

New polyfluoro and perfluoroalkoxy sulfonyl fluorides Part V. Fluorination studies

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Abstract

Two methods of fluorinating the ether containing disulfonyl fluoride, $\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (**1**) have been utilized for preparing new fluorinated derivatives. Static and electrochemical fluorination methods were effective in preparing $\text{CHF}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})$ (**2**) and $\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (**3**). The following new fluorinated ether salt derivatives have also been prepared and characterized: $\text{Ca}[\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_3)_2]$, $\text{Ca}[\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_3)_2]$ and $\text{Na}_2[\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_3)_2]$. Infrared, NMR and mass spectra are presented in order to support the assigned structures.

Introduction

The utilization of fluorocarbon sulfonyl fluorides as ion-exchange resins, surface active agents and in the preparation of strong sulfonic acids continues to make them the subject of considerable interest [1–4]. In previous papers we have reported the preparation of various sulfonyl fluorides and derivatives with ether linkages present in the fluorocarbon chain [5–8]. Since ether functions can add desirable qualities to fluorinated systems, we wish to report our further success in preparing new chemically and thermally stable diether-containing fluorocarbon sulfonyl fluorides and derivatives.

Experimental

Materials

The disulfonyl fluoride starting material, $\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$, was prepared according to literature methods [5]. Other chemicals were obtained

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from commercial sources and used as received. Fluorine was a gift of Kali-Chemie, Hanover, Germany.

General procedures

Gases other than fluorine and hydrogen fluoride were manipulated in a conventional Pyrex-glass vacuum apparatus equipped with a Heise–Bourdon gauge and Televac thermocouple gauge. Infrared spectra of the neat liquids were obtained as capillary films using a Nicolet 20DX spectrometer. The ^1H and ^{19}F NMR spectra were recorded with an AC 80 Bruker spectrometer operating at 80.0 MHz for proton and 75.4 MHz for fluorine resonances or on a AMX400 Bruker spectrometer operating at 400 MHz for proton and 376.5 MHz for fluorine resonances. Carbon-13 NMR spectra were obtained using WH360 and AMX400 Bruker spectrometers operating at 90.5 and 100.6 MHz, respectively. Samples were prepared as 20% solutions in CDCl_3 and D_2O . TMS, CFCl_3 and CD_3CN were used as internal standards. In some cases compounds were purified via gas chromatography using an Aerograph Autoprep (model A-700) gas chromatograph. The mass spectra were recorded with either a Varian MAT CH5 or a Finnigan MAT 8230 system operating at 30 eV. Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, Germany.

Electrochemical fluorination apparatus

The reaction cell consisted of a 60 ml PFA Teflon digestion vessel with molded ferrule fittings. Cylindrical electrodes (anode 22 cm^2 , cathode 11 cm^2) were fabricated from 40 gauge nickel gauze. Current was supplied using an EE&G Princeton Applied Research model 363 potentiostat operating with controlled potential. The cell was fitted with a copper reflux condenser, followed by a -196°C cold trap and a mercury bubbler. Hydrogen fluoride was introduced directly in liquid form. The reaction apparatus was connected to a copper vacuum line constructed from 3/8 in. tubing and equipped with an ACCD Helicoid Gage vacuum gauge.

Preparation of $\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ and $\text{CHF}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$

Static fluorination method

Into a 500 ml pre-fluorinated Monel vessel cooled to -196°C , equipped with a Hoke Monel valve and containing 405 mmol (17.0 g) dried NaF were added 8.74 mmol (3.60 g) $\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ and 16 mmol fluorine. The reaction vessel was warmed slowly to room temperature (1 d) and then maintained at room temperature for an additional day. Analysis of the product mixture via ^{19}F and ^1H NMR spectroscopy showed $\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$, $\text{CHF}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ and $\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ to be present. An additional 11 mmol fluorine was added and the mixture was heated at 37°C for 46 h. Distillation of the products gave 5.18 mmol (2.32 g) $\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ in 59% yield; b.p., $60\text{--}61^\circ\text{C}/21\text{ mmHg}$.

Electrochemical fluorination method

The electrodes were washed with concentrated HNO_3 , rinsed with distilled water and dried. After assembly, the cell was evacuated, purged with dry nitrogen and the condenser brought to -15°C . Anhydrous hydrogen fluoride was then introduced. The cell and electrodes were conditioned at a potential of 5.5 V until a steady base line current was achieved. Following the addition of 18.8 mmol (7.76 g) $\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$, a 5.5 V potential was again applied. The potential was removed after passing 69% of the theoretical current required for total fluorination. The hydrogen fluoride was removed and the brown oily contents of the cell were filtered and then extracted with diethyl ether. Removal of the ether gave 4.43 g of a clear oil. Analysis by vapor phase chromatography and $^{19}\text{F}/^1\text{H}$ NMR spectroscopy showed the product to be a mixture of 31% (3.1 mmol, 16% yield) of the perfluorinated product, 34% (3.5 mmol, 19% yield) of the monofluorinated product and 34% (3.76 mmol, 20% recovered) starting material. A pure fraction of $\text{CHF}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ was obtained via gas chromatography for NMR and IR analyses.

The infrared spectrum of $\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ had the following bands (cm^{-1}): 1466 (vs, sh. at 1451), 1341 (vs), 1246 (vs, sh. at 1267), 1213 (vs, sh. at 1195), 1171 (vs), 1138 (vs), 1102 (vs), 1025 (m, sh. at 1001), 991 (m), 888 (w), 872 (w), 804 (s, sh. at 839), 709 (vw), 697 (sh), 669 (w), 655 (w), 603 (s, sh. at 622, 587, 559), 512 (vw), 489 (w), 461 (w), 391 (w), 372 (s).

The relative band areas in the ^{19}F NMR spectrum were CF_2 (1.0), OCF_2 (2.0), $\text{CF}_2\text{SO}_2\text{F}$ (2.0) and SO_2F (1.1).

No molecular ion was observed in the $(\text{FAB})^+$ mass spectrum. Other main fragment ions were: 315 ($\text{M}-\text{CF}_2\text{SO}_2\text{F}$) $^+$, 289 ($\text{C}_5\text{F}_7\text{S}_2\text{O}_2$) $^+$, 277 ($\text{C}_4\text{F}_7\text{SO}_4$) $^+$, 257 ($\text{C}_5\text{F}_7\text{SO}_2$) $^+$, 244 ($\text{C}_6\text{F}_8\text{O}_2$) $^+$, 235 ($\text{C}_5\text{F}_5\text{SO}_2\text{O}$) $^+$, 198 ($\text{CF}_2\text{OCF}_2\text{CF}_2\text{S}$) $^+$, 187 ($\text{C}_5\text{F}_5\text{O}_2$) $^+$, 182 ($\text{C}_3\text{F}_6\text{O}_2$) $^+$, 168 ($\text{C}_5\text{F}_4\text{O}_2$) $^+$, 166 ($\text{CF}_2\text{OCF}_2\text{CF}_2$) $^+$, 163 ($\text{C}_3\text{F}_5\text{O}_2$) $^+$, 147 ($\text{C}_3\text{F}_5\text{O}$) $^+$, 132 ($\text{C}_2\text{F}_4\text{O}_2$ or $\text{C}_2\text{F}_4\text{S}$) $^+$, 116 ($\text{C}_2\text{F}_4\text{O}$) $^+$, 94 ($\text{C}_2\text{F}_2\text{O}_2$ or $\text{C}_2\text{F}_2\text{S}$) $^+$, 83 (SO_2F) $^+$. The EI (30 eV) mass spectrum revealed 429 ($\text{M}-\text{F}$) $^+$, 314 ($\text{C}_5\text{F}_{10}\text{SO}_2$) $^+$, 265 ($\text{C}_3\text{F}_7\text{SO}_4$) $^+$, 249 ($\text{C}_3\text{F}_7\text{SO}_3$) $^+$ and 213 ($\text{C}_4\text{F}_7\text{O}_2$) $^+$ amongst other peaks.

Analysis: Calcd. for $\text{C}_5\text{F}_{12}\text{S}_2\text{O}_6$: C, 13.40; F, 50.9; S, 14.31%. Found: C, 13.39; F, 51.3; S, 14.42%.

The infrared spectrum of $\text{CHF}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ had the following bands (cm^{-1}): 1464 (vs), 1406 (w), 1338 (ms), 1245 (vs), 1210 (vs), 1172 (vs br), 1143 (vs), 1102 (s, sh. at 1069), 981 (m), 809 (vs, sh. at 851), 657 (wm), 643 (w), 608 (s, sh. at 576), 512 (w), 490 (wm), 464 (wm).

The relative band areas in the ^{19}F NMR spectrum were CFH (1.0), OCF_2 (4.0), $\text{CF}_2\text{SO}_2\text{F}$ (4.0) and SO_2F (2.1).

$\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2 + \text{NaOH (aq)}$

Into a 100 ml Pyrex round-bottom flask equipped with a reflux condenser, a Teflon stirring bar and a dropping funnel charged with 19.7 mmol (8.10 g) $\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ were added 103 mmol (4.10 g) NaOH and 50 ml

H₂O. The sulfonyl fluoride was added over a 25 min period with stirring. The reaction flask was heated to reflux with stirring for 2 d. After cooling, the contents were filtered to give 10.20 g of crude product which was purified by continuous extraction with diethyl ether giving 17.9 mmol (8.07 g) Na₂[CH₂(OCF₂CF₂SO₃)₂] (90.8% yield) which melted at 267–270 °C.

The infrared spectrum of Na₂[CH₂(OCF₂CF₂SO₃)₂] had the following bands (cm⁻¹): 1328 (wm), 1293 (vs), 1279 (vs), 1250 (vs, sh. at 1202), 1145 (vs), 1117 (vs), 1068 (s), 1040 (m), 1019 (m), 984 (ms), 963 (m), 941 (m), 899 (wm, br), 829 (w), 766 (w), 660 (s), 625 (ms), 590 (wm), 541 (m).

The relative band areas in the ¹⁹F NMR spectrum were OCF₂ (1.0) and CF₂SO₃ (1.0).

Analysis: Calcd. for Na₂C₅F₈S₂O₈: C, 13.28; H, 0.45; S, 14.16; F, 33.6%. Found: C, 13.48; H, 0.74; S, 12.72; F, 32.8%.

CH₂(OCF₂CF₂SO₂F)₂ + CaO (aq.)

Into a 50 ml Pyrex round-bottom flask equipped with a reflux condenser, a Teflon stirring bar and a dropping funnel containing 15.4 mmol (6.36 g) CH₂(OCF₂CF₂SO₂F)₂, 61.0 mmol (3.42 g) CaO and 25 ml H₂O were added. The sulfonyl fluoride was added over a 10-min period with stirring. The reaction flask was heated to reflux with stirring for 12 d. After cooling, the contents were filtered in order to remove CaF₂; the filtrate was heated to dryness and then dried *in vacuo* to give Ca[CH₂(OCF₂CF₂SO₃)₂]. The calcium salt was stable to 300 °C.

The infrared spectrum of Ca[CH₂(OCF₂CF₂SO₃)₂] had the following bands (cm⁻¹): 1340 (wm), 1267 (vs), 1246 (vs), 1215 (s), 1174 (s), 1152 (vs), 1126 (vs), 1101 (vs), 1074 (ms), 1032 (m), 995 (s), 941 (s, sh. at 955, 873), 793 (vw), 763 (wm), 671 (m), 601 (m), 588 (m), 565 (m), 528 (ms), 457 (m).

CF₂(OCF₂CF₂SO₂F)₂ + CaO (aq.)

Into a three-neck 100 ml Pyrex round-bottom flask equipped with a Teflon stirring bar, a dropping funnel containing 10.4 mmol (4.68 g) CF₂(OCF₂CF₂SO₂F)₂ and attached to a reflux condenser connected to a trap cooled to -78 °C, 42.1 mmol (2.36 g) CaO and 50 ml H₂O were added. The sulfonyl fluoride was added over a 25-min period with stirring. The reaction flask was heated at 95–100 °C with stirring for 5 d. After cooling, the contents were filtered and the filtrate was heated to dryness and then dried *in vacuo* to give 9.57 mmol (4.61 g) Ca[CF₂(OCF₂CF₂SO₃)₂]; 92% yield. The product was stable to >360 °C.

The infrared spectrum of Ca[CF₂(OCF₂CF₂SO₃)₂] had the following bands (cm⁻¹): 1349 (m, sh. at 1333), 1267 (vs, sh. at 1247), 1181 (s), 1149 (ms), 1097 (s), 1054 (wm), 988 (m, sh. at 999), 838 (w), 703 (vw), 677 (wm), 662 (w) 636 (m), 522 (w).

The relative band areas in the ¹⁹F NMR spectrum were OCF₂O (1.0), OCF₂ (2.1) and CF₂SO₃ (2.2).

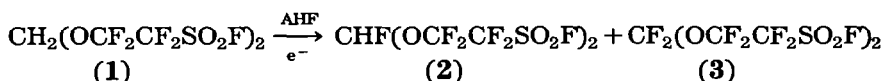
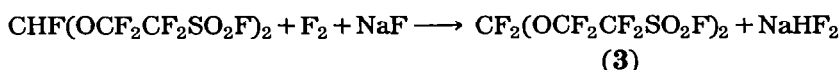
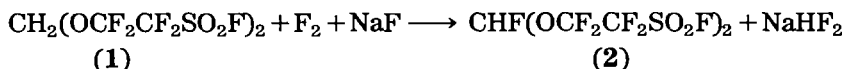
No molecular ion was observed in the (FAB)⁺ mass spectrum, but the following main fragment ions were found: 705 [M₂H₂-C₄F₇SO₃]⁺, 613 (M₂H-CaSO₃C₂F₄OCF₂OCF₂)⁺, 587 (M₂H-CaSO₃C₂F₄OCF₂OCF₄)⁺, 575 (M₂H-CaSO₃C₂F₄OCF₂OF₄)⁺, 525 (M₂H-CaSO₃C₂F₄OCF₂OCF₆)⁺, 401 (MH-CF₂O₂)⁺, 397 (MH-O₃F₂)⁺, 347 (M-OC₂F₅)⁺, 314 (C₅F₁₀SO₂)⁺, 309 (M-OC₂F₇)⁺, 295 (C₅F₉SO₂)⁺, 273 (C₅F₇SO₃)⁺, 261 (M-O₄C₂F₇)⁺, 233 (M-O₅C₃F₇)⁺, 223 (C₄F₅O₃S)⁺, 217 (M-O₆C₃F₇)⁺, 191 (CaC₃FO₄S)⁺, 151 (C₃FSO₄)⁺, 137 (C₄F₃O₂)⁺, 135 (C₃FO₃S)⁺, 132 (C₂F₄O₂)⁺, 131 (C₄FO₂S)⁺, 114 (CF₂SO₂)⁺, 99 (C₄FO₂)⁺, 98 (CF₂SO)⁺, 87 (C₃FO₂)⁺, 59 (C₂FO)⁺, 43 (C₂F)⁺, 40 (Ca)⁺. Among the (FAB)⁻ fragments found were: 925 (2MH-Ca)⁻, 845 (2MH-Ca-SO₃)⁻, 825 (2M-Ca-SO₃F)⁻, 659 (2M-Ca-CF₂OC₂F₄SO₃-F)⁻, 573 [2MH-2(OC₂F₄SO₃)]⁻, 562 (M+SO₃)⁻, 501 [MF or 2MH-Ca-2(SO₃C₂F₄O₂)]⁻, 483 (MH)⁻, 443 (MH-Ca)⁻, 423 (M-Ca-F)⁻, 393 (M-O₂F₃)⁻, 381 (M-CO₂F₃)⁻, 363 (MH-CO₂F₄)⁻, 362 [CF₂(OC₂F₄S)₂O]⁻, 343 (M-CO₂F₅)⁻, 325 (MH-CO₂F₆)⁻, 316 (M-CF₂OC₂F₄)⁻, 255 (MH-O₃C₂F₄SO₃)⁻, 180 (OC₂F₄SO₂)⁻, 177 (OC₂F₃SO₃)⁻, 161 (OC₂F₃SO₂)⁻, 130 (O₂C₅F₂)⁻.

Analysis: Calcd. for CaC₅F₁₀S₂O₈; Ca, 8.31; C, 12.45; F, 39.40; S, 13.30%. Found: Ca, 8.90; S, 12.70; F, 37.5%.

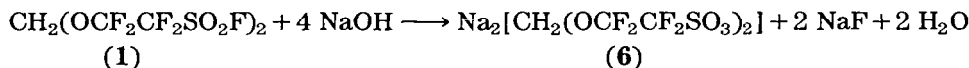
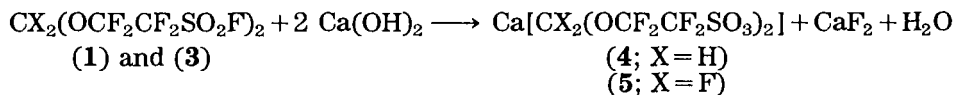
It should be noted that, by convention, resonances appearing downfield from CFCl₃ are assigned positive values, upfield resonances are assigned negative values.

Results and discussion

We have found that static fluorination of compound **1** under mild conditions and in the presence of NaF occurs in several stages. After fluorination for 2 d, the ¹⁹F NMR and ¹H NMR spectra of the product mixture showed compounds **1**, **2** and **3** to be present. Fluorination for an additional 36 h gave, upon distillation, compound **3** in 59% yield. No attempts were made to isolate compound **2** produced in this reaction. In the electrochemical fluorination method the product mixture, after passage of 69% theoretical current required for total fluorination, was separated and analyzed via vapor phase chromatography and ¹⁹F/¹H NMR spectroscopy. The product mixture was found to contain 31% of **3**, 34% of **2** and 34% of **1**. A pure sample of **2** was obtained via gas chromatographic separation of this mixture and used for NMR and IR analyses.



Basic hydrolysis of the starting dihydro material and the perfluorinated product gave stable sulfonate salts:



The structures of all new products were determined from their ^{19}F , ^{13}C and ^1H NMR spectra. The ^{19}F and ^1H NMR chemical shifts and coupling constants for the new compounds can be found in Table 1. Carbon-13 NMR data for the sulfonyl fluorides and the sodium salt are presented in Table 2.

The ^{19}F NMR spectrum of the mono-fluorinated sulfonyl fluoride 2 is interesting in two respects: the CHF resonance is shifted downfield, ($\delta = -88.9$ ppm), from the usual region for geminal H-F groups in hydrocarbons [9], and the OCF_2 set appear as an AB system with resonances at -82.43 and -84.29 ppm with a coupling of 145 Hz. We attribute the deshielding of the CHF group to electron withdrawal by neighboring oxygens. The AB pattern of the OCF_2 group is consistent with the diastereotopic nature of these two fluorines. In $\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{F}$, the OCF_2 resonance is found at -87.76 ppm [10]. The CF_2S fluorines also possess a diastereotopic

TABLE 1

^{19}F and ^1H NMR data for sulfonyl fluorides, $\text{CXY}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$, and sulfonate salts, $\text{M}[\text{CXY}(\text{OCF}_2\text{CF}_2\text{SO}_3)_2]^a$

CXY	OCF_2	CF_2S	SO_2F
$\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (1) ^b			
H 5.8 (s)	-84.5 (d,t)	-112.0 (d,t)	45.2 (t,t)
$\text{CHF}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (2)			
F -88.9 (d,p)	F -82.4 (d,m)	-112.8 (m)	45.0 (t,t)
H 7.0 (d)	F' -84.3 (d,m)		
$J_{\text{H-F}} = 63.4$	$J_{\text{F-F'}} = 145.0$	$J_{\text{CF}_2\text{S-SO}_2\text{F}} = 6.2$	
$J_{\text{CHF-OCF}_2} = 6.2$	$J_{\text{OCF}_2\text{-SO}_2\text{F}} = 6.2$		
$\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (3)			
F -51.4 (p)	-84.0 (m)	-112.6 (d,t)	45.6 (t,t)
$J_{\text{CF}_2\text{-(OCF}_2)_2} = 10.6$	$J_{\text{OCF}_2\text{-CF}_2\text{S}} = 6.1$	$J_{\text{CF}_2\text{S-SO}_2\text{F}} = 6.1$	
$\text{Ca}[\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_3)_2]$ (5)			
F -51.2 (m)	-85.2 (t)	-119.3 (s)	
$J_{\text{CF}_2\text{-(OCF}_2)_2} = 11.6$	$J_{\text{OCF}_2\text{-CF}_2\text{S}} < 1.5$		
$\text{Na}_2[\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_3)_2]$ (6)			
H 5.2 (s)	-85.0 (s)	-118.0 (s)	
	$J_{\text{OCF}_2\text{-CF}_2\text{S}} < 1.5$		

^aChemical shifts in ppm; coupling constants in Hz.

^bValues obtained from the literature [7].

TABLE 2

a b c

 ^{13}C NMR data of sulfonyl fluorides $\text{CXY}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ and $\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na})_2^a$

CXY	OCF_2	CF_2S
$\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (1)		
85.3 (p)	116.8 (t,t,d)	114.0 (t,t,d)
$J_{\text{Fb-a}}=5.3$	$J_{\text{Fb-b}}=280.8$	$J_{\text{Fc-c}}=301.3$
	$J_{\text{Fc-b}}=28.7$	$J_{\text{Fb-c}}=41.0$
	$J_{\text{SO}_2\text{Fb}}=3.4$	$J_{\text{SO}_2\text{Fc}}=36.0$
$\text{CHF}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (2)		
107.4 (d,p)	114.8 (t,t,d,d)	112.6 (t,t,d)
$J_{\text{Fa-a}}=264.4$	$J_{\text{Fb-b}}=285.3$	$J_{\text{Fc-c}}=302.4$
$J_{\text{Fb-a}}=4.9$	$J_{\text{Fc-b}}=29.8$	$J_{\text{Fb-c}}=38.6$
	$J_{\text{SO}_2\text{Fb}}=2.6$	$J_{\text{SO}_2\text{Fc}}=38.6$
	$J_{\text{Fa-b}}=2.6$	
$\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (3)		
118.0 (t)	113.7 (t,t,t,d)	111.8 (t,t,d,t)
$J_{\text{Fa-a}}=278.9$	$J_{\text{Fb-b}}=290.4$	$J_{\text{Fc-c}}=302.5$
	$J_{\text{Fc-b}}=30.1$	$J_{\text{Fb-c}}=38.5$
	$J_{\text{Fa-b}}=1.5$	$J_{\text{SO}_2\text{Fc}}=38.5$
	$J_{\text{SO}_2\text{Fb}}=3.0$	$J_{\text{Fa-c}}=1.2$
$\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na})_2$ (6)		
83.8 (p)	118.2 (t,t)	113.0 (t,t)
	$J_{\text{Fb-b}}=276.2$	$J_{\text{Fc-c}}=286.3$
	$J_{\text{Fc-b}}=32.0$	$J_{\text{Fb-c}}=35.6$
	$J_{\text{Fa-a}}=5.8$	

^aChemical shifts in ppm, coupling constants in Hz. Splitting patterns of **1**, **2** and **6** listed for the proton-decoupled spectra. In the hydrogen-coupled spectra, the splitting patterns and couplings found were: **1**, CH_2 (t,p), OCF_2 (t,t,d,t) and $J_{\text{Hb}}=5.3$, $J_{\text{Hb}}=178.8$ Hz; **2**, CHF (d,d,p), OCF_2 (t,t,d,d,d) and $J_{\text{Hb}}=2.6$, $J_{\text{Hb}}=214.8$ Hz; **6** CH_2 (t,p), OCF_2 (t,t,t) and $J_{\text{Hb}}=5.0$.

relationship, but this group could not be resolved and must be an AA' system with coupling of the order of 1.5 Hz or less. In bromo end-capped perfluoropolyethers the fluorine resonance at -55.3 ppm was attributed to the $-\text{OCF}_2\text{O}-$ grouping [11]. In compound **3** a resonance at -51.4 ppm is found for the $-\text{OCF}_2\text{O}-$ group. The chemical shifts for the FSO_2- and $\text{CF}_2\text{SO}_2\text{F}-$ groups agree with values found for $\text{FSO}_2(\text{CF}_2)_3\text{SO}_2\text{F}$ [12].

For the perfluorinated compounds **3** and **5**, the magnitude of the coupling between the CXY ($\text{X}=\text{F}$, $\text{Y}=\text{F}$) and OCF_2 groups was similar with values of 10.6 and 11.6 Hz. However, coupling between the OCF_2 and CF_2S groups in **3** was found to be 6.1 Hz whilst in the salt **5** this value was less than 1.5 Hz. This small coupling was also seen in the sodium salt **6**. The NMR chemical shifts and coupling constants for the other functionalities fall in the ranges of previously reported values [7–10].

The ^{13}C NMR proton decoupled spectra of compounds **1**, **2** and **3** (see Table 2) show variations in the coupling between the carbon a and the OCF_2

fluorines; values of 5.3 and 4.9 Hz were obtained for compounds **1** and **2**, respectively while with compound **3** no similar type coupling was observed. Also, coupling was observed between the OCF_2 carbon b and the F_a fluorines; values of 2.6 and 1.5 Hz were found for compounds **2** and **3**, respectively. The ^{13}C NMR proton-coupled spectrum of the CH_2 group in **1** and **6** was found to have the expected triple-pentet pattern with a coupling of 178.8 and 177.4 Hz, respectively; for compound **3** the CHF group exhibited a d,d,p pattern with a hydrogen coupling of 214.8 Hz.

The infrared spectra of all the new compounds have common features. The characteristic SO_2 (asym.) and SO_2 (sym.) stretching frequencies were found for the sulfonyl fluorides **2** and **3** in the 1466–1464 and 1246–1245 cm^{-1} regions, respectively. The strong S–F absorption in these compounds, which disappeared when the salts were formed, was seen at 804 and 809 cm^{-1} . These assignments agree well with the results obtained in other fluorosulfonyl derivatives [5–10, 13]. The asym. and sym. SO_3 stretching bands of the salts **5** and **6** were found in the 1250–1267 and 1054–1032 cm^{-1} regions; for salts containing the CF_3SO_3^- group, the corresponding assigned regions are 1270–1290 and 1036–1038 cm^{-1} [13]. The strong carbon fluorine absorption bands found at 1040–1267 cm^{-1} can be attributed to the CF_2 groups and was present in all the compounds [14].

Mass spectra fragments for all new compounds are listed above in the experimental section. Molecular ion peaks were not detected for any of the compounds listed, however $\text{M} - \text{F}$ and other appropriate fragments were found and are supportive of the assigned structures.

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