Journal of Fluorine Chemistry, *43* (1989) 349–369
Received: September 19, 1988; accepted: January 22, 1989

SULFUR TRIOXIDATION OF ACYCLIC FLUORO-ALLYL ETHERS: SYNTHESIS OF NEW FLUORINATED SULTONES AND THEIR DERIVATIVES

JAVID MOHTASHAM, MARIE BRENNEN, ZHONGHENG YU, JAMES L. ADCOCK AND GARY L. GARD

Departments of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 and Portland State University, Portland, OR 97207-0751 (U.S.A.)

SUMMARY

The new fluorinated β-sultones, $CF_3OCF_2CF_2OCF_2\overline{CFCF_2OSO_2}$ and $CF_3OCF_2\overline{CFCF_2OSO_2}$ (1 and 2), have been prepared along with their rearranged isomers, $CF_3OCF_2CF_2OCF_2CF(SO_2F)COF$ and $CF_3OCF_2CF(SO_2F)COF$ (3, 4), and hydrolysis products, $CF_3OCF_2CF_2OCF_2CFHSO_2F$ (5) and $CF_3OCF_2CFHSO_2F$ (6).

New sulfonyl fluoride esters have been synthesized from allyl alcohol and the β-sultones 1 and 2; polymerization of these esters has also been achieved.

INTRODUCTION

Sulfonyl fluorides (RSO_2F, R = hydrocarbon or fluorocarbon group) are receiving considerable attention. It is known that incorporating a sulfonyl fluoride group (SO_2F) into molecular systems can lead to compounds useful as ion-exchange resins, surface-active agents and strong sulfonic acids [1-3].

0022-1139/89/$3.50

Fluorinated β-sultones are probably unequal as precursors to molecular systems containing the sulfonyl fluoride grouping [3-10]. We wish to report our results in using F-allyl ethers to prepare new fluoro β-sultones, $CF_3OCF_2CF_2OCF_2\overline{CFCF_2OS}O_2$ (1) and $CF_3OCF_2\overline{CFCF_2OS}O_2$ (2) which served as precursors to a series of molecular systems containing the fluorosulfonyl group; a number of different reaction pathways; rearrangement, hydrolysis, esterification, and polymerization are explored.

RESULTS AND DISCUSSION

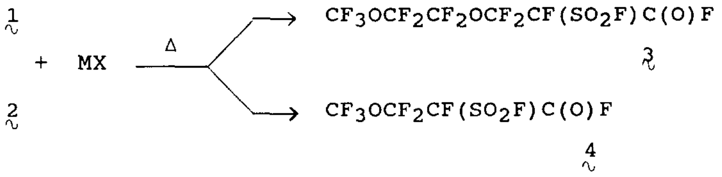
The following new fluoro β-sultones were produced via the reaction of the F-allyl ethers, $CF_3OCF_2CF_2OCF_2CF{=}CF_2$ and $CF_3OCF_2CF{=}CF_2$, with monomeric sulfur trioxide in a modified Carius tube under autogeneous pressure at temperatures greater than 100°C.

$$CF_3OCF_2CF_2OCF_2CF{=}CF_2 + SO_3 \rightarrow \underset{1}{CF_3OCF_2CF_2OCF_2\overline{CFCF_2OS}O_2} \qquad (1)$$

$$CF_3OCF_2CF{=}CF_2 + SO_3 \rightarrow \underset{2}{CF_3OCF_2\overline{CFCF_2OS}O_2} \qquad (2)$$

F-allyl ethers represent a class of compounds capable of producing unsymmetrical allylic cationic intermediates in reactions with sulfur trioxide [4]. The products in reactions (1) and (2) result from the stereospecific addition of SO_3 without isomer formation. By comparison, with F-vinyl ethers ($R_fOCF{=}CF_2$), the cycloaddition reaction with sulfur trioxide occurs in a reverse order [5]; *i.e.*, the oxygen and SO_2 of sulfur trioxide bonds with the olefinic carbon of the CF and the terminal CF_2 groups, repectively; incorporation of the unpaired electron from the ether oxygen into the electron cloud of the π-olefinic system creates a conjugated system such that the olefinic CF_2 carbon carries a partial negative charge and bonds with the sulfur portion of SO_3.

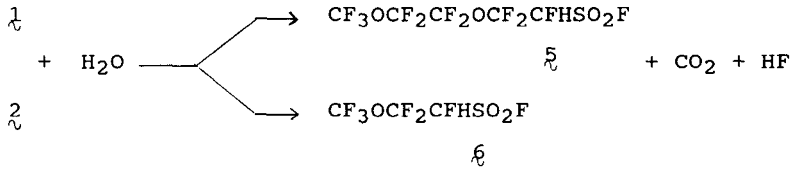
The β-sultones 1 and 2 are thermally stable, colorless liquids. Treatment of these β-sultones with metal halides, MX, (where M = Na or K, and X = F, Br) produced the corresponding isomeric fluorosulfonyl acylfluorides:



$$\mathbf{1} + MX \xrightarrow{\Delta} CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)F \quad \mathbf{3} \qquad (3)$$

$$\mathbf{2} + MX \xrightarrow{\Delta} CF_3OCF_2CF(SO_2F)C(O)F \quad \mathbf{4} \qquad (4)$$

In the presence of water, 1 and 2 undergo rearrangement, and a concerted hydrolysis/decarboxylation reaction:

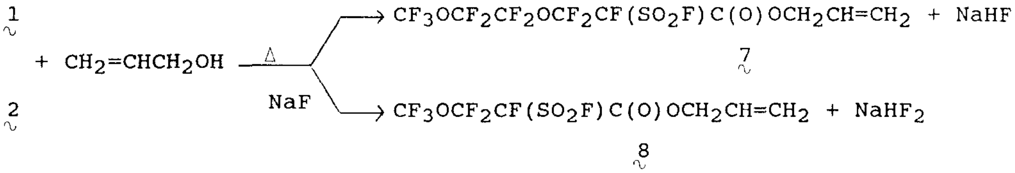


$$\mathbf{1} + H_2O \longrightarrow CF_3OCF_2CF_2OCF_2CFHSO_2F \quad \mathbf{5} \quad + CO_2 + HF \qquad (5)$$

$$\mathbf{2} + H_2O \longrightarrow CF_3OCF_2CFHSO_2F \quad \mathbf{6} \quad + CO_2 + HF \qquad (6)$$

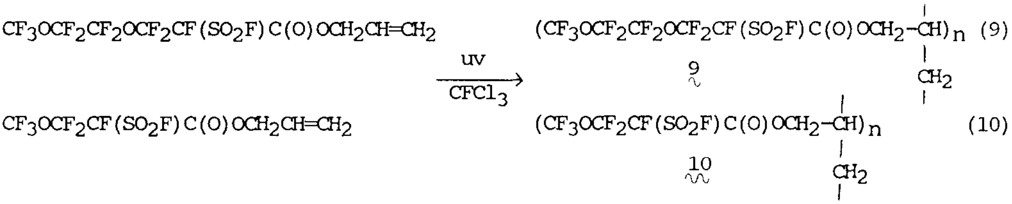
The products, 5 and 6, are also stable colorless liquids.

Allyl alcohol in the presence of sodium fluoride, reacts with the β-sultones 1 and 2 to produce new fluorosulfonyl allyl esters according to the following equations:



$$\mathbf{1}\ \text{or}\ \mathbf{2} + CH_2{=}CHCH_2OH \xrightarrow[NaF]{\Delta} \begin{cases} CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2 + NaHF & \mathbf{7} \\ CF_3OCF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2 + NaHF_2 & \mathbf{8} \end{cases}$$

The new allyl esters, 7 and 8, are thermally stable and colorless liquids; in the presence of ultraviolet irradiation, the new fluorosulfonyl allyl esters undergo polymerization:



$$CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2 \xrightarrow[CFCl_3]{uv} (CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)OCH_2{-}\overset{|}{\underset{\underset{|}{CH_2}}{CH}})_n \quad \mathbf{9} \quad (9)$$

$$CF_3OCF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2 \xrightarrow[CFCl_3]{uv} (CF_3OCF_2CF(SO_2F)C(O)OCH_2{-}\overset{|}{\underset{\underset{|}{CH_2}}{CH}})_n \quad \mathbf{10} \quad (10)$$

The fluorosulfonyl polyesters, 9 and 10, are viscous liquids.

The infrared spectra of the new compounds have several common features. The compounds 1 through 6 contain the asymmetric and symmetric SO_2 stretching vibrations at 1469-1449 and 1242-1220 cm^{-1}, respectively; these values are in good agreement with the other fluorinated β-sultones and their derivatives [3,6-7]. The carbonyl stretching frequency for compounds 3 and 4 is found in the 1883-1867 cm^{-1} region. The S-F stretching vibration of the fluorosulfonyl group in compounds 3-6 is found near the 800 cm^{-1} region. The carbon-hydrogen vibrational bands are located in the 2992-2988 cm^{-1} region.

For the new monomeric and polymeric esters, 7-10, the frequencies and assignments are as follows: carbonyl stretching vibrations are found in 1792-1771 cm^{-1} region; the olefinic stretching frequencies for compounds 7 and 8 are located at 1652 cm^{-1}. It is to be noted that for polymeric systems (compounds 9 and 10) the olefinic stretching vibration at 1652 cm^{-1} is absent. The sulfur-fluorine stretching of the fluorosulfonyl group in monomeric and polymeric systems is located near 800 cm^{-1}. The SO_2 asymmetric and symmetric vibrational frequencies for the compounds are found in the 1458-1454 and 1237-1228 cm^{-1} region, respectively. The C-H vibrational bands for compounds 7-10 are found in the region of 3100-2966 cm^{-1}.

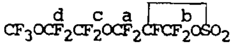
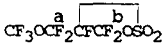
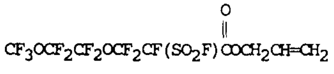
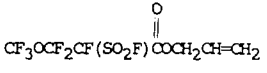
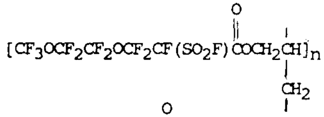
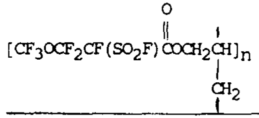
In all cases these assignments are in excellent agreement with literature values [8-10].

The major mass spectral peaks for these compounds are listed in the experimental section. The molecular ions were observed for compounds 7 and 8 and the MH^+ peak found for compounds 1, 2, 4, 6, 7 and 8. Additional $M-X^+$ or $MH-X^+$ peaks, such as a $MH-F^+$, $M-F^+$, $M-OH^+$, $M-SO_2F^+$, $M-CF_3O^+$, were also found.

The ^{19}F nmr chemical shift values are summarized in Table 1. The nonequivalent CF_2 fluorines in the sultones, 1 and 2, are found in the -85.3 to -91.7 ppm range; for a sultone such as $(CF_3)_2CFOCF_2\overline{CFCF_2OSO_2}$, the CF_2 resonance bands are located at -82.4 and -89.5 ppm [11], while for other similar sultones, $CF_3CF_2CF_2O\overline{CFCF_2SO_2O}$ and $C_2H_5O\overline{C(CF_3)CF_2SO_2O}$, the CF_2 resonance bands are located in the -84.1 to -100.5 ppm range [5]. Generally, the range for nonequivalent CF_2 fluorines of fluorinated sultones is reported between -72.8 to -88.5 ppm [3, 6-7, 12-14]. The CF resonance in the sultone ring is located at -154.7 and -153.9 ppm for compounds 1 and 2, respectively; in other sultone systems such as $(CF_3)_2CFOCF_2\overline{CFCF_2OSO_2}$ and $(CF_3)_2CFOCF(\overline{O)CF(S}O_2)CF_2OSO_2F$, the CF fluorine resonance is located at -151.8 and -149.0 ppm, respectively [4]. The ^{19}F nmr for CF_3 groups in

TABLE 1

^{19}F NMR Chemical Shifts

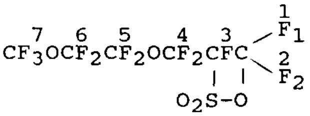
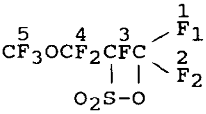
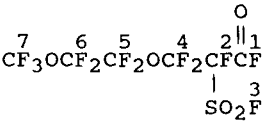
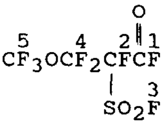
Compound	FSO_2	COF	CF_3	CF_2^{a}	CF_2^{b}		CF_2^{c}	CF_2^{d}	CF	CF^{e}
					F_1	F_2				
 $\overset{d}{CF_3}O\overset{c}{CF_2}CF_2O\overset{a}{CF_2}\overset{b}{CFCF_2}OSO_2$	-	-	-58.4 t	-79.5 m	-85.3 d,d,t	-91.7 d,t	-90.9 m	-93.2 q	-154.7 d,t	-
 $CF_3O\overset{a}{CF_2}\overset{b}{CFCF_2}OSO_2$	-	-	-57.3 t	-80.7 m	-85.4 d,d,t	-90.6 d,t	-	-	-153.9 d,t	-
$CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)F$	52.8 d,t,d	31.6 d,d,t	-57.5 t	-76.9 m	-	-	-90.3 m	-92.4 q	-161.0 d,t,d	-
$CF_3OCF_2CF(SO_2F)C(O)F$	55.6 d,t,d	34.6 d,d,t	-55.6 t	-77.5 m	-	-	-	-	-160.1 d,t,d	-
$CF_3OCF_2CF_2OCF_2\overset{e}{CF}HSO_2F$	53.9 m	-	-55.5 t	-76.9 m	-	-	-89.0 m	-91.0 q	-	-190.2 d,t,d
$CF_3OCF_2\overset{e}{CF}HSO_2F$	51.5 m	-	-57.4 t	-82.5 m	-	-	-	-	-	-192.5 d,t,d
 $CF_3OCF_2CF_2OCF_2CF(SO_2F)\overset{\overset{O}{\Vert}}{C}OCH_2CH{=}CH_2$	50.2 d,t	-	-57.8 t	-77.6 m	-	-	-90.7 m	-92.7 q	-161.7 d,t	-
 $CF_3OCF_2CF(SO_2F)\overset{\overset{O}{\Vert}}{C}OCH_2CH{=}CH_2$	52.6 d,t	-	-54.8 t	-77.8 m	-	-	-	-	-159.8 d,t	-
 $[CF_3OCF_2CF_2OCF_2CF(SO_2F)\overset{\overset{O}{\Vert}}{C}OCH_2\underset{\underset{CH_2}{\vert}}{CH}]_n$	50.5 b,m	-	-57.3 b,m	-76.9 b,m	-	-	-90.5 b,m	-92.6 b,m	-161.1 b,m	
 $[CF_3OCF_2CF(SO_2F)\overset{\overset{O}{\Vert}}{C}OCH_2\underset{\underset{CH_2}{\vert}}{CH}]_n$	49.8 b,m	-	-57.2 b,m	-79.6 b,m	-	-	-	-	-161.4 b,m	

1) Fluorine chemical shifts in ppm from external F-11.
2) d = doublet, t = triplet, q = quartet, m = multiplet and b = broadened

all compounds consisted in general of a triplet in the range of -54.8 to -57.8 ppm. The ^{19}F nmr values for the following functional groupings or arrangements, $-C(O)\underline{F}$, $-SO_2\underline{F}$, $-C\underline{F}_2$, $-OC\underline{F}_2C\underline{F}_2O$, $-C\underline{F}(SO_2F)$ and $-C\underline{F}H$, in compounds **1** to **10** are all in excellent agreement with literature values [3, 6-7, 12-14].

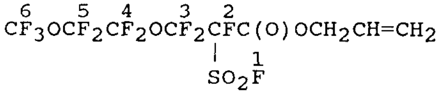
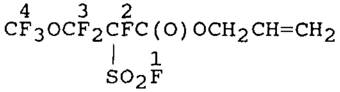
TABLE 2

^{19}F NMR Coupling Constants

Compound	Coupling Constant Hz
 $\underset{O_2S-O}{CF_3OCF_2CF_2OCF_2CFCF_2}$	$J_{2,1}$ = 112.9 $J_{3,1}$ = 6.6 $J_{4,1}$ = 2.4 $J_{4,2}$ = 12.7 $J_{4,3}$ = 7.7 $J_{6,7}$ = 9.4
 $\underset{O_2S-O}{CF_3OCF_2CFCF_2}$	$J_{2,1}$ = 112.9 $J_{3,1}$ = 6.6 $J_{4,1}$ = 2.8 $J_{4,2}$ = 14.1 $J_{4,3}$ = 6.8 $J_{4,5}$ = 9.2
 $CF_3OCF_2CF_2OCF_2\underset{SO_2F}{CF}\overset{O}{C}F$	$J_{2,1}$ = 23.8 $J_{3,1}$ = 16.7 $J_{4,1}$ = 7.6 $J_{3,2}$ = 3.8 $J_{4,2}$ = 8.2 $J_{4,3}$ = 6.5 $J_{6,7}$ = 9.9
 $CF_3OCF_2\underset{SO_2F}{CF}\overset{O}{C}F$	$J_{2,1}$ ≈ 24.0 $J_{3,1}$ = 16.1 $J_{4,1}$ = 7.3 $J_{3,2}$ ≈ 4.0 $J_{4,2}$ = 8.0 $J_{4,5}$ = 9.4

(continued overleaf)

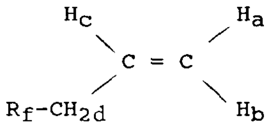
TABLE 2 (cont.)

$\overset{6}{C}F_3O\overset{5}{C}F_2\overset{4}{C}F_2O\overset{3}{C}F_2C\overset{2'}{F}\overset{2}{H}SO_2\overset{1}{F}$	$J_{2,1} \approx$ 2.0	$J_{2',1} =$ 6.6		
	$J_{2',2} =$ 44.6	$J_{3,2} =$ 5.8		
	$J_{3,2'} =$ 11.7	$J_{5,6} =$ 9.17		
$\overset{4}{C}F_3O\overset{3}{C}F_2C\overset{2'}{F}\overset{2}{H}SO_2\overset{1}{F}$	$J_{2,1} =$ 2.1	$J_{2',1} =$ 5.9		
	$J_{2',2} =$ 45.2	$J_{3,2} =$ 5.8		
	$J_{3,4} =$ 9.3			
 $\overset{6}{C}F_3O\overset{5}{C}F_2\overset{4}{C}F_2O\overset{3}{C}F_2\underset{SO_2\overset{1}{F}}{C}\overset{2}{F}C(O)OCH_2CH{=}CH_2$	$J_{2,1} =$ 4.2	$J_{3,1} =$ 9.9		
	$J_{3,2} =$ 8.2	$J_{5,6} =$ 9.4		
 $\overset{4}{C}F_3O\overset{3}{C}F_2\underset{SO_2\overset{1}{F}}{C}\overset{2}{F}C(O)OCH_2CH{=}CH_2$	$J_{2,1} \approx$ 4.0	$J_{3,1} =$ 9.7		
	$J_{3,2} =$ 8.2	$J_{3,4} =$ 8.9		

The ^1H nmr data (chemical shifts and coupling constants) for the new compounds are reported in Tables 2 and 3. 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 [7,15]. The proton nmr spectra for the polymeric esters **9** and **10** showed, in general, broad peaks similar to that reported for other polymeric esters [7,9].

TABLE 3

^1H NMR Data



	Chemical Shifts (ppm)			
R_f	H_d	H_c	H_b	H_a
$CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)O-$	5.10	6.04	5.65	5.56
	d,d,d	d,d,t	d,d,t	d,d,t
$CF_3OCF_2CF(SO_2F)C(O)O^-$	5.06	6.10	5.61	5.54

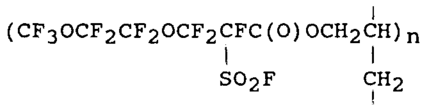
	Coupling Constants (Hz)				
R_f	J_{ac}	J_{bc}	J_{cd}	J_{ab}	J_{bd} or J_{ad}
$CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)O-$	10.4	17.2	6.1	1.3	1.2
$CF_3OCF_2CF(SO_2F)C(O)O^-$	10.6	17.1	6.0	-	-

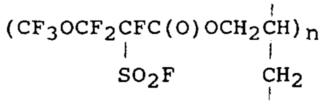
1) Proton chemical shifts in ppm downfield from external TMS.

2) The proton nmr spectrum of $CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)OCH_2CH=CH_2$ was also obtained with a General Electric QE-300 NMR spectrometer.

3) For $CF_3OCF_2CF_2OCF_2CFHSO_2F$ the CH chemical shift is 5.9 ppm.

4) For $CF_3OCF_2CFHSO_2F$ the CH chemical shift is 5.9 ppm.

5) For  $(CF_3OCF_2CF_2OCF_2\underset{SO_2F}{\underset{|}{C}}FC(O)OCH_2\overset{|}{\underset{\overset{|}{CH_2}}{\underset{|}{C}}}H)_n$ the spectrum contained a broad peak at 4.57 ppm and a series of peaks between 0.7 and 3.0 ppm.

6) For  $(CF_3OCF_2\underset{SO_2F}{\underset{|}{C}}FC(O)OCH_2\overset{|}{\underset{\overset{|}{CH_2}}{\underset{|}{C}}}H)_n$ the spectrum contained a broad peak at 4.55 ppm and a series of peaks between 0.7 and 3.5 ppm.

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 $CF_3OCF_2CF=CF_2$ and $CF_3OC_2F_4OCF_2CF=CF_2$ olefins were supplied by Dr. James Adcock. The olefins were prepared by fluorinating (aerosol direct fluorination method) the following esters, $CH_3O(CH_2)_3C(O)OCH_3$ and $CH_3O(CH_2)_2O(CH_2)_3C(O)OCH_3$. The fluorinated derivatives were treated with NaOH to give $CF_3O(CF_2)_3C(O)ONa$ and $CF_3O(CF_2)_2O(CF_2)_3C(O)ONa$. Heating the sodium salts gave $CF_3OCF_2CF=CF_2$ and $CF_3O(CF_2)_2OCF_2CF=CF_2$, respectively; complete details of this work will be published later.

General Procedure. Gases were manipulated in a conventional Pyrex-glass vacuum apparatus with a Heise-Bourdon tube gauge. Infrared spectra were obtained by using liquid or solid 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 Göttingen, West Germany.

$CF_3OC_2F_4OCF_2CF{=}CF_2$ with SO_3

To 21.3 mmol of SO_3 in a 130 ml Pyrex-glass Carius tube, equipped with a Kontes Teflon valve, 17.5 mmol of $CF_3OC_2F_4OCF_2CF{=}CF_2$ was added. The mixture was heated at 115±5°C for 48 h. Distillation of the mixture gave 13.4 mmol of a clear liquid, $CF_3OC_2F_4OCF_2\overline{CFCF_2OS}O_2$, 1, in 76.6% yield, b.p. 88°C/336 mm.

The infrared spectrum had the following bands (cm^{-1}): 1508 (w), 1497 (m), 1473 (w), 1449 (s), 1429 (w), 1403 (w), 1337 (ms), 1293 (s), 1225 (vs), 1149 (s), 1131 (s), 1107 (s), 1090 (s), 1061 (sh), 1024 (sh), 1000 (ms), 921 (ms), 901 (ms), 846 (m), 831 (m), 814 (w), 785 (ms), 763 (ms), 744 (ms), 684 (ms) 671 (sh), 660 (ms), 623 (sh), 579 (w), 566 (sh), 557 (sh), 531 (ms), 503 (m), 476 (m), 428 (sh), 409 (w).

The ^{19}F nmr spectrum of $CF_3OCF_2CF_2OCF''_2\overline{CFCF'_2OS}O_2$ (1) gave the following relative peak areas: CF_3 (3.5), CF''_2 (2.5), CF_2CF_2 (2.0,2.0), CF'_2 (1.0,1.0) and CF (1.0).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 413, MH^+; 393, $[M-F]^+$; 332, $[M-SO_3]^+$; 328, $[MH-CF_3O]^+$; 327, $[M-CF_3O]^+$; 313, $[M-SO_3F]^+$; 213, $CF_3OC_2F_4OC^+$; 185, $CF_3OCF_2CF_2{}^+$; 169, $CF_2OCFC(SO)C^+$; 163, $CF_3OCFCFO^+$; 150, $CF_2OCC(SO)C^+$; 147, $CF_3OCF_2C^+$; 135, $CF_3OCF_2{}^+$; 133, $CF_2CFOCCC^+$; 132, $OCF_2CF_2O^+$; 131, $CF_2CFCF_2{}^+$; 129, $CF(SO)CF_2{}^+$; 128, CF_3OCFC^+; 119, $OCFC(SO)C^+$; 109, CF_3OCC^+; 100, $CF_2CF_2{}^+$; 97, CF_3OC^+; 95, $CFSO_2{}^+$; 81, CF_2CF^+; 79, $CFSO^+$; 75, $OCFCO^+$; 69, $CF_3{}^+$; 64, $SO_2{}^+$;

Anal. Calcd for $C_6F_{12}SO_5$: C, 17.49; F, 55.3; S, 7.78. Found: C 17.47; F, 54.8; S, 7.62%.

$CF_3OC_2F_4OCF_2\overline{CFCF_2OS}O_2$ with NaF

To a 50 ml Pyrex-glass round bottomed flask, equipped with a Teflon coated stirring bar, were added 3.10 mmol of dry NaF, and 4.85 mmol of $CF_3OC_2F_4OCF_2\overline{CFCF_2OS}O_2$. The reaction vessel was connected to a reflux condenser which was attached to a trap cooled to -78°C. The reaction mixture was heated to 100±5°C (48 h). Distillation of the mixture gave 2.74 mmol of a colorless liquid, $CF_3OC_2F_4OCF_2CF(SO_2F)C(O)F$, **3**, in 56.5% yield; b.p. 82±1°C/343 mm.

The infrared spectrum had the following bands (cm^{-1}): 1881 (s), 1871 (s), 1844 (m), 1469 (s), 1402 (m), 1290 (s), 1236 (vs), 1195 (sh), 1152 (vs), 1118 (vs), 1094 (s), 996 (ms), 976 (ms), 901 (s), 824 (s), 807 (s), 763 (ms), 746 (sh), 709 (ms), 682 (ms), 672 (m), 621 (sh), 597 (s), 560 (sh), 526 (w), 486 (m), 459 (m), 418 (vw).

The ^{19}F nmr spectrum of $CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)F$ gave the following relative peak areas: SO_2F (1.0), C(O)F (1.0), CF_3 (3.5), CF_2 (2.1), CF_2CF_2 (2.2,2.1) and CF (1.0).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 393, $[M-F]^+$; 330, $[MH-SO_2F]^+$; 327, $[M-CF_3O]^+$; 313, $[M-SO_3F]^+$; 213, $CF_3OC_2F_4OC^+$; 211, $OCF_2CF(SOF)COF^+$; 185, $CF_3OCF_2CF_2{}^+$; 169, $CF_2OCFC(SO)C^+$; 163, $CF_3OCFCFO^+$; 150, $CF_2OCC(SO)C^+$; 147, $CF_3OCF_2C^+$; 145, $CF(SO_2F)CF^+$; 135, $CF_3OCF_2{}^+$; 133, $CF_2CFOCCC^+$; 132, $OC_2F_4O^+$; 129, CF_2CFSO^+; 128, CF_3OCFC^+; 119, $CC(SO_2F)C^+$; 109, CF_3OCC^+; 100, $CF_2CF_2{}^+$; 97, CF_3OC^+; 95, CSO_2F^+; 83, SO_2F^+; 81, CF_2CF^+; 79, $CFSO^+$; 78, $CFCOF^+$; 69, $CF_3{}^+$; 67, SOF^+; 64, $SO_2{}^+$; 56, CCS^+.

Anal. Calcd for $C_6F_{12}SO_5$: C, 17.49; F, 55.3; S, 7.78. Found: C, 17.51; F, 55.6; S, 7.66%.

$CF_3OC_2F_4OCF_2\overline{CFCF_2OS}O_2$ with H_2O

To a 40 ml Kel-F vessel, equipped with a Teflon stirring bar, was added 6.36 mmol of $CF_3OC_2F_4OCF_2\overline{CFCF_2OS}O_2$. The reaction vessel was cooled to 0°C and 10 ml of distilled H_2O was added dropwise over a period of 45 min. The mixture was allowed to stand at room temperature for 3 h after which the lower layer was separated, and dried over $MgSO_4$. Distillation gave 1.45 mmol of a colorless liquid, $CF_3OC_2F_4OCF_2CFHSO_2F$, $\underset{\sim}{5}$, in 22.8% yield; b.p. 86°C/336 mm.

The infrared spectrum had the following bands (cm^{-1}): 2988 (vw), 1455 (s), 1406 (m), 1356 (ms), 1289 (s), 1253 (s), 1231 (s), 1197 (s), 1147 (vs), 1123 (sh), 1092 (ms), 934 (sh), 916 (m), 907 (m), 894 (m), 882 (m), 866 (w), 824 (ms), 810 (sh), 788 (m), 753 (m), 734 (w), 721 (sh), 683 (w), 671 (m), 647 (sh), 599 (ms), 561 (sh), 527 (vw), 497 (vw), 477 (vw), 458 (vw).

The ^{19}F nmr spectrum of $CF_3OCF_2CF_2OCF_2CFHSO_2F$ gave the following relative peak areas: FSO_2 (1.0), CF_3 (3.1), CF_2 (2.0), CF_2CF_2 (2.1,2.0) and CF (1.1).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 349, $[M-OH]^+$; 347, $[M-F]^+$; 281, $[M-CF_3O]^+$; 195, $CF_2OCF_2CFSO^+$; 185, $CF_3OCF_2CF_2^+$; 165, $CF_2CFHSO_2F^+$; 164, $CF_2CFSO_2F^+$; 163, $OCFCOCCSO_2^+$; 147, $CFCOCCSO_2^+$; 145, $OCCOCC(SO_2)H^+$; 143, $CFOCCOCCS^+$; 135, $CFOCCSO_2^+$; 119, $CFOCCSO^+$; 117, $COCC(SO_2)H^+$; 101, $COCC(SO)H^+$; 100, CF_2CF_2; 97, OCF_2CF^+; 95, $CFSO_2^+$; 87, $CFOCCO^+$; 83, SO_2F^+; 82, CF_2CFH^+; 81, CF_2CF^+; 79, $CFSO^+$; 75, $CFCS^+$; 69, CF_3^+; 67, SOF^+; 64, SO_2^+; 59, $CFCO^+$.

Anal. Calcd for $C_5F_{11}HSO_4$: C, 16.40; H, 0.28; F, 57.1; S, 8.76. Found: C, 16.52; H, 0.27; F, 57.4; S, 8.81%.

$CF_3OCF_2CF{=}CF_2$ with SO_3

To a 24.4 mmol of SO_3 in a 130 ml Pyrex-glass Carius tube with a Kontes Teflon valve, 22.2 mmol of $CF_3OCF_2CF{=}CF_2$ was added. The mixture was heated for 6 days at 110±5°C. Distillation of the mixture gave 14.8 mmol of $CF_3OCF_2CFCF_2OSO_2$, **2**, in 66.7% yield; b.p. 69-72°C.

The infrared spectrum had the following bands (cm^{-1}): 1485 (w), 1470 (m), 1446 (s), 1428 (m), 1344 (s), 1317 (s), 1275 (sh), 1249 (vs), 1210 (sh), 1180 (s), 1138 (s), 1096 (s), 1021 (ms), 1007 (ms), 971 (sh), 932 (m), 920 (m), 908 (sh), 890 (w), 863 (m), 848 (w), 824 (ms), 785 (s), 690 (w), 675 (m), 657 (s), 621 (vw), 603 (vw), 582 (w), 546 (m), 523 (ms), 505 (ms), 469 (sh), 448 (m), 418 (vw).

The ^{19}F nmr spectrum of $CF_3OCF''_2CFCF'_2OSO_2$ gave the following relative peak areas: CF_3 (3.0), CF''_2 (1.92), CF'_2 (1.0,0.96) and CF (0.92).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 297, MH^+; 277, $[MH-HF]^+$; 216, $[M-SO_3]^+$; 211, $[M-CF_3O]^+$; 197, $[M-SO_3F]^+$; 189, $OCCFCF_2OSO_2^+$; 179, $CF_3OCF_2CS^+$; 151, $OCFCCOSO_2^+$; 150, $CF_2OCC(SO)C^+$; 147, $CF_3OCF_2C^+$; 145, $CF(SO_2)CF_2^+$; 135, $CF_3OCF_2^+$; 132, $OCCCOSO_2^+$; 131, $CF_2CFCF_2^+$; 129, $CF(SO)CF_2^+$; 128, CF_3OCFC^+; 125, $OCCFCF_2O^+$; 119, $OCFC(SO)C^+$; 109, CF_3OCC^+; 100, $OCC(SO)C^+$; 97, CF_3OC^+; 95, $CFSO_2^+$; 81, CF_2CF^+; 80, SO_3^+; 79, $CFSO^+$; 69, CF_3^+; 64, SO_2^+.

Anal. Calcd for $C_4F_8SO_4$: C, 16.22; F, 51.3; S, 10.81. Found: C, 16.33; F, 50.8; S, 10.74%.

$CF_3OCF_2CFCF_2OSO_2$ with NaF

To a 50 ml Pyrex-glass round bottom flask equipped with a Teflon coated stirring bar, were added 4.76 mmol of dry NaF, and 7.67 mmol of

$CF_3OCF_2\overline{CFCF_2OS}O_2$. The reaction vessel was connected to a reflux condenser which was attached to a trap cooled to -78°C. The mixture was heated for 24 h at 100°C and room temperature (8 d). Direct transfer of the product from the reaction mixture gave 3.38 mmol of $CF_3OCF_2CF(SO_2F)C(O)F$, **4**, in 44.1% yield.

The infrared spectrum had the following bands (cm^{-1}): 1883 (s), 1867 (sh), 1845 (sh), 1489 (sh), 1467 (s), 1445 (s), 1432 (sh), 1345 (sh), 1317 (s), 1242 (vs), 1176 (sh), 1145 (vs), 1129 (vs), 1095 (s), 1004 (ms), 973 (m), 932 (w), 920 (w), 888 (w), 860 (m), 826 (ms), 801 (ms), 782 (ms), 716 (m), 676 (m), 657 (ms), 619 (ms), 585 (ms), 544 (vw), 523 (w), 504 (vw), 481 (w), 457 (w), 422 (vw), 410 (vw).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 297, MH^+; 278, $[MH-F]^+$; 277, $[M-F]^+$; 231, $[MH-COF,F]^+$; 211, $[M-CF_3O]^+$; 197, $[M-SO_2F,O]^+$; 189, $OCF_2CF(SO_2)CO^+$; 151, $OCFC(SO_2)CO^+$; 150, $CF_2OCC(SO)C^+$; 147, $CF_3OCF_2C^+$; 145, $CF(SO_2)CF_2{}^+$; 135, $CF_3OCF_2{}^+$; 129, $CF(SF)COF^+$; 128, CF_3OCFC^+; 119, $CFC(SO_2)C^+$; 109, CF_3OCC^+; 107, $CFC(SO_2)^+$; 100, $CC(SO_2)C^+$; 97, CF_3OC; 95, CSO_2F^+; 85, CF_3O^+; 83, SO_2F^+; 81, CF_2CF^+; 79, $CFSO^+$; 69, $CF_3{}^+$; 67, SOF^+; 64, $SO_2{}^+$.

Anal. Calcd for $C_4F_8SO_4$: C, 16.22; F, 51.33; S, 10.83. Found: C, 16.26; F, 51.4; S, 10.95%.

$CF_3OCF_2\overline{CFCF_2OS}O_2$ with H_2O

To a 40 ml Kel-F vessel equipped with a Teflon stirring bar was added 12.8 mmol of $CF_3OCF_2\overline{CFCF_2OS}O_2$. The reaction vessel was cooled to 0°C and 10 ml of distilled H_2O was added dropwise over a period of 45 minutes. The mixture was distilled and the resulted product was dried over $MgSO_4$. Distillation gave 5.12 mmol of $CF_3OCF_2CFHSO_2F$, **6**, in 40.0% yield; b.p. 72°C.

The infrared spectrum had the following bands (cm^{-1}): 2992 (m), 1483 (ms), 1450 (vs), 1360 (s), 1310 (s), 1255 (vs), 1231 (vs), 1199 (sh), 1150 (vs), 1131 (vs), 1085 (sh), 1002 (m), 963 (w), 942 (m), 934 (m), 919 (ms), 885 (m), 857 (ms), 829 (s), 795 (s), 782 (sh), 752 (ms) 705 (sh), 681 (m), 666 (vw), 632 (m), 617 (ms), 581 (s), 530 (w), 493 (m), 489 (sh), 470 (m), 440 (m).

The ^{19}F nmr spectrum of $CF_3OCF_2CFHSO_2F$ gave the following relativ peak areas: FSO_2 (1.0), CF_3 (2.8), CF_2 (2.0) and CF (1.0).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 251, MH^+; 233, $[M-OH]^+$; 232, $[MH-F]^+$; 231, $[M-F]^+$; 165, $CF_2CFHSO_2F^+$; 164, $CF_2CFSO_2F^+$; 145, $CF_2CFSO_2^+$; 135, $CFOCCSO_2^+$; 129, CF_3OCFH^+; 128, CF_3OCFC^+; 113, CF_2CFS^+; 101, $COCC(SO)H^+$; 100, $COCCSO^+$; 97, OCF_2CF^+; 83, SO_2F^+; 82, CF_2CFH^+; 81, CF_2CF^+; 79, $CFSO_2^+$; 69, CF_3^+; 67, SOF^+; 64, SO_2^+; 59, $OCFC^+$.

Anal. Calcd for $C_3F_7HSO_3$: C, 14.41; H, 0.40; F, 53.2; S, 12.82. Found: C, 14.64; H, 0.43; F, 53.5; S, 12.79%.

$CF_3OC_2F_4OCF_2\overline{CFCF_2OSO_2}$ with $CH_2=CHCH_2OH$

To a 25 ml Pyrex-glass round bottom flask, equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 6.90 mmol of dried NaF, 3.76 mmol of $CF_3OC_2F_4OCF_2\overline{CFCF_2OSO_2}$ and 3.79 mmol of $CH_2=CHCH_2OH$. The mixture was stirred for 24 h at room temperature. Distillation of the volatile material gave 2.37 mmol of

$CF_3OC_2F_4OCF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2$, $\underset{\sim}{7}$, in 63.0% yield; b.p. 96-99°C/50 mm.

The infrared spectrum had the following bands (cm^{-1}): 3100 (vw), 3030 (vw), 2995 (vw), 2966 (w), 1792 (s), 1771 (s), 1652 (w), 1458 (vs), 1398 (w), 1363 (w), 1281 (s), 1251 (sh), 1230 (vs), 1205 (sh), 1159 (vs), 1124 (vs), 1096 (ms), 1026 (m), 991 (m), 970 (w), 941 (m), 899 (ms), 822 (ms), 787 (ms), 752 (ms), 688 (m), 674 (m), 625 (sh), 604 (ms), 562 (w), 527 (vw), 491 (w), 470 (w).

The ^{19}F nmr spectrum of $CF_3OCF_2CF_2OCF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2$ gave the following relative peak areas: FSO_2 (1.1), CF_3 (3.3), CF_2 (1.9), CF_2CF_2 (2.1,2.0) and CF (1.0). The ^1H nmr spectrum gave the following peak areas: CH_2 (1.9) and C_2H_3 (3.1).

The positive ion $(CI)^+$ mass spectrum (m/e, species): 451, MH^+; 450, M^+; 368, $[MH-SO_2F]^+$; 367, $[M-SO_2F]^+$; 366, $[M-H,SO_2F]^+$; 347, $[MH-F,COOC_3H_5]^+$; 338, $[M-SO_2F,C_2H_5]^+$; 305, $CF_3OC_2F_4OCF_2CCOCH_2^+$; 207, $CCF_2OCF_2CFSO^+$; 195, $CF_2OCF_2CFSO^+$; 185, $CF_3OCF_2CF_2^+$; 164, $CF_2CFSO_2F^+$; 163, $CF_3OCFCFO^+$; 145, $CF_2CFSO_2^+$; 143, $OCCFCOOC_3H_4^+$; 142, $OCCFCOOC_3H_3^+$; 137, $COC_2COOC_3H_5^+$; 136, $COC_2COOC_3H_4^+$; 135, $CFOCCSO_2^+$; 128, $SCFCOC_3H^+$; 123, $OC_2COOC_3H_3^+$; 121, $OC_2COOC_3H^+$; 119, $CFOCCSO^+$; 117, SO_2CCOCH^+; 109, $CCCOOC_3H_5^+$; 106, $CCCOOC_3H_2^+$; 103, $CFCOOC_2H_4^+$; 101, $CFCOOC_2H_2^+$; 100, $CF_2CF_2^+$; 99, $CFCOC_3H_4^+$; 97, OCF_2CF^+; 95, $CFSO_2^+$; 89, $CFCOOCH_2^+$; 85, $COOC_3H_5^+$; 83, SO_2F^+; 82, $COOC_3H_2^+$; 81, $COOC_3H^+$; 80, $COOC_3^+$; 79, $CFSO^+$; 71, $COOC_2H_3^+$; 69, CF_3^+; 67, SOF^+; 64, SO_2^+; 63, SCF^+.

Anal. Calcd for $C_9H_5F_{11}SO_6$: C, 24.01; H. 1.12; F, 46.4; S, 7.12. Found: C, 24.00; H. 1.04; F, 46.8; S, 7.28%.

$CF_3OCF_2\overline{CFCF_2OS}O_2$ with $CH_2{=}CHCH_2OH$

To a 50 ml Pyrex-glass round bottomed flask, equipped with a Teflon coated stirring bar, were added 4.52 mmol of dry NaF, 4.83 mmol of $CH_2{=}CHCH_2OH$, and 6.71 mmol of $CF_3OCF_2\overline{CFCF_2OS}O_2$. The mixture was stirred for 7 days at room temperature and was heated for 6 days at 63±2°C. Distillation of the mixture gave 4.62 mmol of $CF_3OCF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2$, **8**, in 95.7% yield; b.p. 65±1°C/22 mm.

The infrared spectrum had the following bands (cm^{-1}): 3100 (vw), 3037 (vw), 3002 (vw), 2966 (vw), 1785 (s), 1778 (s), 1652 (w), 1455 (s), 1363 (m), 1321 (s), 1293 (sh), 1286 (s), 1237 (vs), 1159 (s), 112 (vs), 1023 (m), 990 (m), 973 (m), 940 (ms), 896 (m), 862 (w), 830 (m), 818 (ms), 794 (ms), 780 (sh), 744 (vw), 707 (w), 680 (w), 658 (sh), 62 (ms), 590 (s), 530 (vw), 513 (vw), 488 (w), 461 (w), 440 (vw), 420 (vw), 410 (vw).

The ^{19}F nmr spectrum of $CF_3OCF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2$ gave the following relative peak areas: FSO_2 (0.86), CF_3 (3.0), CF_2 (1.9) and CF (1.0). The ^1H nmr spectrum gave the following relative peak areas: CH_2 (1.7) and C_2H_3 (2.7).

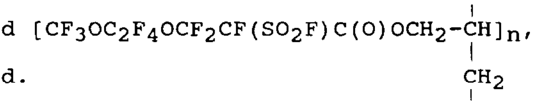
The positive ion $(CI)^+$ mass spectrum (m/e, species): 335, MH^+; 334, M^+; 251, $[M-SO_2F]^+$; 250, $[MH-CF_3O]^+$; 231, $[MH-CF_3O,F]^+$; 222, $CF_2CF(SO_2F)COOCH_2^+$; 203, $CF_2CF(SO_2)COOCH_2^+$; 194, $CF_2C(SO_2)COOCC^+$; 189, $CF_2CF(SO_2)COO^+$; 175, $CFC(SO_2)COOCC^+$; 165, $CFC(SO_2)COOCH_2^+$; 164, $CF_2CFSO_2F^+$; 157, $CF_2CF(SO_2)C^+$; 145, $CF_2CFSO_2^+$; 135, $COC_2COOC_3H_3^+$; 128, $SCFCOC_3H^+$; 121, $OC_2COOC_3H^+$; 119, $CFOCCSO^+$; 117, SO_2CCOCH^+; 109, $CCCOOC_3H_5^+$; 106, $CCCOOC_3H_2^+$; 101, $CFCOOC_2H_2^+$;, 100, $CFCOC_3H_5^+$; 99, $CFCOC_3H_4^+$; 97, OCF_2CF^+; 91, $CCFSO^+$; 87, $CFCOOC^+$; 85, CF_3O^+; 83, SO_2F^+;

82, $COOC_3H_2^+$; 81, $COOC_3H^+$; 79, $CFSO^+$; 73, $COOC_2H_5^+$; 71, $COOC_2H_3^+$; 70, $COOC_2H_2^+$; 69, CF_3^+; 68, $COOC_2^+$; 67, SOF^+; 64, SO_2^+; 59, $CFCO^+$; 57, $OC_3H_5^+$; 55, $COC_2H_3^+$; 54, $COC_2H_2^+$.

Anal. Calcd for $C_7H_5F_7SO_5$: C, 25.16; H, 1.51; F, 39.8; S, 9.59. Found: C, 25.34; H, 1.54; F, 39.6; S, 9.43%.

Polymerization of $CF_3OC_2F_4OCF_2CF(SO_2F)C(O)OCH_2CH=CH_2$

To a 80 ml quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 0.345 g (0.766 mmol) of $CF_3OC_2F_4OCF_2CF(SO_2F)C(O)OCH_2CH=CH_2$ in 1.08 g (7.85 mmol) of $CFCl_3$ was irradiated with ultraviolet light from a 100 watt Hanovia lamp for 21.5 hours. The solution was transferred from the reaction vessel and $CFCl_3$ removed under vacuum to give 0.272 g (0.604 mmol) of the light brown viscous liquid

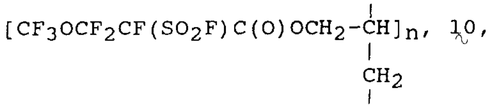


$[CF_3OC_2F_4OCF_2CF(SO_2F)C(O)OCH_2\text{-}\underset{\underset{|}{CH_2}}{\overset{|}{CH}}]_n$, **9**, which was formed in 78.8% yield.

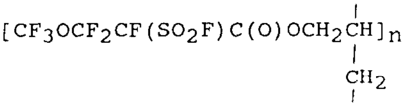
The infrared spectrum had the following bands (cm^{-1}): 2968 (vw), 2878 (vw), 1791, (ms), 1456 (ms), 1419 (vw), 1399 (w), 1291 (vs), 1236 (vs), 1236 (vs), 1196 (vs), 1148 (vs), 1125 (vs), 1028 (m), 902 (ms), 822 (m), 747 (w), 681 (w), 670 (w), 647 (vw), 619 (sh), 599 (m), 562 (sh), 527 (vw), 490 (vw), 459 (vw), 439 (vw).

Polymerization of $CF_3OCF_2CF(SO_2F)C(O)OCH_2CH=CH_2$

To a 80 ml quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 0.348 g (1.04 mmol) of $CF_3OCF_2CF(SO_2F)C(O)OCH_2CH=CH_2$ in 1.36 g (9.89 mmol) of $CFCl_3$ was irradiated with ultraviolet light from a 100 watt Hanovia lamp for 21.5

hours. The liquid was drained from the reaction vessel and $CFCl_3$ was removed under vacuum to give 0.302 g (0.903 mmol) of the light brown viscous liquid  $[CF_3OCF_2CF(SO_2F)C(O)OCH_2-\underset{\substack{|\\ CH_2\\ |}}{\overset{|}{C}H}]_n$, **10**, which was formed in 86.8% yield.

The infrared spectrum had the following bands (cm^{-1}): 2968 (w), 2878 (vw), 1791 (s), 1454 (s), 1417 (vw), 1316 (s), 1291 (s), 1243 (vs), 1228 (vs), 1165 (s), 1130 (vs), 1023 (m), 976 (m), 891 (m), 762 (m), 818 (ms), 796 (ms), 736 (vw), 702 (vw), 683 (w), 658 (sh), 620 (m), 588 (ms), 532 (w), 510 (vw), 488 (w), 459 (w), 422 (vw).

The ^{19}F nmr spectrum of  $[CF_3OCF_2CF(SO_2F)C(O)OCH_2\underset{\substack{|\\ CH_2\\ |}}{\overset{|}{C}H}]_n$ gave the following relative peak areas: FSO_2 (1.0), CF_3 (3.4), CF_2 (1.9) and CF (1.0).

Anal. Calcd for $C_7H_5F_7SO_5$: C, 25.16; H, 1.51; F, 39.80; S, 9.59. Found: C, 25.28; H, 1.55; F, 39.71; S, 9.23%.

ACKNOWLEDGEMENTS

We wish to express our appreciation to the Gas Research Institute (5084-260-1085) and the U.S. Department of Energy, Grant No. DE-FG21-88MC25142, for support of this research. Dr. G.D. Knerr at the University of Idaho obtained with mass spectra.

REFERENCES

1 G.A. Olah, P.S. Iyer and P. Suryer, Synthesis, (1986) 513.

2 C. Bunyagldz, H. Plotrowska and M.H. Aldridge, J. Chem. Eng. Data, 26 (1981) 344.

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

4 C.G. Krespan and D.A. Dixon, J. Org. Chem., 51, (1986) 4460.

5 C.G. Krespan, B.E. Smart and E.G. Howard, J. Am. Chem. Soc., 99 (1977) 1214.

6 R.J. Terjeson, J. Mohtasham and G.L. Gard, Inorg. Chem., 27 (1988) 2916.

7 J. Mohtasham, D.C. Cox, D.J. Burton and G.L. Gard, J. Fluorine Chem., 42 (1988) 119.

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

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

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

11 V.F. Cherstkov, S.R. Sterlin, L.S. German and J.L. Knunyants, Izv. Akad. Nauk. SSSR, Ser. Khim, 12 (1982) 2796.

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

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

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

15 R.J. Terjeson, J. Mohtasham, D.H. Peyton and G.L. Gard, J. Fluorine Chem., 42 (1988) 187.