Journal of Fluorine Chemistry, *42* (1989) 119–136

Received May 24, 1988, accepted July 25, 1988

THE SYNTHESIS OF NEW BIS/MONO FLUORINATED SULTONES AND THEIR DERIVATIVES

J. MOHTASHAM, D.G. COX, D.J. BURTON AND G.L. GARD

Departments of Chemistry, University of Iowa, Iowa City, IA 52242 (U.S.A.)
and Portland State University, Portland, OR 97207 (U.S.A.)

SUMMARY

The fluorinated bis/mono β-sultones, $[CF_2(\overline{O)CF(S}O_2)CF_2]_2$ and $CF_2{=}CF(CF_2)_2CF(\overline{SO_2)CF_2(O})$, **1** and **2** are formed via the reaction of sulfur trioxide with 1,5-perfluorohexadiene. In the presence of NaF, **2** and **1** rearranged to give the isomeric products, $CF_2{=}CF(CF_2)_2CF(SO_2F)C(O)F$ and $[FC(O)CF(SO_2F)CF_2]_2$, respectively. New sulfonyl fluoride esters have been prepared from allyl alcohol and the sultones **1** and **2**; polymerization of these esters has also been achieved.

INTRODUCTION

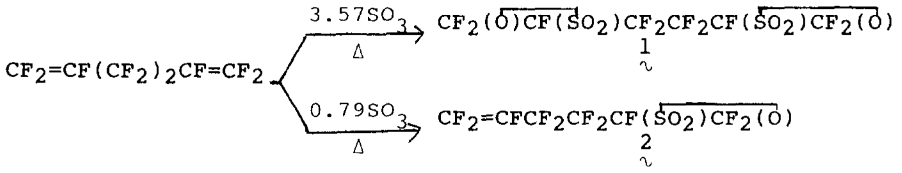
Sulfur trioxide reacts with mono and bis olefins to give mono and bis fluorosultones [1-3]. Fluorinated β-sultones undergo a number of interesting reactions that produce molecular systems containing the fluorosulfonyl group [1-4]. The incorporation of the fluorosulfonyl

0022-1139/89/$3 50

group leads to compounds useful as ion-exchange resins, co-monomers with tetrafluoroethylene, surface active agents and strong sulfonic acids [3-5]. Esters containing the fluorosulfonyl group have been prepared from fluorosultones with fluorinated and nonfluorinated alcohols [1,6-8]; allyl esters can also be prepared via this route. We wish to report our results with the fluorosultones obtained from 1,5-perfluorohexadiene.

RESULTS AND DISCUSSION

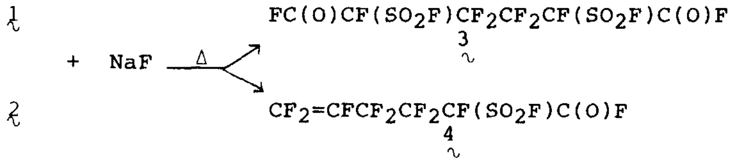
Two fluoro β-sultones were prepared via the reaction of $[CF_2{=}CFCF_2]_2$ with monomeric sulfur trioxide on heating. The product of the reaction is dependent on the ratio between reactants; when a 1:1 molar ratio composition of fluorinated diene and SO_3 is heated, a mixture containing mono- and bis-sultones is formed. If the molar ratio of fluorinated diene to SO_3 is increased to 1.26:1, mono-sultone is formed, and at a 1:3.57 ratio, bis-sultone is obtained:



$$CF_2{=}CF(CF_2)_2CF{=}CF_2 \xrightarrow[\Delta]{3.57SO_3} \underset{\mathbf{1}}{CF_2(\overline{O)CF(S}O_2)CF_2CF_2CF(\overline{SO_2)CF_2(O})} \quad (1)$$

$$CF_2{=}CF(CF_2)_2CF{=}CF_2 \xrightarrow[\Delta]{0.79SO_3} \underset{\mathbf{2}}{CF_2{=}CFCF_2CF_2CF(\overline{SO_2)CF_2(O})} \quad (2)$$

1 and **2** are thermally stable liquids and undergo rearrangement in the presence of MX (where M = Na or K, and X = F) to give the corresponding isomeric fluorosulfonyl acyl fluoride.



$$\mathbf{1} + NaF \xrightarrow{\Delta} \underset{\mathbf{3}}{FC(O)CF(SO_2F)CF_2CF_2CF(SO_2F)C(O)F} \quad (3)$$

$$\mathbf{2} + NaF \xrightarrow{\Delta} \underset{\mathbf{4}}{CF_2{=}CFCF_2CF_2CF(SO_2F)C(O)F} \quad (4)$$

In the presence of water and heat, **1** undergoes rearrangement, and a concerted hydrolysis/decarboxylation reaction:

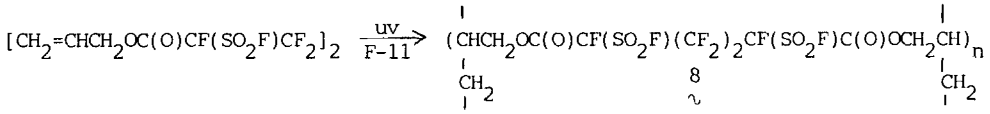
$$\mathbf{1} + H_2O \xrightarrow{\Delta} \underset{\mathbf{5}}{FSO_2CFHCF_2CF_2CFHSO_2F} + CO_2 + HF \qquad (5)$$

Allyl alcohol, with sodium fluoride, reacts with the mono/bis fluorosultones **1** and **2** according to the following equations:

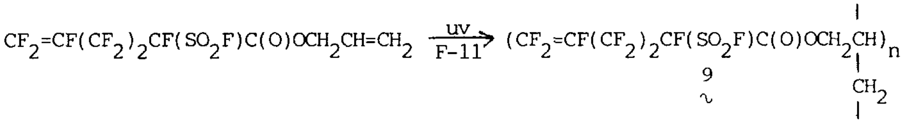
$$\mathbf{1} + CH_2{=}CHCH_2OH + 2NaF \longrightarrow \underset{\mathbf{6}}{[CH_2{=}CHCH_2OC(O)CF(SO_2F)CF_2]_2} + 2NaHF_2 \quad (6)$$

$$\mathbf{2} + CH_2{=}CHCH_2OH + NaF \longrightarrow \underset{\mathbf{7}}{CF_2{=}CFCF_2CF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2} + NaHF_2 \quad (7)$$

The new esters are thermally stable, clear and colorless liquids. In the presence of ultraviolet irradiation they undergo polymerization:



$$[CH_2{=}CHCH_2OC(O)CF(SO_2F)CF_2]_2 \xrightarrow[\text{F-11}]{\text{uv}} \underset{\mathbf{8}}{(\overset{|}{\underset{\underset{|}{CH_2}}{C}}HCH_2OC(O)CF(SO_2F)(CF_2)_2CF(SO_2F)C(O)OCH_2\overset{|}{\underset{\underset{|}{CH_2}}{C}}H)_n} \quad (8)$$



$$CF_2{=}CF(CF_2)_2CF(SO_2F)C(O)OCH_2CH{=}CH_2 \xrightarrow[\text{F-11}]{\text{uv}} \underset{\mathbf{9}}{(CF_2{=}CF(CF_2)_2CF(SO_2F)C(O)OCH_2\overset{|}{\underset{\underset{|}{CH_2}}{C}}H)_n} \quad (9)$$

When washed with CCl_3F, the polydiester in eq. (8) gave an off-white solid polymer which decomposed at ∿265°C. The polyester, **9**, is a viscous liquid.

The infrared spectra for compounds **1** through **5** contain the asymmetric and symmetric SO_2 stretching vibrations at 1462-1441 cm^{-1} and 1223-1209 cm^{-1}, respectively; these values are in agreement with other fluorosultones and comparable derivatives [3]. In compounds **3** and **4**, the carbonyl stretching frequency is found in the 1863-1884 cm^{-1} region, respectively; for compound **4** the olefinic stretching mode is located at 1785 cm^{-1}. The S-F stretching vibration of the fluorosulfonyl group in compounds **3**-**5** is found near the 800 cm^{-1} region.

In the new esters, the group frequencies and assignments are: carbonyl stretching vibration (1799-1764 cm^{-1}); olefinic stretching frequencies ($H_2C=CH$, 1652 cm^{-1} and $F_2C=CF-$, 1785 cm^{-1}); sulfur-fluorine stretching (near 800 cm^{-1}); SO_2 asymmetric and symmetric vibrational frequencies (1455-1448 cm^{-1} and 1223-1216 cm^{-1}); and C-H vibrational bands (2875-3100 cm^{-1}). It is to be noted that for polymeric systems the olefinic stretching vibration at 1652 cm^{-1} is absent.

In all cases these assignments are in excellent agreement with literature values [6-8].

The major mass spectral peaks for these compounds are listed in the experimental section. A molecular ion was observed for compound **2** and the MH^+ peak found for compounds **1**, **4**, **5**, **6**, and **7**. Additional M-X peaks, such as a $M-F^+$, $M-SO_2F^+$, $M-SO_3F^+$, $M-SO_3{}^+$, were also found.

The ^{19}F nmr chemical shift values are summarized in Table I. The nonequivalent CF_2 fluorines in the bis/mono-sultone rings are found in the -84.0 to -87.7 ppm range; for other fluorinated monosultones $\overline{CF_2CF_2OS}O_2$, $CF_3\overline{CFCF_2OS}O_2$, $CF_2ClCFClCF_2\overline{CFCF_2OS}O_2$, and $SF_5\overline{CFCF_2OS}O_2$ the CF_2 resonance bands are located in -72.8 to -88.5 ppm range [1-4]. The CF group in the four membered ring is located at -153.4 and -152.9 ppm for compounds **1** and **2**, respectively; in other sultone systems such as $CF_2ClCFClCF_2\overline{CFCF_2OS}O_2$ and the disultone of perfluoro-1,7-octadiene, the CF fluorine resonance is located at -148 and -150.1 ppm, respectively [1,2]. The ^{19}F nmr spectra for the CF_2 group in all compounds consisted in general of a complex multiplet with a band center in the range -113.2 to -126.3 ppm. The ^{19}F nmr values for the following functional groupings or arrangements, $-C(O)\underline{F}$, $-SO_2\underline{F}$, $-C\underline{F}H$, $-\underline{CF}(SO_2F)$, and $\underline{CF}_2=\underline{CF}$, in compounds **2** to **9** are all in excellent agreement with literature values [1-4].

The ^1H nmr data (chemical shifts and coupling constants) for the new esters are reported in Table 2. The chemical shifts and coupling constants for the $-CH_2CH=CH_2$ moiety are in agreement with values reported for allyl alcohol and $R_fC(O)OCH_2CH=CH_2$ derivatives [7-8]. The proton nmr spectrum for the polymeric ester $\underset{\sim}{9}$ showed, in general, broad peaks similar to that reported for other polymeric esters [8]. The nmr spectrum of the polyester $\underset{\sim}{8}$ formed from the bis-sultone was not obtained because of its insolubility in a number of solvents.

EXPERIMENTAL

Materials. The chemicals used in this work were obtained from commercial sources: SO_3 (MCB); $CH_2=CHCH_2OH$ (Mallinckrodt); NaF (Baker) was dried under vacuum before use. Freon-11 (CCl_3F) was dried over silica gel prior to use. All other reagents were used without further purification. The diene, $CF_2=CF(CF_2)_2CF=CF_2$ was prepared according to the literature.

General Procedure. Gases were manipulated in a conventional Pyrex-glass vacuum apparatus with a Heise-Bourdon tube gauge. Infrared spectra were obtained by using liquids or solids samples between KBr or KRS-5 disks on a Nicolet 20DX spectrometer. The nmr spectra were recorded with a Varian model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for fluorine resonances. TMS and F-11 were used as external standards. The melting/decomposition points were determined by using a Mel-Temp capillary melting point apparatus and are uncorrected. The mass spectra were taken on a VG 7070 HS mass spectrometer with an ionization potential of 70 eV. Perfluorokerosene was used as an internal standard.

Elemental analyses were determined by Beller Microanalytical Laboratory in Gottingen, F.R.G.

TABLE 1

^{19}F NMR Chemical Shifts

Compound	SO_2F	COF	CF_2^a F_1	CF_2^a F_2	CF_2^b F_1	CF_2^b F_2	CF_2^c	CF^d	CF^e	CF^f	CF_2^g
$[\overset{a}{CF_2}(O)\overset{d}{C}F(SO_2)\overset{c}{CF_2}]_2$ 1	-	-	-84.0 (d,t)	-86.7 (d,m)	-	-	-116.3 (d,m)	-153.4 (m)	-	-	-
$\overset{b}{CF_2}=\overset{e}{C}F(\overset{c}{CF_2})_2\overset{d}{C}F(SO_2)\overset{a}{CF_2}(O)$ 2	-	-	-84.5 (d,t)	-87.7 (d,d,t)	-89.3 (d,d,t)	-106.5 (d,d,t,t)	-119.9 (d,d,m) -118.0 (m)	-152.9 (m)	-192.8 (d,d,m)	-	-
$[FC(O)CF(SO_2F)CF_2]_2$ 3	55.8 (m)	31.8 (d,m)	-	-	-	-	-113.6 (d,m)	-160.3 (d,m)	-	-	-
$CF_2=CF(CF_2)_2CF(SO_2F)C(O)F$ 4	54.7 (m)	31.3 (m)	-	-	-89.3 (d,d,t)	-106.2 (d,d,m)	-119.3 -117.8 (m)	-160.0 (m)	-192.8 (d,d,m)	-	-
$[FSO_2\overset{f}{C}FH\overset{g}{CF_2}]_2$ 5	56.0 (m)	-	-	-	-	-	-	-	-	-190.1 (m)	-119.0 -126.3 (d,m)
$[CH_2=CHCH_2O\overset{O}{\overset{\parallel}{C}}CF(SO_2F)CF_2]_2$ 6	53.2 (m)	-	-	-	-	-	-113.2 (m)	-159.3 (d,m)	-	-	-

$CF_2=CF(CF_2)_2CF(SO_2F)\overset{O}{\overset{\|}{C}}OCH_2CH=CH_2$ 7	52.3 (m)	-	-	-	-89.3 (d,d,t)	-106.2 (d,d,m)	-118.8 -118.0 (m)	-160.3 (m)	-192.1 (d,d,m)	-	-
$[\overset{b}{CF_2}=\overset{e}{CF}(CF_2)_2CF(SO_2F)\overset{O}{\overset{\|}{C}}OCH_2\underset{CH_2}{CH}]_n$ 9	52.1 (b,s)	-	-	-	-87.8 (m)	-105.8 (b,d)	-118.2 (m)	-160.3 (s)	-192.8 (m)	-	-

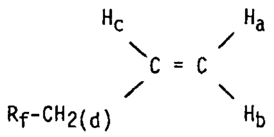
1) Fluorine chemical shifts in ppm from external $CFCl_3$.

2) s = singlet, d = doublet, t = triplet, m = multiplet, b = broadened.

3) a = $\underline{CF_2}(O)-$; b = $\underline{CF_2} = CF$; c = $-CF\underline{CF_2CF_2}CF$; d = $O\underline{CF}(SO_2)-$; e = $CF_2 =\underline{CF}$; f = $\underline{CFH}$; g = $\underline{CF_2}CFH$

TABLE 2

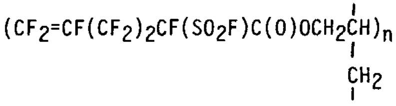
^1H NMR Data

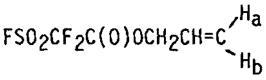


R_f	Chemical Shifts (ppm)				Coupling Constants (Hz)			
	H_d	H_c	H_b	H_a	J_{ac}	J_{bc}	J_{cd}	J_{ab}
$-O(O)CCF(SO_2F)(CF_2)_2CF(SO_2F)C(O)O-$	5.23 (d,d,d)	6.27 (d,d,t)	5.75 (d,d,t)	5.68 (d,d,t)	10.8	16.5	6.0	1.0
$CF_2=CF(CF_2)_2CF(SO_2F)C(O)O-$	5.10 (d,d,d)	6.17 (d,d,t)	5.66 (d,d,t)	5.57 (d,d,t)	10.5	17.2	6.1	0.9

1) Proton chemical shifts in ppm downfield from external TMS. Coupling constants for monoester were obtained with an General Electric QE 300 NMR Spectrometer.

2) For $(FSO_2CFHCF_2)_2$ the CH chemical shift is 7.1 ppm; the $J_{H,F}$ = 44.1 Hz.

3) For  $(CF_2=CF(CF_2)_2CF(SO_2F)C(O)OCH_2\overset{|}{\underset{\underset{|}{CH_2}}{CH}})_n$ the spectrum contained a broad peak at 4.53 ppm and a series of peaks between 1 and 3.5 ppm.

4) J_{ab} for  $FSO_2CF_2C(O)OCH_2CH=C\begin{smallmatrix}\nearrow H_a\\ \searrow H_b\end{smallmatrix}$ was found to be 1.2 Hz.

$(CF_2{=}CFCF_2')_2$ with Excess SO_3

To 85.0 mmol of SO_3 in a 130 ml Pyrex-glass Carius tube, equipped with a Kontes Teflon valve, 23.8 mmol of $(CF_2{=}CFCF_2')_2$ was added. The mixture was heated at 115$\pm$5°C for 14 h. Distillation of the mixture gave 21.7 mmol of a clear liquid, $[CF_2(\overline{O)CF(S}O_2)CF_2']_2$, in 91% yield, b.p. 69+1°C/15 mm.

The infrared spectrum had the following bands (cm^{-1}): 1441 (vs), 1427 (sh), 1342 (m), 1314 (ms), 1272 (ms), 1216 (s), 1180 (sh), 1124 (ms), 1096 (ms), 1061 (ms), 984 (m), 955 (sh), 920 (m), 892 (m), 857 (vw), 815 (sh), 787 (ms), 773 (sh), 738 (ms), 695 (w), 653 (ms), 639 (m), 611 (m), 604 (sh), 583 (w), 569 (w), 541 (sh), 520 (m), 498 (vw), 484 (m), 456 (w), 442 (w), 407 (m).

The ^{19}F nmr spectrum of $[CF_aF_b(\overline{O)CF(S}O_2)CF_2']_2$ gave the following relative peak areas: CF_2 (1.0, 1.0), CF_2' (2.0), and CF (1.0); the J_{ab} coupling value was 110.8 Hz. The positive ion $(CI)^+$ mass spectrum (m/e species): 423, MH^+; 404, $(MH-F)^+$; 403, $M-F^+$; 342, $(M-SO_3)^+$; 339, $(M-SO_2F)^+$; 323, $(M-SO_3F)^+$; 259, $C_6F_9O^+$; 255, $(M-C_2F_5O_3)^+$; 247, $(M-SO_3F_5)^+$; 243, $C_6F_9^+$; 231, $C_6F_5SO_2^+$; 211, $(M-CF_2CFCF_2SO_3)^+$; 209, $C_5F_7O^+$; 193, $C_5F_7^+$; 181, $C_4F_7^+$; 171, $C_5F_5O^+$; 169, $C_4F_3SO_2^+$; 162, $C_4F_6^+$; 159, $C_4F_5O^+$; 143, $C_4F_5^+$; 140, $C_4F_4O^+$; 109, $C_3F_3O^+$; 97, $C_2F_3O^+$; 95, $CFSO_2^+$; 93, $C_3F_3^+$; 81, $C_2F_3^+$; 79, $CFSO^+$; 74, $C_3F_2^+$; 67, SOF^+; 66, CF_2O^+; 64, SO_2^+; 63, CSF^+; 62, $C_2F_2^+$.

Anal. Calcd for $C_6F_{10}S_2O_6$: C, 17.06; F, 45.0; S, 15.17. Found: C, 17.18; F, 44.7; S, 15.01.

$[CF_2(\overline{O)CF(S}O_2)CF_2']_2$ with NaF

To a 50 ml Pyrex-glass round bottomed flask, equipped with a Teflon coated stirring bar, were added 73.8 mmol of dry NaF, and 30.8 mmol of $[CF_2(\overline{O)CF(S}O_2)CF_2']_2$. The reaction vessel was connected to a reflux condenser which was attached to a trap cooled to -78°C. The reaction mixture was heated to 80-100°C (48 h). Distillation of the mixture gave 1.90 mmol of a colorless liquid, $[FC(O)CF(SO_2F)CF_2]_2$, in 62% yield; b.p. 61±1°C/13 mm.

The infrared spectrum had the following bands (cm^{-1}): 1877 (s), 1863 (ms), 1455 (vs), 1237 (vw), 1230 (vs), 1209 (s), 1159 (s), 1138 (s), 1082 (m), 1040 (w), 991 (m), 963 (m), 934 (vw), 913 (vw), 829 (s), 773 (vw), 752 (vw), 716 (m), 653 (m), 611 (m), 590 (m), 576 (m), 562 (sh), 541 (ms), 464 (m), 456 (m).

The ^{19}F nmr spectrum gave the following relative peak areas: SO_2F (1.0), C(O)F (1.0), CF (1.0), and CF_2'(1.8).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 404, $(MH-F)^+$; 403, $(M-F)^+$; 339, $(M-SO_2F)^+$; 323, $(M-SO_3F)^+$; 255, $(M-C_2F_5O_3)^+$; 247, $(M-SO_3F_5)^+$; 211, $(M-SO_3C_3F_5)^+$; 191, $(C_4F_5SO)^+$; 171, $(C_5F_5O)^+$; 169, $C_4F_3SO_2^+$; 162, $C_4F_6^+$; 159, $C_4F_5O^+$; 143, $C_4F_5^+$; 140, $C_4F_4O^+$; 131, $C_3F_5^+$; 128, $C_3F_4O^+$; 119, $C_3FSO_2^+$; 112, $C_3F_4^+$; 109, $C_3F_3O^+$; 100, $C_2F_4^+$; 97, $C_2F_3O^+$; 93, $C_3F_3^+$; 90, $C_3F_2O^+$; 87, C_3FS^+; 83, SO_2F^+; 82, $CFSF^+$; 81, $C_2F_3^+$; 79, $CFSO^+$; 75, C_2FS^+; 74, $C_3F_2^+$; 67, SOF^+; 64, SO_2^+; 63, CFS^+; 59, C_2FO^+; 51, SF^+.

Anal. Calcd for $C_6F_{10}S_2O_6$: C, 17.06; F, 45.0; S, 15.17. Found: C, 17.42; F, 44.2; S, 16.09.

$[CF_2(\overline{O)CF(S}O_2)CF_2']_2$ with H_2O

To a 40 ml Kel-F vessel, equipped with a Teflon stirring bar, was added 17.1 mmol of $[CF_2(\overline{O)CF(S}O_2)CF_2']_2$. The reaction vessel was cooled to 0°C and 341.1 mmol of distilled H_2O was added dropwise over a period of 3 h. The mixture was heated at 40°C (12 h). The solid was recovered via filtration and sublimed in vacuo at 55°. The white solid $(FSO_2CFHCF_2)_2$, 12.09 mmol, was formed in 71% yield; m.p. 43-44°C.

The infrared spectrum had the following bands (cm^{-1}): 2973 (m), 1468 (sh), 1441 (s), 1420 (sh), 1328 (m), 1307 (m), 1293 (m), 1265 (w), 1251 (sh), 1237 (sh), 1209 (ms), 1181 (vw), 1152 (m), 1131 (m), 1033 (vw), 1019 (vw), 991 (m), 871 (m), 850 (sh), 836 (m), 829 (sh), 808 (m), 801 (sh), 773 (m), 759 (m), 752 (m), 702 (m), 625 (vw), 597 (m), 569 (sh), 555 (ms), 548 (ms), 527 (m), 498 (vw), 477 (ms), 470 (m), 449 (sh), 435 (w), 428 (sh), 407 (m).

The ^{19}F nmr spectrum gave the following peak areas: SO_2F (1.0), CF (1.2), and CF_2 (2.1).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 331, MH^+; 311, $(M-F)^+$; 291, $(M-HF_2)^+$; 249, $(MH_2-SO_2F)^+$; 248, $(MH-SO_2F)^+$; 247*, $(M-SO_2F)^+$; 227, $(M-HSO_2F_2)^+$; 195, $CF_2CF_2CFSO_2^+$; 165, $FSO_2CFHCF_2^+$; 163, $CF_2CF_2CFS^+$; 162, $CF(CF_2)_2CF^+$; 161, $FSOCFHCF_2C^+$; 151, $FSO_2CFHC_3^+$; 143, $CCF_2CF_2CF^+$; 141, CF_2CFCSO^+; 131, $CFCF_2CF_2^+$; 115, FSO_2CFH^+; 114, FSO_2CF^+; 113, $CF_2CF_2CH^+$; 111, $SOCHCF_2^+$; 101, $CFHCCCHS^+$; 95, FSO_2C^+; 93, CF_2CFC^+; 91, $SOCCF^+$; 79, $CFSO^+$; 75, $CFCS^+$; 69, $CFHC_3H^+$; 67, SOF^+; 64, SO_2^+ or $SCFH^+$; 63, SCF^+ or $CFHCF^+$; 57, C_2SH^+; 51, SF^+; 50, CF_2^+; 48, SO^+.

Anal. Calcd for $C_4F_8H_2S_2O_4$: C, 14.55; H, 0.61; F, 46.1; S, 19.40. Found: C, 14.57; H, 0.62; F, 46.4; S, 19.62.

Excess $(CF_2{=}CFCF_2)_2$ with SO_3

To a 12.5 mmol of SO_3 in a 130 ml Pyrex-glass Carius tube with a Kontes Teflon valve, 15.7 mmol of $CF_2{=}CF(CF_2)_2CF{=}CF_2$ was added. The mixture was heated for 10 h at 115±5°C. Distillation of the mixture gave 7.34 mmol of $CF_2{=}CF(CF_2')_2\overline{CF'CF_2''OS}O_2$ in 47% yield; b.p. 79±1°C 226 mm.

The infrared spectrum had the following bands (cm^{-1}): 1785 (s), 1441 (vs), 1370 (s), 1335 (sh), 1321 (s), 1279 (s), 1272 (sh), 1216 (vs), 1195 (sh), 1110 (s), 1089 (s), 1075 (sh), 998 (m), 977 (m), 970 (sh), 913 (m), 864 (m), 850 (sh), 815 (m), 787 (s), 766 (s), 745 (vw), 709 (vw), 695 (vw), 674 (sh), 660 (s), 646 (sh), 604 (w), 590 (w), 569 (vw), 540 (m), 519 (m), 484 (w), 428 (w), 407 (m).

The ^{19}F nmr spectrum of $F_cF_dC{=}CF(CF_2')_2\overline{CF'CF_a''F_b''OS}O_2$ gave the following relative peak areas: CF (1.1), CF' (1.0), CF_2'' (1.0, 1.0), CF_2' (4.1), and CF_2 (1.0,1.0); the coupling constants were J_{ab} = 110.1 Hz and J_{cd} = 50.5 Hz.

The positive ion $(CI)^+$ mass spectrum (m/e, species): 342, M^+; 323, $(M-F)^+$; 243, $(M-SO_3F)^+$; 231, $(C_5F_9^+)$; 212, $C_5F_8^+$; 193, $(M-CF_3SO_3)^+$; 181, $C_4F_7^+$; 155, $C_5F_5^+$; 143, $C_4F_5^+$; 131, $C_3F_5^+$; 124, $C_4F_4^+$; 112, $C_3F_4^+$; 109, $C_3F_3O^+$; 100, $C_2F_4^+$; 95, SO_2CF^+; 93, $C_3F_3^+$; 81, $C_2F_3^+$; 79, CFSO; 74, $C_3F_2^+$; 64, SO_2; 62, $C_2F_2^+$; 48, SO^+; 47, CFO^+; 44, CS^+.

Anal. Calcd for $C_6F_{10}SO_3$: C, 21.06; F, 55.5; S, 9.37. Found: C, 21.15; F, 55.0; S, 8.69.

$CF_2{=}CF(CF_2)_2\overline{CFCF_2OS}O_2$ with NaF

To a 50 ml Pyrex-glass round bottom flask, equipped with a Teflon coated stirring bar, were added 1.19 mmol of dry NaF, and 4.50 mmol of $[CF_2{=}CF(CF_2)_2\overline{CFCF_2OS}O_2]$. The reaction vessel was connected to a reflux condenser which was attached to a trap cooled to -78°C. The mixture was heated for 48 h at 147±3°C. Distillation of the mixture gave 2.92 mmol of $CF_2=CF(CF_2)_2CF(SO_2F)COF$, in 65% yield; b.p. 84-5°C/244 mm.

The infrared spectrum had the following bands (cm^{-1}): 1884 (s), 1870 (sh), 1785 (vs), 1462 (vs), 1377 (s), 1321 (vs), 1272 (m), 1244 (sh), 1223 (vs), 1195 (s), 1181 (s), 1166 (sh), 1138 (s), 1082 (s), 1005 (m), 984 (m), 955 (ms), 857 (m), 829 (ms), 794 (ms), 766 (ms), 745 (vw), 723 (m), 695 (m), 660 (m), 646 (sh), 639 (sh), 625 (sh), 611 (m), 590 (sh), 583 (m), 576 (sh), 555 (ms), 505 (w), 497 (m), 463 (m), 435 (m).

The ^{19}F nmr spectrum of $F_aF_bC=CF(CF_2)_2CF(SO_2F)C(O)F$ gave the following relative peak areas: SO_2F (1.0), COF (1.0), CF (1.1), CF (1.3), CF_aF_b (1.0, 1.1), and CF_2 (4.2); the J_{ab} coupling constant was 50.8 Hz.

The positive ion $(CI)^+$ mass spectrum (m/e, species):P 343, MH^+; 342, M^+; 324, $[MH-F]^+$; 323, $[M-F]^+$; 276, $[MH-SOF]^+$; 259, $[M-SO_2F]^+$; 243, $[M-SO_3F]^+$; 237, $CF_2=CF(CF_2)_2CSC^+$; 231, $CF_2=CFCF_2CC(SO_2)C^+$; 213, $[MH-SO_2F, COF]^+$; 212, $[M-SO_2F, COF]^+$; 209, $CFCF_2CF_2CFCOF^+$; 193, $CF_2=CF(CF_2)_2C^+$; 181, $CF_2=CF(CF_2)_2{}^+$; 171, $CFCF_2CF_2CCO^+$; 163, $CF_2CF_2CFS^+$; 162, $CFCF_2CF_2CF^+$; 143, $CF_2=CFCF_2C^+$; 131, $CF_2=CFCF_2{}^+$; 109, CF_2CFCO^+; 100, $CF_2CF_2{}^+$; 93, $CF_2=CFC^+$; 83, SO_2F^+; 81, CF_2CF^+; 79, $CFSO^+$; 67, SOF^+; 64, $SO_2{}^+$.

Anal. Calcd for $C_6F_{10}SO_3$: C, 21.06; F, 55.5; S, 9.37. Found, C, 21.52; F, 55.2; S, 9.74.

$[CF_2\overline{(O)CF(SO_2})CF_2]_2$ with $CH_2=CHCH_2OH$

To a 25 ml Pyrex-glass round bottomed flask, equipped with a

Kontes Teflon valve and a Teflon stirring bar, were added 3.57 mmol of dried NaF, 5.31 mmol of $[CF_2(\overline{O)CF(S}O_2)CF_2]_2$, and 10.34 mmol of $CH_2=CHCH_2OH$. The mixture was stirred for 3 h at room temperature. Distillation of the volatile material gave 2.61 mmol of $[CH_2=CHCH_2OC(O)CF(SO_2F)CF_2]_2$ in 49% yield; b.p. 111±2°C/36mm.

The infrared spectrum had the following bands (cm^{-1}): 3093 (vw), 3037 (vw), 2995 (vw), 2966 (w), 2889 (vw), 1792 (s), 1771 (s), 1652 (w), 1455 (vs), 1384 (sh), 1363 (m), 1307 (ms), 1272 (s), 1258 (ms), 1223 (s), 1188 (ms), 1152 (ms), 1117 (sh), 1082 (m), 1019 (m), 984 (m), 970 (vw), 941 (m), 899 (w), 829 (m), 801 (sh), 787 (m), 759 (vw), 752 (m), 688 (sh), 667 (m), 646 (sh), 604 (m), 576 (vw), 548 (m), 505 (sh), 484 (m), 456 (m).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.1), CF (1.0), and CF_2 (1.7). The ^1H nmr spectrum gave the following peak areas: CH_2 (1.8) and C_2H_3 (2.9).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 499, MH^+; 457, $[M-C_3H_5]^+$; 312, $FSO_2CF(CF_2)_2CFSOF^+$; 311, $C(CF_2)_2CF(SO_2F)COOC_3H_5^+$; 293, $FSO_2CF(CF_2)_2CFSO^+$; 291, $CCFCF_2CF(SO_2F)COOC_3H_4^+$; 261, $CCF_2CF(SO_2F)COOC_3H_5^+$; 235, $CF_2CF(SO_2F)COOC_2H_3^+$; 227, $CFCF(SO_2F)COOC_3H_2^+$; 209, $CCF(SO_2F)COOC_3H_3^+$; 197, $FSO_2CFCOOC_3H_3^+$; 195, $FSO_2CFCOOC_3H^+$; 171, $CF(CF_2)_2CCO^+$; 169, $CFCF_2CCSO_2^+$; 163, $CF_2CF_2CFS^+$; 145, $CF_2CFSO_2^+$; 140, $CF_2CF_2CCO^+$; 131, $CF_2CF_2CF^+$; 121, $SCFCOOCH_2^+$; 115, $CFCOOC_3H_4^+$; 112, $CFCOOC_3H^+$; 101, $CFCOOC_2H_2^+$; 100, $CF_2CF_2^+$; 95, FSO_2C^+; 87, $CFCOOC^+$; 85, $SCCOCH^+$; 83, SO_2F^+; 81, $CCOOCHC^+$; 79, $FSOC^+$; 71, $CFCOO^+$; 69, $CCOOCH^+$; 67, SOF^+; 64, SO_2^+; 63, SFC^+.

Anal. Calcd for $C_{12}H_{10}F_8S_2O_8$: C, 28.92; H, 2.02; F, 30.5; S, 12.87. Found: C, 28.65; H, 2.01; F, 30.0; S, 12.70.

$CF_2{=}CF(CF_2)_2\overline{CFCF_2OSO_2}$ with $CH_2{=}CHCH_2OH$

To a 50 ml Pyrex-glass round bottomed flask, equipped with a Teflon coated stirring bar, were added 3.1 mmol of dry NaF, 5.34 mmol of $CH_2{=}CHCH_2OH$, and 5.53 mmol of $CF_2{=}CF(CF_2)_2\overline{CFCF_2OSO_2}$. The mixture was heated for 20 h at 55±5°C. Distillation of the mixture gave 3.76 mmol of $CF_2{=}CF(CF_2')_2CF'(SO_2F)C(O)OCH_2CH{=}CH_2$, in 68% yield; b.p. 84±2°C/12mm.

The infrared spectrum had the following bands (cm^{-1}): 3100 (w), 3037 (vw), 2995 (vw), 2966 (w), 2896 (vw), 1785 (vs), 1652 (m), 1455 (vs), 1420 (sh), 1363 (s), 1321 (s), 1286 (s), 1251 (s), 1216 (s), 1173 (s), 1089 (s), 1019 (m), 991 (m), 970 (ms), 941 (ms), 892 (m), 857 (m), 829 (ms), 794 (ms), 780 (ms), 766 (ms), 738 (sh), 6985 (w), 681 (m), 653 (m), 618 (ms), 590 (ms), 569 (ms), 498 (m), 484 (m), 456 (m), 434 (m).

The ^{19}F nmr spectrum gave the following relative peak areas: SO_2F (1.0), CF (1.0), CF$'$(1.1), CF_2 (1.0, 1.1), and CF_2' (3.8). The ^1H nmr spectrum gave the following relative peak areas: CH_2 (2.0) and C_2H_3 (3.0).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 381, MH^+; 380, M^+; 379, $[M{-}H]^+$; 297, $[M{-}SO_2F]^+$; 296, $[M{-}H,SO_2F]^+$; 277, $[M{-}HF,SO_2F]^+$; 268, $CF_2{=}CF(CF_2)_2CFCOOC^+$; 249, $CF_2{=}CF(CF_2)_2CCOOC^+$; 240, $CF_2{=}CFCF_2CFCCOC_3H_2{}^+$; 231, $CF(CF_2)_2CFCOOCHC^+$; 221, $CF_2{=}CF(CF_2)_2CCO^+$; 213, $CF(CF_2)_2CCOOC_2H_2{}^+$; 212, $CF_2{=}CF(CF_2)_2CF^+$; 209, $CCF(SO_2F)COOC_3H_3{}^+$;

201, $CF(CF_2)_2CCOOCH_2^+$; 194, $FSO_2CFCOOCCC^+$; 193, $CF_2=CF(CF_2)_2C^+$; 181, $CF_2=CF(CF_2)_2^+$; 171, $CF(CF_2)_2CCO^+$; 165, $CF_2C(S)COOC_2H_3^+$; 163, $CF_2CF_2CFS^+$; 159, $CF_2CF_2CFCO^+$; 151, $CCCCFCOOCH_2CHCH^+$; 145, $CF_2CFSO_2^+$; 143, $CF(CF_2)_2C^+$; 132, $SCFCOOC_2H^+$; 131, $CF_2CF_2CF^+$; 127, $CCFCOOC_3H_4^+$; 124, $CF_2CF_2CC^+$; 121, $SCFCOOCH_2^+$; 115, $CFCOOC_3H_4^+$; 114, $CFSO_2F^+$; 113, $CFCOOCH_2CC^+$; 109, CF_2CFCO^+; 101, $CFCOOC_2H_2^+$; 100, $CF_2CF_2^+$; 95, FSO_2C^+; 94, CF_2COO^+; 93, CF_2CFC^+; 91, $SCFCO^+$; 87, $CFCOOC^+$; 83, SO_2F^+; 81, $CCOOC_2H^+$; 79, $FSOC^+$; 75, $CFCOO^+$; 69, $CCOOCH^+$; 67, SOF^+; 64, SO_2^+; 63, SCF^+; 62, $CFCF^+$.

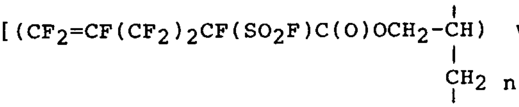
Anal. Calcd for $C_9H_5F_9SO_4$: C, 28.43; H, 1.33; F, 45.0; S, 8.43. Found: C, 28.44; H, 1.44; F, 45.5; S, 8.21.

Polymerization of $[CH_2=CHCH_2OC(O)CF(SO_2F)CF_2]_2$

To a 80 ml quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 0.610 g (1.22 mmol) of $[CH_2=CHCH_2OC(O)CF(SO_2F)CF_2]_2$ in 1.52 g (11.1 mmol) of $CFCl_3$ was irradiated with ultraviolet light from a 100 watt Hanovia lamp for 7 h. The solution was transferred from the reaction vessel, and $CFCl_3$ removed under vacuum to give 0.588 g (1.18 mmol) of an off-white solid; the polydiester was formed in 96% yield. A sample washed with CCl_3F decomposed at 265°C.

The infrared spectrum had the following bands (cm^{-1}): 3100 (vw), 2973 (w), 1799 (s), 1764 (ms), 1448 (vs), 1391 (vw), 1363 (w), 1307 (sh), 1279 (m), 1258 (m), 1230 (s), 1195 (m), 1159 (ms), 1082 (w), 1047 (sh), 1019 (w), 991 (w), 970 (vw), 934 (w), 899 (sh), 885 (vw), 829 (m), 801 (sh), 787 (m), 766 (vw), 752 (w), 667 (w), 604 (sh), Anal. Calcd for $C_{12}H_{10}F_8S_2O_8$: C, 28.92; H, 2.02; F, 30.5; S, 12.87. Found: C, 28.62; H, 2.01; F, 30.7; S, 12.83.

Polymerization of $CF_2=CF(CF_2)_2CF'(SO_2F)C(O)OCH_2CH=CH_2$

To a 80 ml quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 0.52 g (1.38 mmol) of $CF_2=CF(CF_2)_2CF(SO_2F)C(O)OCH_2CH=CH_2$ in 1.77 g (12.9 mmol) of $CFCl_3$ was irradiated with ultraviolet light from a 100 watt Hanovia lamp for 23 h. The liquid was drained from the reaction vessel and $CFCl_3$ was removed under vacuum to give 0.480 g (1.26 mmol) of the light brown viscous liquid  $[(CF_2=CF(CF_2)_2CF(SO_2F)C(O)OCH_2-\overset{|}{C}H)\underset{|}{C}H_2]_n$ which was formed in 92% yield.

The infrared spectrum had the following bands (cm^{-1}): 3100 (vw), 2973 (w), 2875 (vw), 1785 (s), 1455 (s), 1420 (sh), 1370 (s), 1321 (s), 1286 (s), 1251 (s), 1223 (s), 1173 (s), 1089 (s), 1012 (m), 970 (ms), 934 (sh), 892 (m), 864 (m), 829 (ms), 794 (ms), 766 (sh), 738 (sh), 709 (w), 681 (w), 646 (w), 618 (ms), 597 (ms), 569 (ms), 505 (w), 491 (m), 463 (wq), 435 (w), 407 (w).

The ^{19}F nmr spectrum gave the following relative peak areas: SO_2F (1.0), CF(0.9), CF'(1.2), CF_2 (1.0,1.0), and CF_2' (4.6).

Anal. Calcd for $C_9H_5F_9SO_4$: C, 28.43; H, 1.33; F, 45.0; S, 8.43. Found: C, 28.51; H, 1.36; F, 44.4; S, 8.25.

ACKNOWLEDGEMENTS

We wish to express our appreciation to the Gas Research Institute for support of this research. Dr. G.D. Knerr at the University of Idaho obtained the mass spectrum.

REFERENCES

1 D.C. England, M.A. Dietrich and R.V. Linsey, J. Am. Chem. Soc., 82 (1960) 6181.

2 I.I. Krylor, A.P. Kutepov, G.A. Sokolskii and I.L. Knunyants, Izv. Akad. Nauk. SSSR, Ser. Khim., 11 (1982) 2528.

3 J.M. Canich, M.M. Ludvig, G.L. Gard and J.M. Shreeve, Inorg. Chem., 23 (1984) 4403.

4 R. Beckerbauer, U.S. Pat. 3 714 245 (1973).

5 G.A. Olah, P.S. Iyer and P. Surya, Synthesis (1986) 513.

6 T.J. Huang, Z.X. Dong and J.M. Shreeve, Inorg. Chem., 26 (1987) 2304.

7 J. Khalilolahi, J. Mohtasham, M.E. Lerchen, R.M. Sheets and G.L. Gard, Inorg. Chem., 26 (1987) 2307.

8 R.J. Terjeson, J. Mohtasham, R.M. Sheets and G.L. Gard, J. Fluorine Chem., 38 (1988) 3.