(carbamoylmethyl)thiophosphonate fragment are similar to the distances and angles found in metal-coordinated CMP ligands.

The chemical and structural data presented here indicate that bifunctional (carbamoylmethyl)thiophosphonate ligands interact only weakly through their carbonyl base site with relatively hard metal centers that are important constituents in nuclear process solutions. Two important questions related to the coordination ability of these ligands remain to be addressed: How successfully will the neutral ligands complex softer metal centers present in nuclear process solutions, and can an anionic form of the ligand, $[(RO)P(S)(O)CH_2C(O)NR'_2{}^-]$, be prepared and will it provide improved coordination ability with hard metal ions? On the basis of studies of Pinkerton and co-workers,[29] it might be expected that an anionic thiophosphonate would serve as an improved extractant for lanthanide ions. Forthcoming communications from our laboratory will address these points.

Acknowledgment. R.T.P. wishes to recognize financial support for this work from the Department of Energy, Office of Basic Energy Sciences, Contract No. 85ER-40079. He also wishes to recognize NSF Grants CHE-7802921 and CHE-8201374, which facilitated the purchases of the X-ray diffractometer and NMR spectrometer.

Registry No. 1, 108675-65-6; 2, 108675-66-7; 3, 108675-68-9; $UO_2(NO_3)_2(1)_2$, 108675-67-8; $(EtO)_2P(S)H$, 999-01-9; $(BuO)_2P(S)H$, 17529-47-4; La, 7439-91-0; Nd, 7440-00-8; Er, 7440-52-0; *N*,*N*-diethylchloroacetamide, 2315-36-8.

Supplementary Material Available: Tables SI–SIV, listing hydrogen atom positional parameters, thermal parameters, and bond distances and bond angles (4 pages); Table SV, listing calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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(29) Pinkerton, A. A. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 495. Pinkerton, A. A.; Schwarzenback, D. *J. Chem. Soc., Dalton Trans.* **1976**, 2466.

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Synthesis of Polyfluoroalkyl Esters of (Fluorosulfonyl)difluoroacetic Acid and Diesters of Sulfonyldifluoroacetic Acid

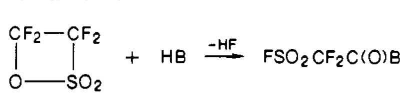
Ting-Ji Huang, Zhi-Xia Dong, and Jean'ne M. Shreeve*

Received October 27, 1986

Several new polyfluoroalkyl(fluorosulfonyl)difluoroacetates, $R_fOC(O)CF_2SO_2F$ (R_f = CF_3CH_2, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$, $(CF_3)_2C(CH_3)$, $CF_3CH(CH_3)$, $(CF_3)_2CH$, $C_7F_{15}CH_2$, $CH_2(CF_2)_3CH_2OC(O)CF_2SO_2F$), diesters of sulfonyldifluoroacetic acid, $R_fOC(O)CF_2SO_2OR_f'$ (R_f = CF_3CH_2, $(CF_3)_2CH$; R_f' = CF_3CH_2, $(CF_3)_2CH$), and alkyl (fluorosulfonyl)difluoroacetates, $RCH_n(CH_2OC(O)CF_2SO_2F)_{3-n}$ ($R = CH_3$, $n = 0$; $R = O_2N$, $n = 0$; $R = OC(O)CF_2SO_2F$, $n = 2$; $R = CH_2OC(O)CF_2SO_2F$, $n = 0$), resulted from the reaction of tetrafluoroethane-β-sultone with polyfluoroalkyl alcohols or polyfluoroalkoxides and alkanediols, -triols, and a -tetraol.

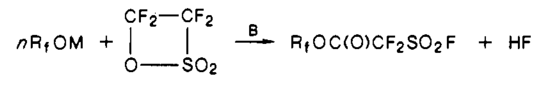
Introduction

Previous investigations dealing with the reactions of tetrafluoroethane-β-sultone with various nucleophilic reagents, such as amines, mercaptans, alcohols, hydrogen sulfide, and carboxylic acids gave rise to the corresponding derivatives of (fluorosulfonyl)difluoroacetic acid.[1,2]

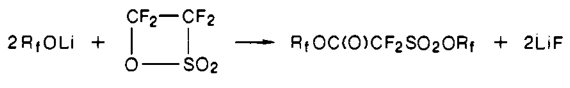


B = e.g., C_6H_5S, C_6H_5NH, $C_6H_5(CH_3)N$, CH_3O, $i\text{-}C_3H_7O$, $\overline{O(CH_2)_2NCH_2CH_2}$, SCN, $(C_6H_5)_2N$, Et_2N

In our continuing efforts toward the syntheses of precursors to new highly conducting, hydrolytically and thermally stable polyfluorinated sulfonic acids, we have taken advantage of the electrophilic sulfur center in sultones to prepare a variety of mono-, di-, tri-, and tetrasulfonyl fluorides. Tetrafluoroethane-β-sultone was reacted with polyfluoroalkyl alcohols to yield new polyfluoroalkyl (fluorosulfonyl)difluoroacetates, and di(polyfluoroalkyl) esters of sulfonyldifluoroacetic acid.

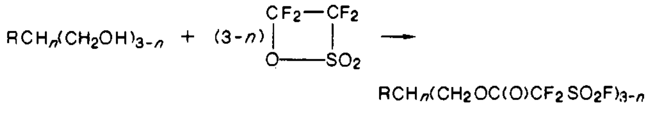


R_f = CF_3CH_2, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$, $C_7F_{15}CH_2$; $M = H$; B = KF, NaF; $n = 1$
= $CF_3(CH_3)CH$, $(CF_3)_2CH$, $(CF_3)_2C(CH_3)$; M = Li; $n = 1$
= $CH_2(CF_2)_3CH_2$; $M = H$; B = KF, NaF; $n = 0.5$



R_f = CF_3CH_2, $(CF_3)_2CH$

In addition, alkyl poly[(fluorosulfonyl)difluoroacetates] were synthesized.



$R = CH_3$, $n = 0$; $R = O_2N$, $n = 0$; R = $OC(O)CF_2SO_2F$, $n = 2$; $R = CH_2OC(O)CF_2SO_2F$, $n = 0$

Results and Discussion

Polyfluoroalkyl (fluorosulfonyl)difluoroacetates were synthesized in good yields by the reaction between tetrafluoroethane-β-sultone and polyfluoroalkoxides or polyfluoroalkyl al-

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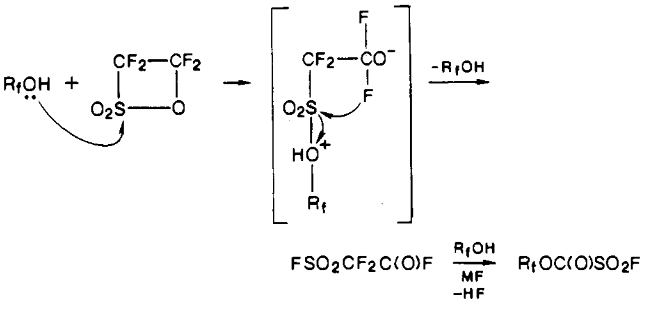
(1) England, D. C.; Dietrich, M. A.; Lindsey, R. V., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 6181.
(2) Knunyants, I. L.; Sokol'ski, G. A. *Angew. Chem.* **1972**, *84*, 623.
(3) Canich, J. M.; Ludvig, M. M.; Gard, G. L.; Shreeve, J. M. *Inorg. Chem.* **1984**, *23*, 4403.
(4) Sokol'ski, G. A.; et al. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 1524.
(5) Sokol'ski, G. A.; et al. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 1613.

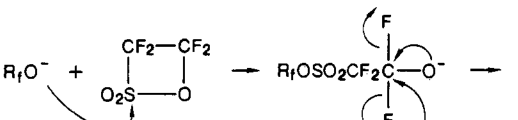
0020-1669/87/1326-2304$01.50/0

cohols (1:1) in the presence of NaF or KF at room temperature. On treatment of tetrafluoro-β-sultone with a 2:1 excess of the polyfluoroalkoxide, diesters, $R_fOC(O)CF_2SO_2OR_f$, were formed.

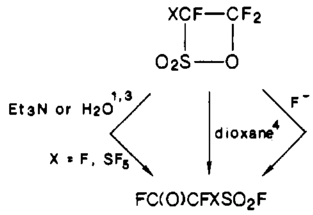
The following mechanism describes the formation of the ester or diester:



or



These routes to the stable products are strongly supported by the following isomerization of β-sultones to their acyclic isomers:



Ethyl (fluorosulfonyl)difluoroacetate when reacted with sodium ethoxide gave sodium (ethoxycarbonyl)difluoromethanesulfonate.[6] It is likely that $C_2H_5OC(O)CF_2SO_2OC_2H_5$ was formed in the first stage of the reaction, and it then alkylates the sodium salt. The overall reaction is described by

$$C_2H_5OC(O)CF_2SO_2F + C_2H_5ONa \rightarrow [C_2H_5OC(O)CF_2SO_2OC_2H_5 + NaF] \rightarrow C_2H_5OC(O)CF_2SO_2ONa + C_2H_5F$$

In contrast when $(CF_3)_2CHOC(O)CF_2SO_2F$ was reacted with lithium 2,2,2-trifluoroethoxide, $(CF_3)_2CHOC(O)CF_2SO_2OCH_2CF_3$ was obtained due to the inductive effect of the polyfluorinated ethyl substituent, i.e.

$$(CF_3)_2CHOC(O)CF_2SO_2F + CF_3CH_2OLi \rightarrow (CF_3)_2CHOC(O)CF_2SO_2OCH_2CF_3$$

The new mono- and diesters described in this work are all colorless, slightly volatile or involatile liquids at 25 °C. They are stable toward water. The carbonyl stretching vibrations for these esters fall typically in the 1780–1820-cm^{-1} region. The ^{19}F NMR resonance for the fluorosulfonyl group is found invariably in the range ϕ 42.00 ± 0.75 as a triplet. The conversion of these materials to ethers and finally to their sulfonic acid derivatives will be reported in due course.

Experimental Section

Materials. Tetrafluoroethane-β-sultone was prepared according to the literature.[1] The other materials were obtained as follows: $(CF_3)_2CHOH$, $CF_3CH(CH_3)OH$, $CH_3C(CF_3)_2OH$, $CF_3CF_2CF_2CH_2OH$, $C_7F_{15}CH_2OH$, and $HOCH_2(CF_2)_3CH_2OH$ from PCR; $CF_3CF_2CH_2OH$ from Fairfield; CF_3CH_2OH, $C(CH_2OH)_4$, $CH_3C(CH_2OH)_3$, $HOCH_2CH_2OH$, and $O_2NC(CH_2OH)_3$ from Aldrich. They were used as received.

General Procedures. A conventional Pyrex glass vacuum line equipped with Heise Bourdon tube and Televac pressure gauges was used to manipulate the volatile starting materials and to free products from impurities. On occasion, products were purified by using bulb-to-bulb distillation. Volatile compounds were measured quantitatively by using *PVT* techniques. Infrared spectra were recorded with a Perkin-Elmer 599 spectrometer as liquid films between KBr disks. ^{19}F NMR spectra were obtained on a JEOL FX-90Q Fourier transform spectrometer operating at 84.26 MHz. $CDCl_3$ was used as the solvent with $CFCl_3$ as an external reference. Chemical shifts upfield from $CFCl_3$ were assigned negative values. ^{1}H NMR spectra were obtained at an operating frequency of 89.94 MHz. Mass spectra were recorded with a VG 7070 HS mass spectrometer with an ionization potential of 17 or 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Preparation of $CF_3CH_2OC(O)CF_2SO_2F$. 2,2,2-Trifluoroethanol (2 mmol) was condensed into a Pyrex reaction flask charged with tetrafluoroethane-β-sultone (2.5 mmol) and sodium fluoride (3 mmol) at −196 °C; the mixture was warmed very slowly to 25 °C, and stirred for 24 h. The reaction mixture was distilled by using trap-to-trap techniques. Unreacted $FC(O)CF_2SO_2F$ was held in the trap at −196 °C. The product and traces of CF_3CH_2OH were retained in a trap at −40 °C. A 90% yield of the pure, colorless liquid $CF_3CH_2OC(O)CF_2SO_2F$ was obtained by passing the material over P_4O_{10}. The infrared spectrum of $CF_3CH_2OC(O)CF_2SO_2F$ has bands as follows: 2982 w, 1808 s, 1500 w, 1465 s, 1410 m, 1320 s, 1276 s, 1240 s, 1190 s, 1150 s, 1075 w, 1043 m, 970 m, 830 s, 806 s, 725 w, 650 m, 590 w, 560 w cm^{-1}. The ^{1}H NMR spectrum consists of a quartet at δ 4.72 ($J_{CH_2-CF_3}$ = 7.69 Hz). The ^{19}F NMR spectrum has a triplet of quartets at ϕ 41.87 (SF) (J_{SF-CF_2} = 5.85 Hz, J_{SF-CF_3} = 0.36 Hz), a triplet of doublets at ϕ −74.13 (CF_3), and a doublet at ϕ −104.07 (CF_2). The mass spectrum (CI$^+$) is as follows (*m/e*, species, %): 260, M$^+$, 1.3; 177, $CF_3CH_2OC(O)CF_2^+$, 2.3; 127, $CF_3CH_2OC(O)^+$, 43.3; 83, SO_2F^+, 100; 69, CF_3^+, 9.7.

Anal. Calcd for $C_4H_2F_6O_4S$: C, 18.46; H, 0.76; F, 43.85. Found: C, 18.58; H, 0.76; F, 43.6.

Several compounds were prepared in a similar manner from tetrafluoroethane-β-sultone and R_fOH or R_fOLi. Yields were based on the amount of alcohol originally introduced. The materials are colorless liquids at room temperature.

$(CF_3)_2CHOC(O)CF_2SO_2F$ (70% Yield). IR: 2983 w, 1818 vs, 1463 vs, 1380 s, 1364 s, 1290 s, 1242 vs, 1216 s, 1148 s, 1120 s, 1068 m, 998 w, 912 s, 827 s, 802 m, 738 w, 718 w, 650 w, 562 w, 530 w, 480 w, cm^{-1}. ^{1}H NMR: δ 5.82 (CH, sept). ^{19}F NMR: ϕ 42.68 (SF, tr), −73.38 ($(CF_3)_2C$, d), −104.4 (CF_2, d); $J_{(CF_3)_2C-H}$ = 5.37 Hz, J_{CF_2-SF} = 6.34 Hz. MS (CI$^+$) (*m/e*, species, %): 329, M$^+$ + 1, 0.2; 309, M − F$^+$, 2.1; 245, M − SO_2F^+, 19.2; 225, M − $SO_2F_2H^+$, 43.2; 195, $(CF_3)_2CHOC(O)^+$, 29.2; 161, $C(O)CF_2SO_2F^+$, 2.1; 133 $CF_2SO_2F^+$, 4.6; 83, SO_2F^+, 3.4; 69, CF_3^+, 100.

Anal. Calcd for $C_5HF_9O_4S$: C, 18.29; H, 0.30; F, 52.13. Found: C, 18.51; H, 0.36; F, 52.4.

$CF_3(CH_3)CHOC(O)CF_2SO_2F$ (82% Yield). IR: 3002 w, 2990 w, 1801 vs, 1462 vs, 1387 w, 1344 w, 1307 m, 1288 s, 1241 s, 1210 vs, 1182 s, 1160 s, 1126 m, 1082 s, 1022 m, 863 w, 818 s, 735 w, 648 m, 603 w, 570 w, cm^{-1}. ^{1}H NMR: δ 5.48 (CH, ~sept), 1.55 (CH_3, d). ^{19}F NMR: ϕ 41.99 (SF, tr), −78.94 (CF_3, d of tr), −104.1 (CF_2, d of q); J_{CH_3-H} = 6.59 Hz, J_{CF_3H} = J_{CF_2-SF} = 5.85 Hz, $J_{CF_3-CF_2}$ = 0.61 Hz. MS (CI$^+$) (*m/e*, species, %): 275, M + 1$^+$, 1.1; 256, M + 1 − F$^+$, 7.2; 205, M − CF_3^+, 4.0; 191, M − SO_2F^+, 8.0; 141, $CF_3(CH_3)CHOC(O)^+$, 2.6; 133, $CF_2SO_2F^+$, 2.6; 97, $CF_3(CH_3)CH^+$, 34.1; 77, $CH_3C_2F_2^+$, 100; 69, CF_3, 8.8.

Anal. Calcd for $C_5H_4F_6O_4S$: C, 21.90; H, 1.46; F, 41.61. Found: C, 21.84; H, 1.53; F 41.6.

$(CF_3)_2(CH_3)COC(O)CF_2SO_2F$ (60% Yield). IR: 3001 w, 2987 w, 1820 vs, 1461 vs, 1400 w, 1318 vs, br, 1250 vs, br, 1160–1140 vs, 1100 s, 1015 w, 900 w, 838 w, 812 m, 730 w, 703 w, 638 m, 568 w cm^{-1}. ^{1}H NMR: δ 2.05 (CH_3, sept). ^{19}F NMR: ϕ 42.45 (SF, tr of sept), −76.50 ($(CF_3)_2C$, overlap q), −103.8 (CF_2, d); J_{CF_3-SF} = 0.80 Hz, $J_{(CF_3)_2C-CH_3}$ = 1.1 Hz, J_{CF_2-SF} = 6.34 Hz. MS (CI$^+$) (*m/e*, species, %): 343 M + 1$^+$, 0.8; 259, M − SO_2F^+, 24.1; 165 $(CF_3)_2C(CH_3)$, 24.4; 145 $CF_3(CF_2)C(CH_2)^+$, 100; 95, $CF_3C_2H_2^+$, 15.3; 93, $C_3F_3^+$, 14.8; 77, $CH_3C_2F_2^+$, 42.4; 69, CF_3^+, 61.8.

Anal. Calcd for $C_6H_3F_9O_4S$: C, 21.05; H, 0.88; F, 50.0. Found: C, 20.98; H, 0.96; F, 49.9.

$CF_3CF_2CH_2OC(O)CF_2SO_2F$ (65% Yield). IR: 2988 w, 1808 vs, 1462 vs, 1401 w, 1354 w, 1307 s, 1264 m, 1242–1214 vs, br, 1160 s, 1113 s, 1065 w, 1031 m, 980 w, 942 w, 815 s, 730 w, 650 m, 625 w, 600 w, 578 w, 522 w, 482 w, 460 w cm^{-1}. ^{1}H NMR: δ 4.86 (CH_2, tr of q). ^{19}F NMR: ϕ 42.22 (SF, tr of mult), −83.98 (CF_3, mult), −103.7 (CF_2S, d), −123.5 (CF_2C, tr of q); $J_{CF_2C-CH_2}$ = 11.96 Hz, J_{CF_2-SF} = 5.73 Hz, $J_{CF_3-CF_2C}$ = 0.49 Hz, $J_{CH_2-CF_3}$ = 0.98 Hz. MS (EI$^+$) (*m/e*, species, %):

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[6] Dmitriev, M. A.; Sokol'ski, G. A.; Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 1227.

227, $CF_3CF_2CH_2OC(O)CF_2^+$, 0.3; 226, $CF_3CF_2CHCO_2CF_2^+$, 11.9; 177, $CF_3CF_2CH_2CO_2^+$, 0.8; 176, $CF_3CF_2CHCO_2^+$, 24.7; 133, $CF_3CF_2CH_2^+$, 2.8; 132, $CF_3CF_2CH^+$, 97.5; 69, CF_3^+, 100.

Anal. Calcd for $C_5H_2F_8O_4S$: C, 19.35; H, 0.65; F, 49.03. Found: C, 19.42; H, 0.59; F, 48.9.

$CF^{A}_{3}CF^{B}_{2}CF^{C}_{2}CH_2OC(O)CF^{D}_{2}SO_2F^{E}$ (60% Yield). IR: 2980 w, 1818 s, 1463 vs, 1400 w, 1350 w, 1303 m, 1240 vs, 1212 s, 1198 m, 1152 s, 1043 w, 1023 m, 967 w, 911 m, 816 m, 740 w, 650 w, 630 w, 578 w, 536 w, 482 w cm^{-1}. ^1H NMR: δ 4.84 (CH_2, tr of tr). ^{19}F NMR: ϕ 41.99 (E, tr), −81.14 (A, tr), −104.0 (D, d), −120.6 (C, mult), −127.8 (B, mult); $J_{D-E} = 5.73$ Hz, $J_{A-B} = 9.15$ Hz, $J_{C-H} = 12.45$ Hz, $J_{B-H} = 1.22$ Hz. MS (EI^+) (*m/e*, species, %): 276, M − SO_2FH^+, 8.5; 227, $CF_3CF_2CF_2CH_2CO_2^+$, 5.7; 183, $CF_3CF_2CF_2CH_2^+$, 28.7; 169, $CF_3CF_2CF_2^+$, 1.8; 133, $CF_2SO_2F^+$, 17.7; 119, $CF_3CF_2^+$, 25.9; 83, SO_2F^+, 9.1; 69, CF_3^+, 86.4; 67, SOF^+, 57.5; 64, SO_2^+, 9.7; 51, SF^+, 100.

Anal. Calcd for $C_6H_2F_{10}O_4S$: C, 20.00; H, 0.56; F, 52.78. Found: C, 19.92; H, 0.51; F, 53.0.

$CF^{A}_{3}CF^{B}_{2}CF^{C}_{2}CF^{D}_{2}CF^{E}_{2}CF^{F}_{2}CF^{G}_{2}CH_2OC(O)CF^{H}_{2}SO_2F^{I}$ (85% Yield). IR: 2992 w, 1800 vs, 1457 vs, 1400 w, 1314 s, 1260–1135 vs, br, 1062 w, 1029 m, 978 w, 892 w, 812 s, 752 m, 742 m, 730 m, 710 m, 651 s, 610 w, 570 m, 533 w cm^{-1}. ^1H NMR: δ 4.90 (CH_2, tr). ^{19}F NMR: ϕ 42.05 (I, tr), −81.14 (A, mult), −103.9 (H, d), −119.7 (G, mult), −122.2 (E, F, mult), −123.3 (C, *D*, mult), −126.4 (B, mult); $J_{CH_2-G} = 12.55$ Hz, $J_{H-I} = 5.73$ Hz. MS: (EI^+) (*m/e*, species, %): 540, M − HF^+, 0.7; 477, M − SO_2F^+, 0.9; 476, $(CF_3(CF_2)_6CHCO_2CF_2^+$, 9.1; 133, $CF_2SO_2F^+$, 14.8; 119, $CF_3CF_2^+$, 19.3; 117, CF_2SOF^+, 3.5; 83, SO_2F^+, 30.9; 69, CF_3^+, 88.5; 67, SOF^+, 49.8; 51, SF^+, 100.

Anal. Calcd for $C_{10}H_2F_{18}SO_4$: C, 21.43; H, 0.36; F, 61.07. Found: C, 21.48; H, 0.30; F, 60.7.

$FSO_2CF_2C(O)OCH_2CF_2CF_2CF_2CH_2OC(O)CF_2SO_2F$ (55% Yield). IR: 2979 w, 1795 s, 1450 s, 1400 w, 1310 s, 1235 s, 1203 s, 1150 s, br, 1120 m, 1100 w, 1029 m, 962 w, 898 w, 804 s, 646 m, 606 w, 570 m, br, 490 w cm^{-1}. ^1H NMR: δ 4.72 (CH_2, tr). ^{19}F NMR: 41.99 (SF, tr), −103.7 (CF_2SO_2, d), −119.5 (CH_2CF_2, mult), −125.2 ($CF_2C\mathit{F}_2CF_2$, mult); $J_{SF-SCF_2} = 5.55$ Hz, $J_{CH_2-C\mathit{F}_2CH_2} = 12.2$ Hz. MS (EI^+) (*m/e*, species, %): 513, M − F^+, 0.2, 399, M − $CF_2SO_2F^+$, 0.2; 355, M − $CO_2CF_2SO_2F^+$, 18.8; 291, $FSO_2CF_2CO_2CH_2CF_2CF_2^+$, 21.3; 241, $FSO_2CF_2CO_2CH_2CF_2^+$, 7.4; 161, $COCF_2SO_2F^+$, 5.5; 133, $CF_2SO_2F^+$, 27.1; 67, SOF^+, 100.

Anal. Calcd for $C_9H_4F_{12}O_8S_2$: C, 20.30; H, 0.75; F, 42.86. Found: C, 20.47; H, 0.83; F, 42.4.

$FSO_2CF_2C(O)OCH_2CH_2OC(O)CF_2SO_2F$ (80% Yield). IR: 2990 w, 1785 s, 1450 s, 1380 w, 1310 s, 1236 s, 1203 s, 1155 s, br, 1123 m, 1100–1018 m, br, 875–810 s, br, 730 w, 650 s, 610–570 m, br, 488 w, 462 w cm^{-1}. ^1H NMR: δ 4.71 (CH_2, s). ^{19}F NMR: ϕ 41.58 (SF, tr), −103.7 (CF_2, d); $J_{CF_2-SF} = 5.85$ Hz. MS (EI^+) (*m/e*, species, %): 281, $FSOCF_2CO_2CHCHCO_2CF_2^+$, 0.2; 231, $FSOCF_2CO_2CHCHCO_2^+$, 0.9; 205, $FSO_2CF_2CO_2CH_2CH_2^+$, 26.9; 161, $FSO_2CF_2CO^+$, 6.4; 133, $FSO_2CF_2^+$, 29.9; 83, SO_2F^+, 5.9; 67, SOF^+, 100.

Anal. Calcd for $C_6H_4F_6O_8S_2$: C, 18.85; H, 1.05; F, 29.84. Found: C, 19.00; H, 1.10; F, 30.2.

$C(CH_2OC(O)CF_2SO_2F)_4$ (88% Yield). IR: 2989 w, 1790 vs, 1445 vs, 1302 s, 1234 vs, 1202 s, 1050 w, 1012 m, 928 w, 848 w, 819 m, 648 m, 632 w, 606 w, 557 w, 488–446 w, br cm^{-1}. ^1H NMR: δ 4.52 (CH_2, s). ^{19}F NMR: ϕ 41.18 (SF, tr), −103.8 (CF_2, d); $J_{SF-CF_2} = 4.15$ Hz. MS (EI^+) (*m/e*, species, %): 693, M − SO_2F^+, 0.4; 692, M − HSO_2F^+, 2.8; 599, M − $CO_2CF_2SO_2F^+$, 1.1; 242, $CF_2CO_2CH_2C(CH_2)CH_2CO_2CF_2^+$, 15.0; 133, $CF_2SO_2F^+$, 0.3; 132, $C(CH_2O)_4^+$, 12.4; 97, $C_5H_5O_2^+$, 20.7; 83, SO_2F^+, 100; 67, SOF^+, 40.7.

Anal. Calcd for $C_{13}H_8F_{12}O_{16}S_4$: C, 20.10; H, 1.03; F, 29.38. Found: C, 20.04; H, 1.07; F, 29.6.

$CH_3C(CH_2OC(O)CF_2SO_2F)_3$ (80% Yield). IR: 2970 w, br, 1780, vs, 1440 vs, 1380 w, 1300 s, 1230 s, 1195 s, 1145 s, 1010 m, br, 950 m, 842–800 s, 720 w, 647 m, 606 m, 558 m, 485 w, 460 w cm^{-1}. ^1H NMR: δ 4.42 (CH_2, s), 1.22 (CH_3, s). ^{19}F NMR: ϕ 41.24 (SF, tr), −103.7 (CF_2, d); $J_{CF_2-SF} = 4.51$ Hz. MS (CI^+) (*m/e*, species, %): 517, M − SO_2F^+, 0.1; 423, M − $CO_2CF_2SO_2F^+$, 5.9; 409, M − $CH_2CO_2CF_2SO_2F^+$, 1.4; 133, $CF_2SO_2F^+$, 2.3; 83, SO_2F^+, 3.3; 69, $CH_3C(CH_2)_3^+$, 1.5; 67, SOF^+, 100.

Anal. Calcd for $C_{11}H_9F_9O_{12}S_3$: C, 22.00; H, 1.50; F, 28.5. Found: C, 22.52; H, 1.49; F, 27.8.

$O_2NC[CH_2OC(O)CF_2SO_2F]_3$ (70% Yield). IR: 2982 w, 1786 s, 1565 s, 1441 s, 1381 w, 1343 w, 1295 s, 1230–1140 s, br, 1052 w, 1020 m, 960 w, 850 m, 809 s, 720 w, 650 s, 608 m, 561 m, 488 w, 460 w cm^{-1}. ^1H NMR: δ 4.97 (CF_2, s). ^{19}F NMR: ϕ 41.76 (SF, tr), −103.8 (CF_2, d); $J_{SF-CF_2} = 5.5$ Hz. MS (EI^+) (*m/e*, species, %): 585, M − NO_2^+, 0.7; 407, $(FSO_2CF_2CO_2CH_2)_2C_2H^+$, 2.7; 133, $CF_2SO_2F^+$, 11.5; 83, SO_2F^+, 1.0; 69, $C_4H_5O^+$, 100, 67, SOF^+, 50.

Anal. Calcd for $C_{10}H_6F_9O_{14}S_3N$: C, 19.02; H, 0.95; F, 27.10. Found: C, 19.61; H, 0.98; F, 28.00.

Preparation of $CF_3CH_2OC(O)CF_2SO_2OCH_2CF_3$ (65.4% Yield). Tetrafluoroethane-β-sultone (2 mmol) was condensed into a flask charged with $LiOCH_2CF_3$ (4 mmol) at −196 °C and was warmed to 0 °C for 4 h. After trap-to-trap distillation, the diester product was retained in the trap at −10 °C. IR: 2998 w, 1793 s, 1450–1420 s, br, 1325–1240 s, 1272 s, br, 1185 s, 1145 s, 1050 m, 1024 s, 990 m, 970 s, 890 w, 831 s, 805 s, 730 w, 671 m, 645 s, 602 w, 558 m, 492 w cm^{-1}. ^1H NMR: δ 4.76 (CH_2OC, q), 4.70 (CH_2OS, q). ^{19}F NMR: ϕ −73.84 (CF_3CH_2OC, tr), −74.54 (CF_3CH_2OS, tr), −105.8 (CF_2, s); $J_{CH_2-CF_3} = 7.57$ Hz. MS (CI^+) (*m/e*, species, %): 341, M + 1^+, 4.7; 257, $CF_3CH_2OC(O)CF_2SO_2O^+$, 19.6; 177, $CF_3CH_2OC(O)CF_2^+$, 38.6; 163, $CF_3CH_2OSO_2^+$, 5.9; 147, $CF_3CH_2OSO^+$, 59.4; 127, $CF_3CH_2OC(O)^+$, 20.4; 83, $CF_3CH_2^+$, 100; 69, CF_3^+, 12.5.

Anal. Calcd for $C_6H_4F_8O_5S$: C, 21.18; H, 1.18; F, 44.71. Found: C, 21.33; H, 1.24; F, 44.7.

$(CF_3)_2CHOC(O)CF_2SO_2OCH(CF_3)_2$ (58% Yield). IR: 2979 m, 1805 s, 1430 s, 1369 s, 1295 s, 1235 s, 1200 s, 1137 s, 1112 s, 1050 s, 990 w, 905 s, 878 m, 835 s, 805 m, 735 m, 715 w, 695 s, 650 w, 625 m, 595 w, 564 w, 525 w cm^{-1}. ^1H NMR: δ 5.79 ($(CF_3)_2CHOC$, sept), 5.29 ($(CF_3)_2CHOS$, sept). ^{19}F NMR: ϕ −73.61 (CF_3, d), −105.2 (CF_2, s); $J_{CF_3-H} = 5.37$ Hz. MS (CI+) (*m/e*, species, %): 477, M + 1^+, 0.5; 309, $(CF_3)_2CHOC(O)CF_2SO_2^+$, 1.2; 245, $(CF_3)_2CHOC(O)CF_2^+$, 36.8; 215, $(CF_3)_2CHOSO^+$, 61.0; 195, $(CF_3)_2CHOCO^+$, 27.5; 151, $(CF_3)_2CH^+$, 42.9; 69, CF_3^+, 100.

Anal. Calcd for $C_8H_2F_{14}O_5S$: C, 20.17; H, 0.42; F, 55.88. Found: C, 20.28; H, 0.41; F, 54.6.

$(CF_3)_2CHOC(O)CF_2SO_2OCH_2CF_3$ (65% Yield). This mixed diester was formed from the reaction of $(CF_3)_2CHOC(O)CF_2SO_2F$ (6 mmol) with $LiOCH_2CF_3$ (6 mmol) at 0 °C. Separation of the product was accomplished with trap-to-trap distillation. IR: 2900 w, 1792 s, 1421 s, 1367 m, 1320–1270 s, br, 1248 s, 1182 s, 1145 s, 1115 m, 1050 s, 986 w, 960 m, 909 w, 881 m, 836 m, 806 w, 729 w, 693 m, 642 w, 592 w, 552 w cm^{-1}. ^1H NMR: δ 5.30 (CH, sept), 4.76 (CH_2, q). ^{19}F NMR: ϕ −73.09 ($(CF_3)_2CH$, d), −73.90 (CF_3CH_2, tr), −104.4 (CF_2, s); $J_{CF_3-CH_2} = 7.57$ Hz, $J_{(CF_3)_2C-H} = 5.37$ Hz. MS (CI^+) (*m/e*, species, %): 409, M + 1^+, 1.1; 389, M − F^+, 5.4; 325, $(CF_3)_2CHOC(O)CF_2SO_2O^+$, 12.2; 245, $(CF_3)_2CHOC(O)CF_2^+$, 2.7; 195, $(CF_3)_2CHOCO^+$, 6.9; 163, $CF_3CH_2OSO_2^+$, 1.2; 151, $(CF_3)_2CH^+$, 9.3; 99, $CF_3CH_2O^+$, 2.2; 83, $CF_3CH_2^+$, 100; 69, CF_3^+, 57.8.

Anal. Calcd for $C_7H_3F_{11}O_5S$: C, 20.59; H, 0.74; F, 51.23. Found: C, 20.79; H, 0.74; F, 51.1.

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