Inorg. Chem. **1987**, *26*, 2307–2309 **2307**

Contribution from the Department of Chemistry,
Portland State University, Portland, Oregon 97207

New Sulfonyl Fluoride Esters

Jilla Khalilolahi, Javid Mohtasham, Megan E. Lerchen, Roger M. Sheets, and Gary L. Gard*

Received November 3, 1986

New sulfonyl fluoride esters $FSO_2CF_2C(O)OR_f$ ($R_f = CF_3CH_2$, $(CF_3)_3C$, C_6F_5), $FSO_2CF(CF_3)C(O)OR_f'$ ($R_f' = CF_3CH_2$, $(CF_3)_2CH$, C_6F_5), and $FSO_2CF(CF_3)C(O)OR$ ($R = CH_3CH_2$, $H_2C{=}CHCH_2$) have been prepared by using the perfluorosultones $\overline{CF_2CF_2OSO_2}$ and $CF_3\overline{CFCF_2OSO_2}$ with appropriate polyfluoro/perfluoro alcohols or hydrocarbon alcohols in the presence of sodium fluoride. In a like manner the diester $[FSO_2CF(CF_3)C(O)OCH_2]_2$ was prepared from ethylene glycol and $CF_3\overline{CFCF_2OSO_2}$. Unlike the fluorinated esters with fluorine at the alkoxy α-carbon atoms, these esters are stable in the presence of fluoride ion at 25 °C or higher temperature. Their IR, NMR, and mass spectra are reported.

Introduction

Sulfonyl fluorides (RSO_2F) and their derivatives, where R represents hydrocarbon and fluorocarbon moieties, continue to be subjects of considerable study. The incorporation of the 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] While a few methods exist for preparing selected derivatives, their overall usefulness is limited. From an earlier study of the β-sultone $\overline{CF_2CF_2OSO_2}$ with $H(CF_2)_4CH_2OH$, it was found that the polyfluoro ester $FSO_2CF_2C(O)OCH_2(CF_2)_4H$ was produced.[4] It was thought that this method with different β-sultones would be a productive way of preparing new sulfonyl fluoride derivatives. We now wish to report our results using the sultones $\overline{CF_2CF_2OSO_2}$ and $CF_3\overline{CFCF_2OSO_2}$.

Results and Discussion

The reactions of $\overline{CF_2CF_2OSO_2}$ and $CF_3\overline{CFCF_2OSO_2}$ with polyfluoro/perfluoro alcohols and hydrocarbon alcohols provide a convenient route to esters of the fluorinated acids $FSO_2CF_2C(O)OH$ and $FSO_2CF(CF_3)C(O)OH$:

$$\overline{CF_2CF_2OSO_2} + R_fOH + NaF \rightarrow FSO_2CF_2C(O)OR_f + NaHF_2 \tag{1}$$

$$R_f = CF_3CH_2,\ (CF_3)_3C,\ C_6F_5$$

$$CF_3\overline{CFCF_2OSO_2} + R_f'OH + NaF \rightarrow FSO_2CF(CF_3)C(O)OR_f' + NaHF_2 \tag{2}$$

$$R_f' = CF_3CH_2,\ (CF_3)_2CH,\ C_6F_5$$

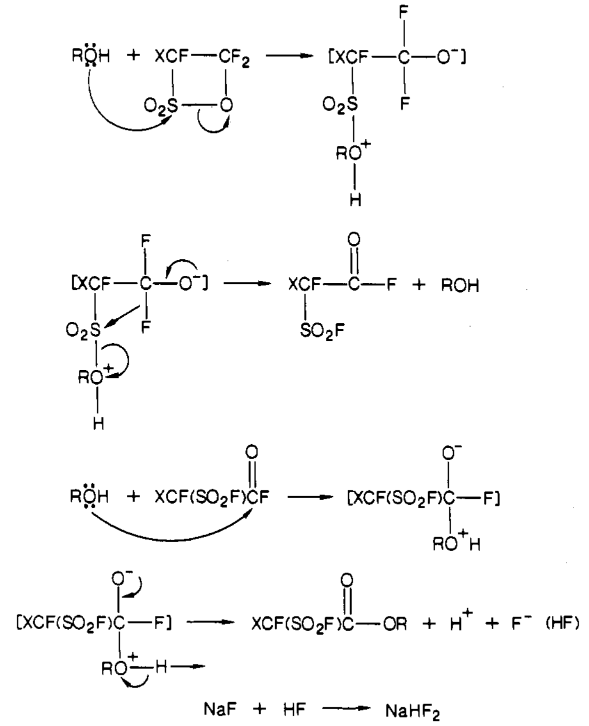
$$CF_3\overline{CFCF_2OSO_2} + ROH + NaF \rightarrow FSO_2CF(CF_3)C(O)OR + NaHF_2 \tag{3}$$

$$R = CH_3CH_2,\ H_2C{=}CHCH_2$$

$$2CF_3\overline{CFCF_2OSO_2} + HOCH_2CH_2OH + 2NaF \rightarrow [FSO_2CF(CF_3)C(O)OCH_2]_2 + 2NaHF_2 \tag{4}$$

The new sulfonyl fluoride esters are all clear, colorless liquids. Some of the new esters appear to have good thermal stability; for example, heating $FSO_2CF(CF_3)C(O)OCH_2CF_3$ for 2 h at 100 °C, 2 h at 160 °C, and 2 h at 171 °C resulted in no decomposition. While it was reported[5] that a number of fluorinated esters of the type $R_fC(O)OCF(CF_3)_2$, where $R_f = F$, CF_3, C_2F_5, and C_3F_7, disproportionated readily in the presence of fluoride ion at room temperature, we have found that all sulfonyl fluoride esters synthesized in this work are stable and can be prepared at room temperature or above in the presence of sodium fluoride.

Scheme I. Rearrangement and Reaction



The possible mechanisms for the rearrangement of the sultone and reaction with alcohols are given in Scheme I; support for the rearrangement mechanism is found by examining reaction mixtures prior to final workup. In these reaction mixtures, it was found via infrared spectral studies that the sultone had rearranged during the course of the reaction to $XCF(SO_2F)C(O)F$ ($X = F$, CF_3).

The infrared spectra of the new sulfonyl fluoride esters have several common features. The carbonyl stretching frequency is characteristically found in the 1792–1771-cm^{-1} region for esters prepared from the nonfluorinated alcohols and in the 1790–1834-cm^{-1} region for esters prepared from fluorinated alcohols. The carbonyl frequencies for the highly fluorinated esters are significantly higher than for the partially fluorinated esters, in line with the expected inductive effect. The carbonyl bands for the new esters agree closely with those found for other perfluoro/polyfluoro esters.[5,6] In all esters, the asymmetric and symmetric $-SO_2-$ bands can be tentatively assigned to the regions 1453–1468 and 1210–1246 cm^{-1}, respectively. This assignment is complicated by the appearance of strong carbon–fluorine absorption bands in the 1110–1300-cm^{-1} region, but in any case the above assignment agrees closely with that found for CF_3SO_2F and

---

(1) Olah, G. A.; Iyer, P. S.; Surya Prakash, G. K. *Synthesis* **1986**, 513.
(2) Bunyagldj, C.; Plotrowska, H.; Aldridge, M. H. *J. Chem. Eng. Data* **1981**, *26*, 344.
(3) Canich, J. M.; Ludvig, M. M.; Gard, G. L.; Shreeve, J. M. *Inorg. Chem.* **1984**, *23*, 4403.
(4) England, D. C.; Dietrich, M. A.; Lindsey, R. V. *J. Am. Chem. Soc.* **1960**, *82*, 6181.
(5) De Marco, R. A.; Couch, D. A.; Shreeve, J. M. *J. Org. Chem.* **1972**, *37*, 3332.
(6) Majid, A.; Shreeve, J. M. *J. Org. Chem.* **1973**, *38*, 4028.

0020-1669/87/1326-2307$01.50/0

other fluorosulfonyl derivatives.[7] For the fluorosulfonyl group, the intense S–F absorption band is located in the 790–821-cm^{-1} region and is in the region found for other sulfonyl fluorides.[8] The C–H absorption bands for the hydrogen containing esters are located in the 2987–3100-cm^{-1} region.

In the mass spectra, parent peaks were found for $C_6F_5OC(O)CF(CF_3)SO_2F$ and $H_2C{=}CHCH_2OC(O)CF(CF_3)SO_2F$; for the ethyl ester $CH_3CH_2OC(O)CF(CF_3)SO_2F$, the highest peak observed was $(M - 1)^+$. The base peak for these compounds was 67, $(SOF)^+$. For the other esters, $CF_3CH_2OC(O)CF(CF_3)SO_2F$, and $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$, the highest fragment found was $(M - F)^+$. For all esters studied a consistent cracking pattern was found where fragments were observed corresponding to $(M - OR)^+$, $(C_3F_4O)^+$, $(C_2F_5)^+$, $(SO_2F)^+$, $(CF_3)^+$, $(SOF)^+$, and $(SO_2)^+$. This result, except for $(SO_2F)^+$, $(SOF)^+$, and $(SO_2)^+$ fragments, is consistent with the spectra of previously reported fluorinated esters.[5,6]

The ^{19}F NMR spectra for all new esters reported in this paper have some common features. The $FSO_2CF(CF_3)$ group is found in all esters prepared from $CF_3\overline{CFCF_2OSO_2}$ and is characterized by having the appropriate resonance bands for FSO_2, CF, and CF_3 at ϕ 50.1–51.6, –161.8 to –164.3, and –74.3 to –75.0, respectively. With the sultone $\overline{CF_2CF_2OSO_2}$, the resonance bands for the FSO_2 and CF_2 groups are located in the corresponding esters at ϕ 40.1–40.7 and –105.7 to –106.4, respectively. In a number of sulfonyl fluoride derivatives, CF_3CHFSO_2F, $SF_5CF(COF)SO_2F$, and SF_5CFHSO_2F, the corresponding SO_2F resonances were found at ϕ 50.5, 51.8, and 51.3, respectively.[3,9] The ^{19}F NMR spectra of $C_6F_5OC(O)CF(CF_3)SO_2F$ and $C_6F_5OC(O)CF_2SO_2F$ have resonance signals for the C_6F_5 group (ortho, para, and meta) at ϕ –155.1, –157.7, and –164.3 and ϕ –155.7, –159.2, and –166.7, respectively. In other perfluorophenyl systems the respective ortho, para, and meta assignments are in good agreement.[10,11] It is of interest to note that in $C_6F_5OC(O)CF(CF_3)SO_2F$ there appears to be through-space coupling between the *m*-fluorines of the C_6F_5 group and the SO_2F group of ~2 Hz. This through-space coupling has been observed in only a few perfluorinated esters.[6] For all esters with a saturated CH_2 group, the proton chemical shift is found in the δ 4.56–5.08 region and is in close agreement with that reported for other fluorinated esters with similar structures.[6] The resonance signal for the methyl group is located at δ 1.45 and again agrees with that found for fluorinated esters containing a CH_3 group.[6]

Experimental Section

Materials. The fluorosultones $\overline{CF_2CF_2OSO_2}$ and $CF_3\overline{CFCF_2OSO_2}$ were prepared by reacting monomeric sulfur trioxide with the respective fluoroolefin.[4] The fluoroolefins $CF_2{=}CF_2$ and $CF_3CF{=}CF_2$ and the fluoroalcohols CF_3CH_2OH, $(CF_3)_3COH$, $(CF_3)_2CHOH$, and C_6F_5OH were obtained from SCM Specialty Chemicals and used as received. Allyl alcohol and sulfur trioxide (MCB), ethylene glycol (Mallinckrodt, AR), and ethyl alcohol (U.S. Industrial Chemicals Co., 200 proof) were also used as received. Sodium fluoride (Baker) was dried in vacuo prior to use.

General Procedure. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise-Bourdon tube gauge and a Televac thermocouple gauge. Infrared spectra were obtained by using a Pyrex glass cell with KBr windows or were obtained as solids between KBr 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. Me_4Si, $CFCl_3$, and trifluoroacetic acid were used as external standards.

The mass spectra were recorded with a VG 7070 HS mass spectrometer with an ionization potential of 17 or 70 eV.

Elemental analyses were determined by Beller Microanalytical Laboratory, Gottingen, West Germany.

$CF_3\overline{CFCF_2OSO_2}$ with CF_3CH_2OH. Into a 100-mL Pyrex glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 253.4 mmol of dried NaF, 58.64 mmol of CF_3CH_2OH, and 58.04 mmol of $CF_3\overline{CFCF_2OSO_2}$. The mixture was stirred magnetically for 3 days at 40 °C. Distillation of the volatile material gave 41.79 mmol of $CF_3CH_2OC(O)CF(CF_3)SO_2F$ in 72% yield; bp 123–124 °C.

The infrared spectrum had the following bands (cm^{-1}): 3050 (vw), 2994 (w), 1806 (s, sh at 1790), 1461 (s), 1412 (m), 1314 (s), 1278 (s), 1243 (s, br), 1187 (s), 1165 (s), 1060 (ms), 1032 (m), 983 (m), 962 (m), 878 (m), 821 (ms), 793 (m), 744 (wm), 688 (w), 660 (wm), 603 (ms), 559 (w), 546 (w), 515 (vw), 490 (w), 465 (w), 440 (w).

The ^{19}F NMR spectrum contained the following resonance bands: ϕ –76.6 (triplet), –75.0 (doublet of doublets), –163.6 (quartet of doublets), +49.6 (quartet of doublets) with relative $\mathit{CF_3}CH_2$:$\mathit{CF_3}CF$:CF:$SO_2\mathit{F}$ band areas of 3.1:2.7:1.0:1.0, theoretical 3.0:3.0:1.0:1.0. Coupling constants were $J_{CF_3-SO_2F} = 9.16$, $J_{CF-SO_2F} = 3.94$, $J_{CF-CF_3} = 7.75$, and $J_{CF_3-CH_2} = 7.5$ Hz. The ^1H NMR spectrum contained a quartet at $\delta = 4.82$. A molecular ion was not found but other appropriate fragments were present. Mass spectrum (*m/e*): 291, $(M - F)^+$; 241, $(M - CF_3)^+$; 227 $(M - CF_3CH_2)^+$; 211, $(M - CF_3CH_2O)^+$; 208, $(M - CF_4CH_2)^+$; 128, $(C_3F_4O)^+$; 127, $[M - CF(CF_3)SO_2F]^+$; 100, $(C_2F_4)^+$; 83, $(CF_3CH_2, SO_2F)^+$; 69, $(CF_3)^+$; 67, $(SOF)^+$; 64, $(C_2H_2F_2, SO_2)^+$; 63, $(C_2HF_2, CSF)^+$; 51, $(SF)^+$; 50, $(CF_2)^+$; 48, $(SO)^+$; 44, $(CO_2)^+$.

Anal. Calcd for $C_5H_2F_8SO_4$: C, 19.36; H, 0.65; F, 49.0; S, 10.34. Found: C, 19.49; H, 0.67; F, 49.2; S, 10.37.

$CF_3\overline{CFCF_2OSO_2}$ with $(CF_3)_2CHOH$. Into the same reaction vessel described previously (100 mL) were added 128.8 mmol of dried NaF, 37.10 mmol of $(CF_3)_2CHOH$, and 32.60 mmol of $CF_3\overline{CFCF_2OSO_2}$. The mixture was stirred at room temperature for 13 days. Distillation of the volatile material gave 17.28 mmol of $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$ in 53% yield; bp 109–110 °C.

The infrared spectrum had the following bands (cm^{-1}): 2987 (w), 1820 (ms, sh at 1806), 1468 (s), 1384 (ms), 1368 (m), 1284 (s), 1246 (s, br), 1212 (s), 1165 (s), 1118 (s), 1078 (m), 1059 (m), 1009 (w), 987 (w, sh at 973), 912 (m), 900 (m), 828 (m, sh at 813), 793 (m), 750 (wm), 725 (m), 693 (m), 675 (w), 631 (vw), 600 (ms), 550 (w), 528 (w), 490 (w), 481 (w), 468 (w), 453 (w), 431 (w).

The ^{19}F NMR spectrum contained a doublet of doublets at ϕ –74.8, a broad singlet at ϕ –75.4, a quartet of doublets at ϕ –164.3, and a quartet of doublets at ϕ 50.8. Relative CF_3:$(CF_3)_2C$:CF:SO_2F band areas were 2.8:6.0:1.0:1.0; theoretical 3.0:6.0:1.0:1.0. Coupling constants were $J_{CF_3-SO_2F} = 9.2$, $J_{CF_3-CF} = 8.2$, $J_{CF_3-CH} = 5.7$, and $J_{SO_2F-CF} = 3.9$ Hz. The ^1H NMR spectrum contained a septet at δ 4.93.

A molecular ion was not found but other appropriate fragments were found. Mass spectrum (*m/e*): 359, $(M - F)^+$; 276, $(M - SO_2F_2)^+$; 275, $(M - SO_2F_2H)^+$; 211, $[M - (CF_3)_2CHO]^+$; 195, $[M - (CF_3)_2CHO_2]^+$; 151, $[(CF_3)_2CH]^+$; 147, $(C_3F_5O)^+$; 128, $(C_3F_4O)^+$; 109, $(C_3F_3O)^+$; 100, $(C_2F_4)^+$; 83, $(SO_2F)^+$; 69, $(CF_3)^+$; 67, $(SOF)^+$; 64, $(SO_2)^+$; 63, $(CSF)^+$; 51, $(SF)^+$; 50, $(CF_2)^+$; 44, $(CO_2)^+$.

Anal. Calcd for $C_6HF_{11}SO_4$: C, 19.06; H, 0.27; F, 55.3; S, 8.48. Found: C, 19.19; H, 0.38; F, 55.6; S, 8.68.

$CF_3\overline{CFCF_2OSO_2}$ with C_6F_5OH. Into the same reaction vessel described previously (100 mL) were added 403.2 mmol of dried NaF, 31.10 mmol of C_6F_5OH, and 29.60 mmol of $CF_3\overline{CFCF_2OSO_2}$. The mixture was stirred for 13 days at 60 °C. Distillation of the volatile material gave 12.73 mmol of $C_6F_5OC(O)CF(CF_3)SO_2F$ in 43% yield; bp 88 ± 1 °C (5 mm).

The infrared spectrum had the following bands (cm^{-1}): 1820 (ms, sh at 1806), 1653 (w), 1521 (vs), 1462 (s), 1365 (w), 1321 (w), 1284 (ms), 1240 (s, br), 1165 (ms), 1131 (ms), 1030 (s), 1015 (s), 1003 (s, sh at 971), 943 (wm), 846 (wm), 812 (ms), 750 (m), 715 (w), 678 (w), 634 (w), 625 (w), 600 (ms), 568 (w), 546 (w), 509 (vw), 487 (w), 468 (w), 456 (w), 437 (w).

The ^{19}F NMR spectrum contained a doublet of doublets at ϕ –74.7, a quartet of doublets at ϕ –162.7, a quartet of doublets of triplets at ϕ 51.0, a triplet at ϕ –157.7 (para), and multiplets at ϕ –155.1 (ortho) and –164.3 (meta). Relative ortho:meta:para:CF:CF_3:SO_2F band areas for $C_6F_5OC(O)CF(CF_3)SO_2F$ were 2.2:2.2:1.0:1.0:3.0:1.0; theoretical 2.0:2.0:1.0:1.0:3.0:1.0. Coupling constants were $J_{CF_3-SO_2F} = 9.16$, $J_{CF_3-CF} = 8.12$, $J_{CF-SO_2F} = 3.9$, $J_{o-p} = 25.4$, $J_{o-m} = 19.7$, $J_{m-p} = 19.7$, and $J_{FSO_2-m} = 2.0$ Hz. In addition to the molecular ion 394, $(M)^+$, additional appropriate fragments were found. Mass spectrum (*m*/e): 211, $(M - C_6F_5O)^+$; 183, $(C_6F_5O)^+$; 167, $(C_6F_5)^+$; 155, $(C_5F_5)^+$; 128, $(C_3F_4O)^+$; 119, $(C_2F_5)^+$; 100, $(C_2F_4)^+$; 83, $(SO_2F)^+$; 69, $(CF_3)^+$; 67, $(SOF)^+$; 64, $(SO_2)^+$; 63, $(SCF)^+$; 51, $(SF)^+$; 50, $(CF_2)^+$; 44, $(CO_2)^+$.

Anal. Calcd for $C_9F_{10}SO_4$: C, 27.42; F, 48.2; S, 8.13. Found: C, 27.53; F, 47.9; S, 7.89.

$CF_3\overline{CFCF_2OSO_2}$ with $HOCH_2CH_2OH$. Into the same reaction vessel

---

(7) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1956**, 173.

(8) Ham, N. S.; Hambly, A. N.; Laby, R. H. *Aust. J. Chem.* **1960**, *13*, 443.

(9) Dean, R. R.; Lee, J. *Trans. Faraday Soc.* **1968**, *64*, 1409.

(10) Sartori, P.; Bauer, G. *J. Fluorine Chem.* **1978**, *12*, 203.

(11) Canich, J. M.; Lerchen, M. E.; Gard, G. L.; Shreeve, J. M. *Inorg. Chem.* **1986**, *25*, 3030.

described previously (100 mL) were added 68.0 mmol of dried NaF, 9.66 mmol of $HOCH_2CH_2OH$, and 19.30 mmol of $CF_3\overline{CFCF_2OSO_2}$. The mixture was stirred for 23 days at room temperature. Distillation of the mixture gave 3.57 mmol of $[FSO_2CF(CF_3)C(O)OCH_2]_2$ in 37% yield.

The infrared spectrum had the following bands (cm^{-1}): 2980 (w), 1792 (s), 1775 (s), 1461 (s), 1409 (w), 1377 (w), 1300 (ms), 1243 (s, br), 1164 (ms, sh at 1125), 1053 (wm), 1018 (wm), 983 (w), 821 (m, sh at 865), 800 (m), 747 (wm), 686 (w), 605 (ms), 547 (w), 486 (w), 459 (w).

The ^{19}F NMR spectrum contained a doublet of doublets at ϕ −75.2, a quartet of doublets at ϕ −163.6, and a quartet of doublets at ϕ 51.6. The relative CF_3:CF:SO_2F band areas were 3.1:1.1:1.0; theoretical 3.0:1.0:1.0. Coupling constants were $J_{CF_3-SO_2F} = 9.9$, $J_{FSO_2-CF} = 3.5$, and $J_{CF_3-CF} = 7.8$ Hz. The ^1H NMR spectrum contained a broadened singlet at δ 4.98.

Anal. Calcd for $C_8H_4F_{10}S_2O_8$: C, 19.92; H, 0.84; F, 39.4; S, 13.30. Found: C, 20.17; H, 0.91; F, 38.9; S, 13.34.

$CF_3\overline{CFCF_2OSO_2}$ with CH_3CH_2OH. Into a similar reaction vessel described earlier (70 mL) were added 221.6 mmol of dried NaF, 48.80 mmol of CH_3CH_2OH, and 43.70 mmol of $CF_3\overline{CFCF_2OSO_2}$. The mixture was stirred for 14 days at room temperature. Distillation of the volatile material gave 27.53 mmol of $CH_3CH_2OC(O)CF(CF_3)SO_2F$ in 63% yield.

The infrared spectrum contained the following bands (cm^{-1}): 2994 (w), 2952 (vw), 2910 (vw), 1792 (s), 1771 (s), 1454 (s), 1398 (w), 1370 (wm), 1307 (ms), 1244 (s, br), 1159 (ms), 1117 (vw), 1090 (w), 1033 (m), 1012 (m), 984 (w, sh at 970), 853 (wm), 829 (m), 801 (m, sh at 780), 747 (m), 689 (w), 606 (ms), 548 (w), 573 (w), 484 (w), 463 (w), 435 (vw).

The ^{19}F NMR spectrum contained a doublet of doublets at ϕ −75.7, a quartet of doublets at ϕ −163.6, and a quartet of doublets at ϕ 50.2. The relative CF_3:CF:SO_2F band areas were 3.1:1.0:1.0; theoretical 3.0:1.0:1.0. Coupling constants were $J_{CF_3-CF} = 8.4$, $J_{CF_3-SO_2F} = 9.4$, and $J_{FSO_2-CF} = 3.9$. The ^1H NMR spectrum contained a quartet at δ 4.56 and a triplet at δ 1.45. The coupling constant was $J_{CH_3-CH_2} = 6.6$ Hz.

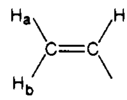
A molecular ion was not observed but other appropriate fragments were found. Mass spectrum (*m*/*e*): 255, $(M-H)^+$; 241, $(M-CH_3)^+$; 211, $(M-CH_3CH_2O)^+$; 173, $(M-SO_2F)^+$; 128, $(C_3F_4O)^+$; 119, $(C_2F_5)^+$; 100, $(C_2F_4)^+$; 83, $(SO_2F)^+$; 69, $(CF_3)^+$; 67, $(SOF)^+$; 64, $(SO_2)^+$; 63, $(CSF)^+$; 51, (SF^+); 50, $(CF_2)^+$; 45, $(CH_3CH_2O)^+$; 44, $(C_2H_4O, CO_2)^+$; 43, $(C_2H_3O)^+$.

Anal. Calcd for $C_5H_5F_5SO_4$: C, 23.44; H, 1.97; F, 37.1; S, 12.52. Found: C, 23.54; H, 1.99; F, 37.4; S, 12.61.

$CF_3\overline{CFCF_2OSO_2}$ with $H_2C{=}CHCH_2OH$. Into a similar reaction vessel (70 mL) were added 178.3 mmol of dried NaF, 32.64 mmol of $H_2C{=}CHCH_2OH$, and 32.34 mmol of $CF_3\overline{CFCF_2OSO_2}$. The mixture was stirred at room temperature for 10 days. Distillation of the volatile material gave 20.70 mmol of $H_2C{=}CHCH_2OC(O)CF(CF_3)SO_2F$ in 64% yield; bp 142–143 °C.

The infrared spectrum contained the following bands (cm^{-1}): 3100 (w), 3037 (w), 3002 (w), 2966 (w), 1792 (s), 1775 (ms), 1651 (w), 1456 (s), 1384 (vw), 1365 (w), 1303 (ms), 1236 (s, br), 1159 (ms), 1084 (w), 1025 (wm), 983 (wm), 893 (w, br), 821 (m), 790 (m), 746 (wm), 690 (w), 603 (ms), 546 (w), 487 (w), 459 (w).

The ^{19}F NMR spectrum contained a doublet of doublets at ϕ −74.3, a quartet of doublets at ϕ −161.8, and a quartet of doublets at ϕ 50.1. Relative CF_3:CF:SO_2F band areas were 2.7:1.0:1.0; theoretical 3.0:1.0:1.0. The ^1H NMR spectrum contained a doublet at δ 5.08; the olefinic protons



contained for H_c a doublet of doublets of triplets at δ 6.10, for H_a a doublet of doublets at δ 5.55, and for H_b a doublet of doublets at δ 5.81. Relative band areas for CH_2 vs. C_2H_3 were 2.0:3.1; theoretical 2.0:3.0. Coupling constants were $J_{CH_2-C} = 6.0$, $J_{b-c} = 17.1$, $J_{a-c} = 11.4$, $J_{a-b} = 4.8$ Hz. In addition to the molecular ion 268 (M^+), the mass spectrum contained the following fragments (*m*/*e*): 211, $(M - C_3H_5O)^+$; 185. $(M - SO_2F)^+$; 164, $(C_2F_4SO_2)^+$; 128, $(C_3F_4O)^+$; 119, $(C_2F_5)^+$; 100, $(C_2F_4)^+$; 83, $(SO_2F)^+$; 69, $(CF_3)^+$; 67, $(SOF)^+$; 64, $(SO_2)^+$; 63 $(SCF)^+$; 57, $(C_3H_5O)^+$; 56, $(C_3H_4O)^+$; 55, $(C_3H_3O)^+$; 51, $(SF)^+$; 50, $(CF_2)^+$; 45, $(C_2H_5O)^+$; 44, $(CO_2)^+$; 43, $(C_2H_3O)^+$.

Anal. Calcd for $C_6H_5F_5SO_4$: C, 26.87; H, 1.88; F, 35.4; S, 11.96. Found: C, 26.71; H, 1.96; F, 35.4; S, 12.17.

$\overline{CF_2CF_2OSO_2}$ with CF_3CH_2OH. Into a 100-mL Pyrex glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 23.80 mmol of dried NaF, 11.30 mmol $\overline{CF_2CF_2OSO_2}$, and 12.25 mmol of CF_3CH_2OH. The mixture was stirred magnetically for 3 days at room temperature. The product, $CF_3CH_2OC(O)CF_2SO_2F$ (10.17 mmol), was obtained by distillation of the volatile material in 90% yield; bp 57 ± 1 °C (54 mm).

The infrared spectrum had the following bands (cm^{-1}): 3058 (vw), 2994 (w), 1803 (s), 1453 (vs), 1422 (m), 1322 (s), 1297 (s), 1275 (s), 1237 (s), 1181 (vs), 1147 (vs), 1091 (m), 1069 (m), 1031 (m), 981 (m), 962 (m), 887 (w), 828 (s), 803 (s), 734 (m), 644 (s), 606 (m), 556 (m), 487 (mw), 462 (w).

The ^{19}F NMR spectrum contained a triplet at ϕ 40.7, a triplet at ϕ −76.9, and a doublet at ϕ −106.4. The relative CF_3:CF_2:SO_2F band areas were 3.2:2.2:1.0; theoretical 3.0:2.0:1.0. Coupling constants were $J_{CF_2-SO_2F} = 5.6$ and $J_{CF_3-CH_2} = 7.8$ Hz. The ^1H NMR spectrum contained a quartet at δ 4.72.

Anal. Calcd for $C_4H_2F_6SO_4$: C, 18.47; H, 0.78; F, 43.82; S, 12.33. Found: C, 18.84; H, 0.82; F, 43.90; S, 11.95.

$\overline{CF_2CF_2OSO_2}$ with $(CF_3)_3COH$. Into the same reaction vessel described previously (100 mL) were added 23.80 mmol of dried NaF, 13.14 mmol of $(CF_3)_3COH$, and 11.21 mmol of $\overline{CF_2CF_2OSO_2}$. The mixture was stirred magnetically for 30 days at room temperature. Distillation of the volatile material gave 4.48 mmol of $(CF_3)_3COC(O)CF_2SO_2F$ in 40% yield; bp 104.5 ± 0.5 °C.

The infrared spectrum had the following bands (cm^{-1}): 1834 (ms), 1463 (ms), 1281 (s), 1274 (s), 1260 (s), 1233 (m), 1211 (m), 1135 (ms), 1088 (wm), 1010 (m), 987 (ms), 832 (m), 804 (m), 722 (w), 731 (m), 712 (vw), 634 (m), 594 (w), 575 (w), 561 (wm), 545 (w), 537 (w), 501 (w), 479 (w).

The ^{19}F NMR spectrum contained a triplet at ϕ 40.1, a singlet at ϕ −71.0, and a doublet at ϕ −105.7; $J_{CF_2-SO_2F} = 6.3$ Hz.

Anal. Calcd for $C_6F_{12}SO_4$: C, 18.19; F, 57.56; S, 8.09. Found: C, 18.08; F, 59.20; S, 7.85.

$\overline{CF_2CF_2OSO_2}$ with C_6F_5OH. Into the same reaction vessel described previously (100 mL) were added 35.71 mmol of dried NaF, 14.20 mmol of C_6F_5OH, and 10.86 mmol of $\overline{CF_2CF_2OSO_2}$. The mixture was stirred magnetically for 6 h at 55–70 °C. Distillation of the volatile material gave 5.10 mmol of $C_6F_5OC(O)CF_2SO_2F$ in 47% yield: bp 102.5 ± 0.5 °C (40 mm).

The infrared spectrum had the following bands (cm^{-1}): 1820 (ms), 1650 (w), 1522 (vs), 1457 (s), 1290 (m), 1234 (ms), 1210 (m), 1150 (m), 1123 (ms), 1011 (ms), 1000 (ms), 976 (m, sh at 953), 861 (w), 812 (m, br), 728 (vw), 709 (vw), 659 (w), 621 (m), 591 (w), 581 (w), 557 (wm), 487 (w), 466 (w).

The ^{19}F NMR spectrum contained a triplet at ϕ 40.5, a doublet at ϕ −106.2, and a complex doublet, a complex triplet, and a complex triplet at ϕ −155.7 (ortho), −159.2 (para), and −166.7 (meta), respectively. The relative SO_2F:CF_2:ortho:para:meta band areas were 1.0:1.9:2.0:1.0:2.0; theoretical 1.0:2.0:2.0:1.0:2.0. Coupling constants were $J_{CF_2-SO_2F} = 6.3$, $J_{o-p} = 24.6$, $J_{m-o} = 12.7$, and $J_{m-p} = 12.9$ Hz.

Anal. Calcd for $C_8F_8SO_4$: C, 27.92; F, 44.2; S, 9.32. Found: C, 27.86; F, 44.4; S, 9.37.

Acknowledgment is made to the Gas Research Institute for support of this research. We thank Dr. Gary Knerr for mass spectral data.

Registry No. $CF_3\overline{CFCF_2OSO_2}$, 773-15-9; $\overline{CF_2CF_2OSO_2}$, 697-18-7; CF_3CH_2OH, 75-89-8; $(CF_3)_2CHOH$, 920-66-1; C_6F_5OH, 771-61-9; $HOCH_2CH_2OH$, 107-21-1; CH_3CH_2OH, 64-17-5; $H_2C{=}CHCH_2OH$, 107-18-6; $(F_3C)_3COH$, 2378-02-1; NaF, 7681-49-4; $CF_3CH_2OC(O)CF(CF_3)SO_2F$, 108344-38-3; $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$, 108344-39-4; $C_6F_5OC(O)CF(CF_3)SO_2F$, 108344-40-7; $[FSO_2CF(CF_3)C(O)OCH_2]_2$, 108344-41-8; $CH_3CH_2OC(O)CF(CF_3)SO_2F$, 18343-96-9; $H_2C{=}CHCH_2OC(O)CF(CF_3)SO_2F$, 108344-42-9; $CF_3CH_2OC(O)CF_2SO_2F$, 108344-43-0; $(CF_3)_3COC(O)CF_2SO_2F$, 108365-50-0; $C_6F_5OC(O)CF_2SO_2F$, 89847-86-9.