

## A useful synthesis of $\omega$ -iodoperfluoroalkanesulfonyl fluorides and perfluoroalkane- $\alpha,\omega$ -bis-sulfonyl fluorides

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### Abstract

$\omega$ -Iodoperfluoroalkanesulfonyl fluorides and perfluoroalkane- $\alpha,\omega$ -bis-sulfonyl fluorides have been prepared via deiodosulfonation, chlorination, and then chlorine–fluorine exchange reaction of  $\alpha,\omega$ -diiodoperfluoroalkanes  $I(CF_2)_nI$  ( $n=3, 4, 6$ ). Similar reaction of  $I(CF_2)_2O(CF_2)_2SO_2F$  affords  $FSO_2(CF_2)_2O(CF_2)_2SO_2F$ .

### Introduction

Fluorinated sulfonyl fluorides and fluorinated  $\alpha,\omega$ -bis-sulfonyl fluorides are important compounds in organic synthesis and material science [1]. Most preparations of fluorinated sulfonyl fluorides have been achieved by electrochemical fluorination (ECF) of the corresponding sulfonyl fluorides or chlorides [2]. Fluorinated sulfonyl fluorides have also been synthesized by the reaction of the corresponding fluorinated sulfonyl chlorides with CsF [3] and KF [4], the reaction of a fluorinated sulfonic anhydride with NaF [5], the reaction of fluorinated olefin with sulfuryl fluoride and CsF [6], the rearrangement and decarboxylation of fluorinated sultone [7], and the reaction of  $ClSO_2F$  with tetrafluoroethene [8]. Recently, Cherstkov *et al.* [9] reported the synthesis of fluorinated sulfonyl fluorides and fluorinated bis-sulfonyl fluorides by an anodic oxidation of fluorinated  $\omega$ -fluorosulfonylcarboxylic acid,  $FSO_2CF_2[CF_2OCF(CF_3)]_nCO_2H$  ( $n=1, 2$ ). Treatment of  $I(CF_2)_2O(CF_2)_2SO_2F$  with zinc afforded the bis-sulfonyl fluoride,  $FSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2F$  [10], but the  $\omega$ -iodoperfluoroalkanesulfonyl fluorides  $I(CF_2)_nSO_2F$  ( $n > 1$ ) have not yet been reported. ( $ICF_2SO_2F$  has been prepared by photodecarbonylation of  $FSO_2CF_2C(O)I$  [11];  $I(CF_2)_2O(CF_2)_2SO_2F$  has been synthesized by the reaction of tetrafluorosultone with KF,  $I_2$  and  $CF_2=CF_2$  [12].) Herein, we report a useful synthesis of  $\omega$ -iodoperfluoroalkanesulfonyl fluorides  $I(CF_2)_nSO_2F$  ( $n=3, 4, 6$ ) and perfluoroalkane- $\alpha,\omega$ -bis-sulfonyl fluorides  $FSO_2(CF_2)_nSO_2F$  ( $n=3, 4, 6$ ) from the corresponding  $\alpha,\omega$ -diiodoperfluoroalkanes.

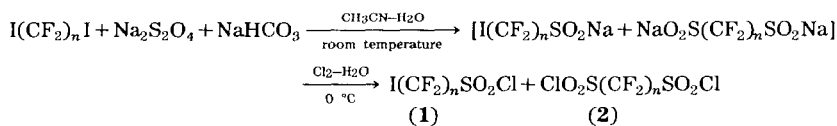
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## Results and discussion

Reaction of  $\alpha,\omega$ -diiodoperfluoroalkane with one equivalent of sodium dithionite and sodium bicarbonate in acetonitrile–water (10:3) gave a mixture of  $\omega$ -iodoperfluoroalkanesulfinate, perfluoroalkane- $\alpha,\omega$ -bis-sulfinate and traces of reduced products. The sulfinate  $\text{I}(\text{CF}_2)_n\text{SO}_2\text{Na}$  and  $\text{NaSO}_2(\text{CF}_2)_n\text{SO}_2\text{Na}$  were treated with chlorine gas at 0 °C to produce the corresponding sulfonyl chlorides  $\text{I}(\text{CF}_2)_n\text{SO}_2\text{Cl}$  (**1**) and  $\text{ClSO}_2(\text{CF}_2)_n\text{SO}_2\text{Cl}$  (**2**). Fractional distillation gave the  $\omega$ -iodoperfluoroalkanesulfonyl chlorides in 28–39% yields with 80–90%  $^{19}\text{F}$  nuclear magnetic resonance (NMR) purities. Pure **1b** was obtained by redistillation. Treatment of the chlorides **1a–1c** with potassium fluoride in acetonitrile at room temperature afforded  $\omega$ -iodoperfluoroalkanesulfonyl fluorides **3a–3c** in good yields. Similarly, when the  $\alpha,\omega$ -diiodoperfluoroalkane was reacted with two equivalents of sodium dithionite and sodium bicarbonate in acetonitrile–water (1:1), the perfluoroalkane- $\alpha,\omega$ -bis-sulfinate were formed, which were subsequently converted to perfluoroalkane- $\alpha,\omega$ -bis-sulfonyl fluorides **4** through the chlorination and halide exchange reaction in good yields. The results of sulfination and chlorination are summarized in Table 1, and the results of the halide exchange reaction are summarized in Table 2.

The reaction of  $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$  with sodium dithionite and sodium bicarbonate afforded  $\text{NaSO}_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{Na}$  which was converted to the corresponding bis-sulfonyl chloride **5** in 55% yield by chlorination. Treatment of **5** with potassium fluoride at room temperature produced 74% of bis-sulfonyl fluoride **6**:

TABLE 1

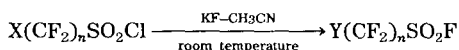
Sulfination and chlorination of  $\alpha,\omega$ -diiodoperfluoroalkanes

$n$ in $\text{I}(\text{CF}_2)_n\text{I}$	$\text{I}(\text{CF}_2)_n\text{I}:\text{Na}_2\text{S}_2\text{O}_4$ ratio	$\text{CH}_3\text{CN}:\text{H}_2\text{O}$ ratio	Product	Yield (purity <sup>a</sup> ) (% (%))
3	1:1	10:3	$\text{I}(\text{CF}_2)_3\text{SO}_2\text{Cl}$ ( <b>1a</b> )	28 (80)
4	1:1	10:3	$\text{I}(\text{CF}_2)_4\text{SO}_2\text{Cl}$ ( <b>1b</b> )	25 (90)
6	1:1	20:3	$\text{I}(\text{CF}_2)_6\text{SO}_2\text{Cl}$ ( <b>1c</b> )	39 (84)
3	1:2	1:1	$\text{ClSO}_2(\text{CF}_2)_3\text{SO}_2\text{Cl}$ ( <b>2a</b> )	73 (100)
4	1:2	1:1	$\text{ClSO}_2(\text{CF}_2)_4\text{SO}_2\text{Cl}$ ( <b>2b</b> )	83 (100)
6	1:2	1:1	$\text{ClSO}_2(\text{CF}_2)_6\text{SO}_2\text{Cl}$ ( <b>2c</b> )	75 (>98)

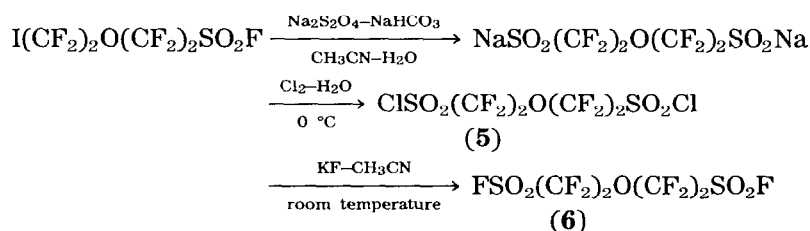
<sup>a</sup>Isolated yields; the purity was determined by  $^{19}\text{F}$  NMR analysis.

TABLE 2

Halide exchange reaction of the sulfonyl and bis-sulfonyl chlorides



<i>n</i>	X	Y	Yield (purity) <sup>a</sup> (% (%))
3	I	I	73 (95) ( <b>3a</b> )
4	I	I	83 (100) ( <b>3b</b> )
6	I	I	75 (100) ( <b>3c</b> )
3	ClSO <sub>2</sub>	FSO <sub>2</sub>	86 (100) ( <b>4a</b> )
4	ClSO <sub>2</sub>	FSO <sub>2</sub>	81 (100) ( <b>4b</b> )
6	ClSO <sub>2</sub>	FSO <sub>2</sub>	74 (> 98) ( <b>4c</b> )

<sup>a</sup>Isolated yields; the purity was determined by <sup>19</sup>F NMR analysis.

We have also investigated the reaction of I(CF<sub>2</sub>)<sub>4</sub>MgBr, generated from I(CF<sub>2</sub>)<sub>4</sub>I and RMgBr [13], with sulfonyl fluoride or sulfonyl chloride fluoride. Unfortunately, no expected ω-iodoperfluoroalkanesulfonyl fluorides **3** were observed. The formation of the Grignard reagents and the ratio of mono- and bis-Grignard reagents {I(CF<sub>2</sub>)<sub>4</sub>MgBr: BrMg(CF<sub>2</sub>)<sub>4</sub>MgBr: I(CF<sub>2</sub>)<sub>4</sub>I, 60:20:20} have been confirmed by hydrolysis of the Grignard reagents at low temperatures to form the corresponding reduction products. It is possible that I(CF<sub>2</sub>)<sub>4</sub>MgBr did not react with FSO<sub>2</sub>X (X≡F, Cl) at low temperature and I(CF<sub>2</sub>)<sub>4</sub>MgBr decomposed before reaching the temperature at which I(CF<sub>2</sub>)<sub>4</sub>MgBr may react with FSO<sub>2</sub>X (X≡F, Cl).

## Experimental details

All boiling points were determined during distillation and are uncorrected. <sup>19</sup>F NMR (83.9 MHz) spectra were recorded on a JEOL FX90Q spectrometer. <sup>13</sup>C NMR (75 MHz) spectra were recorded on a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per million downfield (positive) of the standard. <sup>19</sup>F NMR chemical shifts are reported relative to internal CFCl<sub>3</sub>. <sup>13</sup>C NMR chemical shifts are reported relative to internal tetramethylsilane. CDCl<sub>3</sub> served as solvent for all NMR spectra. IR spectra were recorded on a Mattson Cygnus 100 spectrometer. Gas chromatography (GC)–mass spectroscopy (MS) spectra were recorded on a VG TRIO-1 spectrometer operating at 70 eV.

### Preparation of 3-iodoperfluoropropanesulfonyl chloride (**1a**)

A mixture of 50 g (124 mmol) of  $\text{I}(\text{CF}_2)_3\text{I}$ , 25.5 g (124 mmol) of  $\text{Na}_2\text{S}_2\text{O}_4$ , 12.5 g (150 mmol) of  $\text{NaHCO}_3$ , 75 ml of  $\text{CH}_3\text{CN}$  and 20 ml of water was stirred at room temperature for 2 h.  $^{19}\text{F}$  NMR analysis indicated that 44% of  $\text{I}(\text{CF}_2)_3\text{I}$  remained while 32% of  $\text{I}(\text{CF}_2)_3\text{SO}_2\text{Na}$ , 12% of  $\text{NaSO}_2(\text{CF}_2)_3\text{SO}_2\text{Na}$  and 12% of reduced product were formed. Inorganic salts were removed by filtration. The filtrate was concentrated and dried under vacuum to give a solid residue. This residue was dissolved in 200 ml of water and treated with  $\text{Cl}_2$  at 0 °C to afford a liquid (bottom layer of the reactive mixture) which contained  $\text{I}(\text{CF}_2)_3\text{I}$ , **1a** and **2a**. Distillation of the liquid gave three fractions A (10 g), B (12.9 g) and C (distillation residue, 2 g). A is a mixture of  $\text{I}(\text{CF}_2)_3\text{I}$  and **1a** (ratio 1:1); B is a mixture of  $\text{I}(\text{CF}_2)_3\text{I}$ , **1a** and **2a** (ratio, 12:80:8) yield 28%; C is a mixture of **1a** and **2a** (ratio, 1:1). Redistillation of B gave two fractions D (6 g, a mixture of  $\text{I}(\text{CF}_2)_3\text{I}$ , **1a** and **2a** in the ratio 2:93:5) (b.p., 74 °C at 45 Torr), and E (3 g, a mixture of  $\text{I}(\text{CF}_2)_3\text{I}$ , **1a** and **2a** in the ratio 1:89:10). **1a**  $^{19}\text{F}$  NMR: -60.4 (tt,  $J=15, 5$  Hz,  $2\text{F}, \text{CF}_2\text{I}$ ), -103.8 (t,  $J=12$  Hz,  $2\text{F}, \text{CF}_2\text{S}$ ), -111.3 (s,  $2\text{F}, \text{CF}_2\text{CF}_2\text{I}$ ) ppm. Fourier transform IR (FTIR)  $\nu_{\text{max}}$ : 1421 (m), 1209 (s), 1183 (vs), 1156 (s)  $\text{cm}^{-1}$ .

### Preparation of 4-iodoperfluorobutanesulfonyl chloride (**1b**)

A mixture of 59 g (130 mmol) of  $\text{I}(\text{CF}_2)_4\text{I}$ , 26.6 g (130 mmol) of  $\text{Na}_2\text{S}_2\text{O}_4$ , 12.8 g (150 mmol) of  $\text{NaHCO}_3$ , 77 ml of  $\text{CH}_3\text{CN}$  and 23 ml of water was stirred at room temperature for 2 h.  $^{19}\text{F}$  NMR analysis indicated that 27% of  $\text{I}(\text{CF}_2)_4\text{I}$  remained while 50% of  $\text{I}(\text{CF}_2)_4\text{SO}_2\text{Na}$ , 19% of  $\text{NaSO}_2(\text{CF}_2)_4\text{SO}_2\text{Na}$  and 4% of reduced product were formed. Inorganic salts were removed by filtration. The filtrate was concentrated and dried under vacuum to give a solid residue. This residue was dissolved in 200 ml of water and treated with  $\text{Cl}_2$  at 0 °C to afford a liquid (bottom layer of the reaction mixture) which contained  $\text{I}(\text{CF}_2)_4\text{I}$ , **1b** and **2b**. Distillation of the liquid gave three fractions A (2 g), B (14 g) and C (3.5 g). A is a mixture of  $\text{I}(\text{CF}_2\text{CF}_2)_2\text{I}$  and **1b** (ratio, 1:2); B is a mixture of **1b** and **2b** (ratio, 9:1) of yield 25%; C is a mixture of **1b** and **2b** (ratio, 1:1). Redistillation of B gave pure **1b** (8.4 g, 15%, 100% purity based on  $^{19}\text{F}$  NMR analysis) (b.p., 74 °C at 28 Torr).  $^{19}\text{F}$  NMR: -60.1 ( $2\text{F}, \text{CF}_2\text{I}$ ), -104.6 ( $2\text{F}, \text{CF}_2\text{S}$ ), -113.4 ( $2\text{F}, \text{CF}_2\text{CF}_2\text{I}$ ), -118.8 ( $2\text{F}, \text{CF}_2\text{CF}_2\text{S}$ ) ppm. FTIR  $\nu_{\text{max}}$ : 1423 (s), 1213 (vs), 1149 (vs)  $\text{cm}^{-1}$ .

### Preparation of 6-iodoperfluorohexanesulfonyl chloride (**1c**)

A mixture of 95 g (170 mmol) of  $\text{I}(\text{CF}_2)_6\text{I}$ , 35 g (170 mmol) of  $\text{Na}_2\text{S}_2\text{O}_4$ , 18.5 g (220 mmol) of  $\text{NaHCO}_3$ , 200 ml of  $\text{CH}_3\text{CN}$  and 30 ml of water was stirred at room temperature for 20 h. Inorganic salts were removed by filtration. The filtrate was concentrated and dried under vacuum to give a solid residue which was dissolved in 250 ml of water. The bottom layer of  $\text{I}(\text{CF}_2)_6\text{I}$  was removed. The water solution was treated with  $\text{Cl}_2$  at 0–5 °C until the iodine color had disappeared. The reaction mixture was extracted

with methylene chloride (twice in 50 ml) and the combined organic extracts were concentrated to give 35 g (crude yield, 39%) of **1c** which contained 14% of **2c** and 2% of I(CF<sub>2</sub>)<sub>6</sub>I. **1c** <sup>19</sup>F NMR: -60.1 (CF<sub>2</sub>I), -104.6 (CF<sub>2</sub>S), -113.4 (CF<sub>2</sub>CF<sub>2</sub>I), -118.8 (CF<sub>2</sub>CF<sub>2</sub>S) ppm. FTIR  $\nu_{\max}$ : 1421 (s), 1207 (s), 1156 (s) cm<sup>-1</sup>.

#### *Preparation of 3-iodoperfluoropropanesulfonyl fluoride (3a)*

A mixture of 6 g (93% purity) of **1a**, 1.8 g (30 mmol) of KF and 10 ml of CH<sub>3</sub>CN was stirred at room temperature overnight. <sup>19</sup>F NMR analysis indicated that the sulfonyl chloride was converted into the corresponding sulfonyl fluoride. After 50 ml of water were added to the reaction mixture, the bottom layer was separated and washed with water (twice in 50 ml) to give an organic liquid which was distilled to afford 4.2 g (73% yield) of crude **3a** (95% purity). Crude **3a** was purified by preparative scale GC to give pure **3a** (b.p., 61 °C at 145 Torr). <sup>19</sup>F NMR: +45.3 (SO<sub>2</sub>F), -60.0 (t, *J*=15 Hz, CF<sub>2</sub>I), -107.4 (CF<sub>2</sub>S), -112.2 (CF<sub>2</sub>CF<sub>2</sub>I). <sup>13</sup>C NMR: 92.2 (tt, *J*=322, 42 Hz), 108.0 (tp, *J*=267, 30 Hz), 113.7 (tq, *J*=303, 38 Hz) ppm. FTIR  $\nu_{\max}$ : 1461 (s), 1204 (s), 1144 (s), 908 (s) cm<sup>-1</sup>. GC-MS *m/z*: 360 (M<sup>+</sup>, 0.2), 277 (M<sup>+</sup>-SO<sub>2</sub>F, 2.8), 233 (M<sup>+</sup>-I, 6.4), 177 (ICF<sub>2</sub><sup>+</sup>, 21.8).

#### *Preparation of 4-iodoperfluorobutanesulfonyl fluoride (3b)*

A mixture of 6.5 g (15.2 mmol) of **1b**, 1.8 g (30 mmol) of KF and 10 ml of CH<sub>3</sub>CN were stirred at room temperature overnight. <sup>19</sup>F NMR analysis indicated that the sulfonyl chloride was converted into the corresponding sulfonyl fluoride. After 50 ml of water were added to the reaction mixture, the bottom layer was separated and washed with 50 ml of water to give an organic liquid which was distilled to afford 5.2 g (83% yield) of **3b** (100% purity based on <sup>19</sup>F NMR analysis) (b.p., 75 °C at 70 Torr). <sup>19</sup>F NMR: +46.2 (SO<sub>2</sub>F), -60.2 (CF<sub>2</sub>I), -108.0 (CF<sub>2</sub>S), -113.4 (CF<sub>2</sub>CF<sub>2</sub>I), -119.7 (CF<sub>2</sub>CF<sub>2</sub>S) ppm. <sup>13</sup>C NMR: 92.7 (tt, *J*=321, 42 Hz), 115.3 (tq, *J*=305, 37 Hz), 104.4-113.8 (m) ppm. FTIR  $\nu_{\max}$ : 1462 (s), 1212 (vs), 1150 (vs) cm<sup>-1</sup>. GC-MS *m/z*: 410 (M<sup>+</sup>, 0.2), 327 (M<sup>+</sup>-SO<sub>2</sub>F, 1.6), 283 (M<sup>+</sup>-I, 17.6), 177 (ICF<sub>2</sub><sup>+</sup>, 19.1).

#### *Preparation of 6-iodoperfluorohexanesulfonyl fluoride (3c)*

A mixture of 35 g of **1c** (containing 14% **2c**), 6 g (103 mmol) of KF and 50 ml of CH<sub>3</sub>CN was stirred at room temperature for 5 days. <sup>19</sup>F NMR analysis indicated that the sulfonyl chlorides were converted into the corresponding sulfonyl fluorides. After 100 ml of water were added to the reaction mixture, the bottom layer was isolated and washed with 50 ml of water to give a liquid. Distillation of the liquid afforded 25.5 g of crude **3c** (containing 11% **4c**) which was further purified by silica gel column chromatography using pentane as eluent to give 21.9 g (75% yield) of **3c** (100% purity based on <sup>19</sup>F NMR analysis) (b.p., 74-75 °C at 11 Torr). <sup>19</sup>F NMR: +46.2 (SO<sub>2</sub>F), -59.8 (t, *J*=19 Hz, CF<sub>2</sub>I), -108.1 (CF<sub>2</sub>S), -113.5 (CF<sub>2</sub>CF<sub>2</sub>I), -120.5 (CF<sub>2</sub>CF<sub>2</sub>S), -121.6 (all other F) ppm. <sup>13</sup>C NMR: 93.2 (tt, *J*=321,

42 Hz), 114.9 (tq,  $J=305$ , 37 Hz), 104.7–114.8 (m) ppm. FTIR  $\nu_{\max}$ : 1463 (s), 1221 (s), 1154 (s), 909 (s)  $\text{cm}^{-1}$ . GC–MS  $m/z$ : 510 ( $\text{M}^+$ , 0.4), 427 ( $\text{M}^+ - \text{SO}_2\text{F}$ , 0.2), 383 ( $\text{M}^+ - \text{I}$ , 0.2), 177 ( $\text{ICF}_2^+$ , 24.2).

*General procedure for the preparation of perfluoroalkane- $\alpha,\omega$ -bis-sulfonyl chlorides (2a–2c)*

*Preparation of perfluoropropane-1,3-bis-sulfonyl chloride (2a)*

A mixture of 7.5 g (18.6 mmol) of  $\text{I}(\text{CF}_2)_3\text{I}$ , 8.5 g (41.5 mmol) of  $\text{Na}_2\text{S}_2\text{O}_4$ , 4.6 g (55 mmol) of  $\text{NaHCO}_3$ , 15 ml of acetonitrile and 15 ml of water was stirred at room temperature for 1 h.  $^{19}\text{F}$  NMR analysis indicated that the corresponding sulfinic acid ( $-123.2$  ppm ( $\text{CF}_2\text{CF}_2\text{S}$ ),  $-103.2$  ppm ( $\text{CF}_2\text{S}$ )) was formed. After filtration, the filtrate was concentrated to give a solid residue which was dissolved in 50 ml of water and treated with chlorine gas at  $0^\circ\text{C}$  until the iodine color had disappeared. After 50 ml of methylene chloride were added to the reaction mixture, the methylene chloride solution was separated and concentrated to give a residue. Vacuum distillation of the residue afforded 4 g (62% yield) of **2a** (100% purity based on  $^{19}\text{F}$  NMR analysis) (b.p.  $85\text{--}86^\circ\text{C}$  at 160 Torr).  $^{19}\text{F}$  NMR:  $-104.4$  (s, 4F,  $\text{CF}_2\text{S}$ ),  $-117.0$  (s, 2F,  $\text{CF}_2\text{CF}_2\text{S}$ ) ppm.  $^{13}\text{C}$  NMR: 110.9 (tp,  $J=272$ , 31 Hz), 115.1 (tt,  $J=314$ , 36 Hz) ppm. FTIR  $\nu_{\max}$ : 1425 (s), 1213, (s), 1149 (s)  $\text{cm}^{-1}$ .

*Preparation of perfluorobutane-1,4-bis-sulfonyl chloride (2b)*

Similarly, **2b** (6.3 g, 72% yield) was prepared by the general procedure from 10 g (22 mmol) of  $\text{I}(\text{CF}_2)_4\text{I}$ , 9.9 g (48 mmol) of  $\text{Na}_2\text{S}_2\text{O}_4$ , 5.3 g (63.1 mmol) of  $\text{NaHCO}_3$ , 15 ml of acetonitrile and 15 ml of water followed by chlorination. **2b** (100% purity based on  $^{19}\text{F}$  NMR analysis) (m.p.,  $45\text{--}46^\circ\text{C}$ ).  $^{19}\text{F}$  NMR:  $-104.6$  ( $\text{CF}_2\text{S}$ ),  $-119.1$  ( $\text{CF}_2\text{CF}_2\text{S}$ ) ppm;  $^{13}\text{C}$  NMR: 106.9–119.9 (m) ppm. FTIR  $\nu_{\max}$ : 1424 (s), 1220 (vs), 1189 (s), 1153 (s)  $\text{cm}^{-1}$ .

*Preparation of perfluorohexane-1,6-bis-sulfonyl chloride (2c)*

Similarly, **2c** (5 g, 83% yield) was prepared by the general procedure from 10 g (18 mmol) of  $\text{I}(\text{CF}_2)_6\text{I}$ , 8.1 g (39.6 mmol) of  $\text{Na}_2\text{S}_2\text{O}_4$ , 4.3 g (51.2 mmol) of  $\text{NaHCO}_3$ , 15 ml of acetonitrile and 15 ml of water followed by chlorination. **2c** (greater than 98% purity based on  $^{19}\text{F}$  NMR analysis) (m.p.,  $67\text{--}69^\circ\text{C}$ ).  $^{19}\text{F}$  NMR:  $-104.5$  (4F,  $\text{CF}_2\text{S}$ ),  $-119.3$  (4F,  $\text{CF}_2\text{CF}_2\text{S}$ ),  $-121.4$  (4F) ppm.  $^{13}\text{C}$  NMR: 105.9–119.2 (m) ppm. FTIR  $\nu_{\max}$ : 1424 (s), 1225 (vs), 1158 (m)  $\text{cm}^{-1}$ .

*General procedure for the preparation of perfluoroalkane- $\alpha,\omega$ -bis-sulfonyl fluorides (4a–4c)*

*Preparation of perfluoropropane-1,3-bis-sulfonyl fluoride (4a)*

A mixture of 2.45 g (7 mmol) of **2a**, 1.0 g (17 mmol) of KF and 10 ml of acetonitrile was stirred at room temperature for 6 h.  $^{19}\text{F}$  NMR analysis indicated that the chlorides were converted into the corresponding fluorides. After 30 ml of water were added to the reaction mixture, the bottom layer was separated and distilled to afford 1.9 g (86% yield) of **4a** (100% purity

based on  $^{19}\text{F}$  NMR analysis) (b.p., 102–104 °C (105.5 °C [14]).  $^{19}\text{F}$  NMR: +47.1 (1F,  $\text{SO}_2\text{F}$ ) –108.2 (4F,  $\text{CF}_2\text{S}$ ), –119.1 (2F,  $\text{CF}_2\text{CF}_2\text{S}$ ) ppm.  $^{13}\text{C}$  NMR: 109.9 (tt,  $J=273$ , 30 Hz), 114.8 (tq,  $J=306$ , 37 Hz) ppm. FTIR  $\nu_{\text{max}}$ : 1466 (vs), 1242 (s), 1217 (s), 1150 (s)  $\text{cm}^{-1}$ .

*Preparation of perfluorobutane-1,4-bis-sulfonyl fluoride (4b)*

Similarly, **4b** (2.6 g, 81% yield) was prepared by the general procedure from 3.5 g (8.8 mmol) of **2b**, 2.2 g (38 mmol) of KF and 8 ml of acetonitrile. **4b** (100% purity based on  $^{19}\text{F}$  NMR analysis) (b.p., 122–124 °C).  $^{19}\text{F}$  NMR: +46.8 (2F,  $\text{SO}_2\text{F}$ ), –108.3 (4F,  $\text{CF}_2\text{S}$ ), –120.2 (4F,  $\text{CF}_2\text{CF}_2\text{S}$ ) ppm.  $^{13}\text{C}$  NMR: 106.6–119.3 (m) ppm. FTIR  $\nu_{\text{max}}$ : 1465 (vs), 1248 (s), 1237 (s), 1220 (vs), 1154 (s)  $\text{cm}^{-1}$ .

*Preparation of perfluorohexane-1,6-bis-sulfonyl fluoride (4c)*

Similarly, **4c** (2.2 g, 74% yield) was prepared by the general procedure from 3.2 g (6.4 mmol) of **2c**, 1.6 g (28 mmol) of KF and 10 ml of acetonitrile. **4c** (greater than 98% purity based on  $^{19}\text{F}$  NMR analysis) (b.p., 80–81 °C at 10 Torr).  $^{19}\text{F}$  NMR: +46.5 (2F,  $\text{SO}_2\text{F}$ ), –108.2 (4F,  $\text{CF}_2\text{S}$ ), –120.4 (4F,  $\text{CF}_2\text{CF}_2\text{S}$ ), 121.9 (4F) ppm.  $^{13}\text{C}$  NMR: 106.3–119.6 (m) ppm. FTIR  $\nu_{\text{max}}$ : 1464 (s), 1224 (vs), 1158 (s)  $\text{cm}^{-1}$ .

*Preparation of 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-chloro-sulfonylethoxy)-ethanesulfonyl chloride (5)*

A mixture of 10 g (23.5 mmol) of  $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$ , 8.5 g (47 mmol) of  $\text{Na}_2\text{S}_2\text{O}_4$ , 4.6 g (55 mmol) of  $\text{NaHCO}_3$ , 15 ml of acetonitrile and 15 ml of water was stirred at room temperature for 1 h.  $^{19}\text{F}$  NMR analysis indicated that the corresponding sulfinate was formed. After filtration, the filtrate was concentrated to give a solid residue which was dissolved in 50 ml of water and treated with chlorine gas at 0 °C until the iodine color disappeared. 50 ml of methylene chloride was added to the reaction mixture. The methylene chloride solution was separated and concentrated to give a residue which was distilled to form 4.5 g (55% yield) of **5** (100% purity based on  $^{19}\text{F}$  NMR analysis) (b.p., 90 °C at 10 Torr).  $^{19}\text{F}$  NMR: –109.1 (s, 4F,  $\text{CF}_2\text{S}$ ), –79.7 (s, 4F,  $\text{CF}_2\text{CF}_2\text{S}$ ) ppm.  $^{13}\text{C}$  NMR: 112.5 (tt,  $J=310$ , 37 Hz), 114.7 (tt,  $J=295$ , 31 Hz) ppm. FTIR  $\nu_{\text{max}}$ : 1423 (s), 1219 (s), 1149 (s)  $\text{cm}^{-1}$ .

*Preparation of 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-fluoro-sulfonylethoxy)-ethanesulfonyl fluoride (6)*

A mixture of 3.4 g (8.2 mmol) of **5**, 1.5 g (25 mmol) of KF and 10 ml of acetonitrile was stirred at room temperature for 16 h.  $^{19}\text{F}$  NMR analysis indicated that the chlorides were converted into the fluoride. After 40 ml of water were added to the reaction mixture, the bottom layer was isolated and distilled to afford 2.3 g (74% yield) of **6** (100% purity based on  $^{19}\text{F}$  NMR analysis) (b.p., 52 °C at 35 Torr).  $^{19}\text{F}$  NMR: +45.0 (s, 2F,  $\text{SO}_2\text{F}$ ), –82.1 (s, 4F,  $\text{CF}_2\text{CF}_2\text{S}$ ), –112.6 (s, 4F,  $\text{CF}_2\text{S}$ ) ppm.  $^{13}\text{C}$  NMR: 107.9–120.0 (m) ppm. FTIR  $\nu_{\text{max}}$ : 1465 (vs), 1246 (s), 1214 (s), 1152 (s)  $\text{cm}^{-1}$ .

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