyl proton at δ 3.2 ppm (CD_3CN).

^cHydroxyl proton observed at δ 2.85 ppm in CDCl_3 .

^dHydroxyl protons observed at δ 4.3 ppm in CDCl_3 and under H^X and H^Y peaks in CD_3CN .

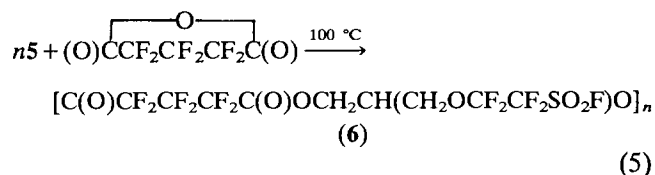
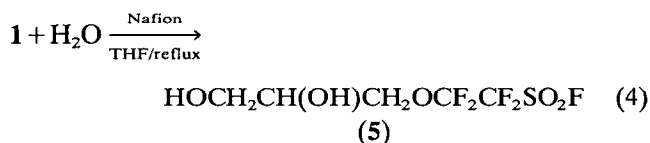
^eO(O)CCF₂CF₂CF₂C(O)O (unresolved broad overlapping resonances at δ 5.5 and 5.3 ppm).

TABLE 2. ^{19}F NMR spectral data for $\text{R}^1\text{CH}_2\text{CH}(\text{R}^2)\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}^a$

Compound	R^1	R^2	OCF_2	CF_2S	SO_2F
2 ^b	$(\text{C}_6\text{H}_5\text{CH}_2\text{O}/\text{HO})$		-82.9 (d,t)	-116.7 (d,t)	43.9 (t,t)
3			$^3J_{\text{FF}} = 4.0$		$^4J_{\text{FF}} = 5.4$ $^3J_{\text{FF}} = 5.2$
4	Cl	HO	-86.8 (d,t) $^3J_{\text{FF}} = 5.1$	-113.6 (d,t)	44.2 (t,t) $^4J_{\text{FF}} = 4.8$ $^3J_{\text{FF}} = 5.1$
5	HO	HO	-85.5 (d,t) $^3J_{\text{FF}} = 5.3$	-113.3 (d,t)	43.0 (d,t) $^4J_{\text{FF}} = 5.8$ $^3J_{\text{FF}} = 5.8$
6	$\text{O}(\text{O})\text{CCF}_2\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{O}$ $\text{O}(\text{O})\text{CCF}_2$ $-\text{CF}_2-$		-86.8 (broad) -121.3 (broad) -126.6 (p) $^3J_{\text{FF}} = 16$	-114.3 (broad)	43.0 (broad)

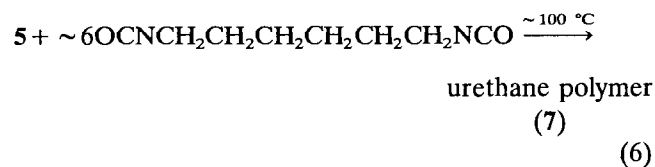
^aChemical shifts in ppm; coupling constants in Hz.^bFrom unseparated mixture of 2 and 3.TABLE 3. ^{13}C NMR spectral data for $\text{R}^1\text{CH}_2\text{CH}(\text{R}^2)\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$

Compound	R^1	R^2	R^1CH_2	CHR^2	CH_2O	CF_2	CF_2S
2	HO	$\text{C}_6\text{H}_5\text{CH}_2$ benzylic 73.9; aromatic 129.2; 128.6; 128.5; 128.4	62.9 $^1J_{\text{CH}} = 142.9$	70.0 $^1J_{\text{CH}} = 142.9$	68.8 $^3J_{\text{CF}} = 4.0$	116.9 $^1J_{\text{CF}} = 271.3$; $^2J_{\text{CF}} = 27.5$; $^3J_{\text{CF}} = 3.5$	114.5 $^1J_{\text{CF}} = 291.7$; $^2J_{\text{CF}} = 42.8$; $^2J_{\text{CF}} = 30.2$
3	$\text{C}_6\text{H}_5\text{CH}_2$ benzylic 72.8; aromatic same as 2	HO	71.7 $^1J_{\text{CH}} = 142.9$	68.5 $^1J_{\text{CH}} = 142.9$	68.9 $^3J_{\text{CF}} = 4.5$	same as 2	same as 2
4	Cl	HO	44.9 $^1J_{\text{CH}} = 151.5$	68.9 $^1J_{\text{CH}} = 141.4$	66.6 $^3J_{\text{CF}} = 4.2$	116.0 $^1J_{\text{CF}} = 275.9$; $^2J_{\text{CF}} = 28.0$; $^3J_{\text{CF}} = 3.8$	113.7 $^1J_{\text{CF}} = 301.8$; $^2J_{\text{CF}} = 41.6$; $^2J_{\text{CF}} = 34.4$
5	HO	HO	63.0 $^1J_{\text{CH}} = 142.3$	70.1 $^1J_{\text{CH}} = 143.3$	68.7 $^3J_{\text{CF}} = 4.1$	116.9 $^1J_{\text{CF}} = 273.4$; $^2J_{\text{CF}} = 27.9$; $^3J_{\text{CF}} = 3.7$	114.6 $^1J_{\text{CF}} = 300.5$; $^2J_{\text{CF}} = 42.7$; $^2J_{\text{CF}} = 34.3$



Diol was analyzed as an ABMXY ^1H NMR spectrum and the results are presented in Table 1. Its infrared spectrum showed a broad hydroxyl stretch at 3381 cm^{-1} and C-H stretches at 2966, 2946 and 2898 cm^{-1} .

Diol 5 is a valuable intermediate in the preparation of unique polymeric materials containing the $-\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ grouping:



Compound **6** showed two broad unresolved ^1H NMR resonances in CD_3CN with chemical shift values of δ 5.5 and 5.3 ppm (Table 1). In the ^{19}F NMR spectrum, a pentet at δ -126.6 ppm was found for the internal CF_2 group in the polymer backbone. All other resonances were broad and unresolved. The infrared spectrum showed a strong carbonyl band at 1792 cm^{-1} and agrees with those reported for fluorocarbon esters [13, 14].

The urethane polymer **7** was found to be very tough and flexible, insoluble in alcohol, acetone, water, acetonitrile, hexane, hexafluoropropanol, concentrated ammonia and 1 mol potassium hydroxide. It swelled with trifluoroacetic acid and appeared to dissolve in concentrated hydrochloric or concentrated sulfuric acid. The infrared spectrum of the product, after extraction with acetone, contained no bands attributable to the starting diisocyanate reactant. The bands at 3339 , 1714 and 1532 , and 765 cm^{-1} may be assigned to the N-H stretching, carbonyl stretching and $(\text{CH}_2)_6$ rocking motions, respectively [12]. Strong SO_2 asymmetric and symmetric stretchings and S-F band were observed at 1445 , 1250 and 811 cm^{-1} , respectively, while the carbon-fluorine bands were found at 1145 and 1068 cm^{-1} . We were unable to determine the structure of this polymer accurately, but based on elemental analysis an approximate composition formed from one diol to six diisocyanate molecules is possible.

The ^{19}F NMR spectra (Table 2) of the $-\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ grouping were very similar with chemical shift values of δ 44.2–43.0 ppm, δ -82.9 to -86.8 ppm and δ -113.3 to -116.7 ppm for the SO_2F , OCF_2 and CF_2S groups, respectively. These results agree with literature values [15–19]. For the polyester **6**, the fluorine resonances for $\text{CF}_2\text{CF}_2\text{CF}_2$ and $\text{CF}_2\text{CF}_2\text{CF}_2$ had integral values of two and four relative to the SO_2F group, respectively (Table 2).

All ^{13}C NMR spectral data (Table 3) were similar in that the methylene groups nearest the fluoroalkyl groups had chemical shifts ranging from δ 66.6 to 68.9 ppm and exhibited $^3J_{\text{CF}}$ couplings values of 4.0–4.5 Hz. The methine carbons, recognized as the only doublets in the ^1H coupled spectra, were found in the range δ 68.5–70.1 ppm and showed similar $^1J_{\text{CH}}$ couplings of 141.4–143.3 Hz. For the mixture of **2** and **3**, the chemical shift value of δ 70.0 ppm was assigned to the ether group ($\text{HCOCH}_2\text{C}_6\text{H}_5$), while the value of δ 68.5 ppm was assigned to the alcohol portion (HCOH). The low chemical shift of δ 44.9 ppm and $^1J_{\text{CH}}$ coupling of 151.5 Hz for the chlorine-substituted methylene carbon in **4** helped confirm the structure [20]. The $\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ portions of the spectra are all quite similar and agree with published results [15].

The infrared spectra of all new compounds listed above in the Experimental section exhibit the features

of the tetrafluoroethylsulfonyl fluoride group [15–21]. The characteristic SO_2 asymmetric and symmetric stretching frequencies were found in the 1455 – 1456 and 1243 – 1250 cm^{-1} regions. The S-F absorption was found between 810 – 817 cm^{-1} . The strong carbon fluorine absorption bands found at 1202 – 1043 cm^{-1} are attributed to the CF_2 groups. Bands characteristic of the epoxide ring at 3069 and 3016 (terminal C-H stretch), 1270 (symmetric ring stretch) and 907 (asymmetric ring stretch) cm^{-1} [22] were present in compound **1** but were absent in all the products.

Mass spectral fragments listed in the Experimental section were supportive of the assigned structures. For most compounds, the molecular ion peaks were not found. However, the relative instability of the halogenated and hydroxy compounds towards fragmentation was quite helpful in assigning structural isomers and is addressed above for these compounds.

Acknowledgment

We express our appreciation to Drs. Michael Riscoe and Rolf Winter of the Portland Veterans Hospital for the use of the GC-MS instrument.

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