



Table 1  
Preparation of compounds 3 and 5

| Reactants |    |    |    | Products        |                         |                             |                 |                         |                             |
|-----------|----|----|----|-----------------|-------------------------|-----------------------------|-----------------|-------------------------|-----------------------------|
| 1         | 2  | or | 4  | 3               | Yields (%) <sup>b</sup> | M.p. (°C) or b.p. (°C/mmHg) | 5               | Yields (%) <sup>b</sup> | M.p. (°C) or b.p. (°C/mmHg) |
| 1a        | 2a | or | 4a | 3a <sup>a</sup> | 74                      | 48–50                       | 5a              | 51                      | 43–45                       |
| 1b        | 2a | or | 4a | 3b <sup>a</sup> | 72                      | 47                          | 5b <sup>a</sup> | 54                      | 98–100/1                    |
| 1c        | 2a | or | 4a | 3c              | 88                      | 46–48                       | 5c <sup>a</sup> | 46                      | 96–98/1                     |
| 1d        | 2a | or | 4a | 3d              | 76                      | 104–105                     | 5d              | 53                      | 90–91                       |
| 1a        | 2b |    |    | 3e <sup>a</sup> | 72                      | 120–122/1                   |                 | –                       | –                           |
| 1b        | 2b |    |    | 3f <sup>a</sup> | 75                      | 122–124/1                   |                 | –                       | –                           |
| 1c        | 2b | or | 4b | 3g              | 77                      | 118–120/1                   | 5g              | 57                      | 125–127/1                   |
| 1d        | 4b |    |    |                 |                         |                             | 5h              | 57                      | 107–110                     |

<sup>a</sup> Known compounds identical with authentic samples prepared from R<sub>f</sub>SO<sub>2</sub>N<sub>3</sub> and the corresponding sulfides or sulfoxides [8].

<sup>b</sup> Isolated yields based on 1.

case both sulfilimines 3 and sulfoximides 5 are obtained from this reaction process.

In both above reactions the intermediate nitrene R<sub>f</sub>SO<sub>2</sub>N: may be involved [12]. All these results are summarized in Table 1.

Oxidation of the *N*-perfluoroalkanesulfonyl sulfilimines 3 should be an attractive route to the sulfoximides 5. For example, there are reports in the literature that ArSO<sub>2</sub>N=S(O)Me<sub>2</sub> may be obtained from the oxidation of ArSO<sub>2</sub>N=SMe<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> or NaOCl [13]. However, following the same reaction procedure, oxidation of 3 gave only a low yield (<10%) of 5.

The chemical properties and reactions of the new compounds 3 and 5 are now under investigation.

In conclusion, in view of the readily available starting materials together with the convenient preparative process and good yields, this synthesis provides an attractive route to *N*-perfluoroalkanesulfonyl sulfilimines and sulfoximides.

### 3. Experimental details

Melting points were measured on a Thiele apparatus. Melting and boiling points are reported uncorrected. <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra were recorded on a Varian 360L instrument using TMS and TFA (δ<sub>CFCl<sub>3</sub></sub> = 77.0 + δ<sub>TFA</sub>, and upfield as positive) as internal or external standards, respectively. CDCl<sub>3</sub> was used as solvent. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Mass spectra were obtained on a Finnigan GC-MS 4021 instrument. Elemental analyses were performed by the Analysis Department of this Institute.

#### 3.1. Preparation of compound 3

A typical procedure was as follows. *n*-C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>NH<sub>2</sub> (1d) (0.70 g, 2.3 mmol), lead tetra-acetate (1.0 g, 2.3 mmol) and pyridine (0.5 ml) were mixed in a flask

fitted with a magnetic stirring bar. Dimethyl sulfide (2a) (2 ml) was dropped into the flask when the colour of the mixture changed from brown into white within several minutes. After stirring for 1 h at room temperature, water (10 ml) was added. The water layer was extracted twice with ether. The organic phases were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was obtained after removing the solvent. Recrystallization from ether/CH<sub>2</sub>Cl<sub>2</sub> gave pure white crystal 3d (0.64 g, 76%). Other compounds 3 were prepared similarly. Compounds 3e–g were purified by distillation under vacuum.

Compounds 3c, H(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>N=SMe<sub>2</sub>: <sup>1</sup>H NMR δ: 5.60 (t, <sup>2</sup>J<sub>HF</sub> = 54.0 Hz); 2.82 (s, CH<sub>3</sub>) ppm. <sup>19</sup>F NMR δ: 5.2 (m, OCF<sub>2</sub>); 12.6 (m, CF<sub>2</sub>O); 40.8 (s, CF<sub>2</sub>S); 62.4 (d, HCF<sub>2</sub>) ppm. MS *m/z* (%): 357 (M<sup>+</sup>, 50.63); 140 (+SO<sub>2</sub>N=SMe<sub>2</sub>, 100.0). IR (KBr) ν (cm<sup>-1</sup>): 2960 (w); 1560 (m); 1335 (s); 1280 (s); 1220–1110 (vs); 985 (s); 930 (m); 860 (m); 760 (m). Analysis: Calc. for C<sub>6</sub>H<sub>7</sub>F<sub>8</sub>NO<sub>3</sub>S<sub>2</sub>: C, 20.17; H, 1.69; N, 3.93; F, 42.55%. Found: C, 20.03; H, 1.81; N, 4.12; F, 42.86%.

Compound 3d, *n*-C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>N=SMe<sub>2</sub>: <sup>1</sup>H NMR δ: 2.43 (s, CH<sub>3</sub>) ppm. <sup>19</sup>F NMR δ: 4.5 (s, 3F); 36.6 (s, CF<sub>2</sub>S); 44.5 (m, 2F); 49.3 (m, 2F) ppm. MS *m/z* (%): 360 (M<sup>+</sup>H, 10.02); 140 (+SO<sub>2</sub>N=SMe<sub>2</sub>, 100.0). IR (KBr) ν (cm<sup>-1</sup>): 1430 (s); 1340 (m); 1320 (m); 1230–1120 (vs); 1040 (s); 960 (s); 865 (m); 740 (s); 580 (s). Analysis: Calc. for C<sub>6</sub>H<sub>6</sub>F<sub>8</sub>NO<sub>2</sub>S<sub>2</sub>: C, 20.06; H, 1.67; N, 3.90; F, 47.63%. Found: C, 20.17; H, 1.54; N, 3.87; F, 47.55%.

Compound 3g, H(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>N=S(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>: <sup>1</sup>H NMR δ: 5.61 (t, 1H); 2.70 (m, 4H); 1.98 (m, 4H) ppm. <sup>19</sup>F NMR δ: 5.3 (m, OCF<sub>2</sub>); 12.7 (m, CF<sub>2</sub>O); 41.0 (s, CF<sub>2</sub>S); 62.4 (d, HCF<sub>2</sub>) ppm. MS *m/z* (%): 384 (M<sup>+</sup>H, 1.53); 383 (M<sup>+</sup>, 1.49); 209 (HCF<sub>2</sub>CF<sub>2</sub>SONSCH<sub>2</sub><sup>+</sup>, 41.17); 106 (SONSC<sup>+</sup>, 100.0); 88 (C<sub>4</sub>H<sub>8</sub>S<sup>+</sup>, 31.90). IR (film) ν (cm<sup>-1</sup>): 2940 (m); 1580 (m); 1560 (m); 1450 (m); 1380 (vs); 1330 (s); 1280 (s); 980 (s); 747 (m); 605 (m). Analysis: Calc. for C<sub>8</sub>H<sub>9</sub>F<sub>8</sub>NO<sub>3</sub>S<sub>2</sub>: C, 25.07;

H, 2.35; N, 3.65; F, 39.94%. Found: C, 25.18; H, 2.51; N, 3.12; F, 39.28%.

### 3.2. Preparation of compound 5

A typical procedure was as follows.  $n\text{-C}_4\text{F}_9\text{SO}_2\text{NH}_2$  (**1d**) (0.70 g, 2.3 mmol), lead tetra-acetate (1.0 g, 2.3 mmol) and pyridine (0.5 ml) were mixed in a flask. DMSO (2 ml) was added rapidly. The mixture was stirred for 4 h at 60 °C. After the brown colour had turned pink, water (10 ml) was added to the flask and the mixture extracted twice with ether. The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed. Recrystallization from acetone/ $\text{CH}_2\text{Cl}_2$  gave pure **5d** (0.46 g, 53%). Other compounds **5** were prepared similarly. Compounds **5b,c,g** were purified by distillation under vacuum.

Compound **5a**,  $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{N}=\text{S}(\text{O})\text{Me}_2$ :  $^1\text{H}$  NMR  $\delta$ : 3.43 (s,  $\text{CH}_3$ ) ppm.  $^{19}\text{F}$  NMR  $\delta$ : -10.0 (s,  $\text{ICF}_2$ ); 2.8 (m,  $\text{CF}_2\text{O}$ ); 7.3 (m,  $\text{CF}_2\text{O}$ ); 39.0 (s,  $\text{CF}_2\text{S}$ ) ppm. MS  $m/z$  (%): 500 ( $\text{M}^+\text{H}$ , 4.27); 372 ( $\text{M}^+ - \text{I}$ , 8.56); 156 ( $\text{M}^+ - \text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2$ , 100.0). IR (film)  $\nu$  ( $\text{cm}^{-1}$ ): 2900 (m); 1660 (s); 1540 (s); 1390 (s); 1350 (s); 1300 (s); 1230–1120 (vs); 910 (s); 760 (s); 720 (s). Analysis: Calc. for  $\text{C}_6\text{H}_6\text{F}_8\text{INO}_4\text{S}_2$ : C, 14.43; H, 1.20; N, 2.81; F, 30.46%. Found: C, 14.13; H, 1.31; N, 2.76; F, 30.40%.

Compound **5d**,  $n\text{-C}_4\text{F}_9\text{SO}_2\text{N}=\text{S}(\text{O})\text{Me}_2$ :  $^1\text{H}$  NMR  $\delta$ : 3.47 (s,  $\text{CH}_3$ ) ppm.  $^{19}\text{F}$  NMR  $\delta$ : 2.8 (s, 3F); 35.0 (s,  $\text{CF}_2\text{S}$ ); 43.3 (m, 2F); 48.0 (m, 2F) ppm. MS  $m/z$  (%): 376 ( $\text{M}^+\text{H}$ , 7.01); 156 ( $\text{M}^+ - \text{C}_4\text{F}_9$ , 100.0). IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 1240–1140 (vs); 1090 (s); 1030 (s); 950 (s); 820 (s); 730 (s); 645 (s). Analysis: Calc. for  $\text{C}_6\text{H}_6\text{F}_9\text{NO}_3\text{S}_2$ : C, 19.20; H, 1.60; N, 37.33; F, 45.60%. Found: C, 19.43; H, 1.55; N, 37.04; F, 45.63%.

Compound **5g**,  $\text{H}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{N}=\overline{\text{S}(\text{O})(\text{CH}_2)_3}\text{CH}_2$ :  $^1\text{H}$  NMR  $\delta$ : 5.63 (t,  $^1\text{H}$ ); 3.46 (m, 4H); 1.13 (m, 4H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : 3.7 (m,  $\text{CF}_2\text{O}$ ); 11.0 (m,  $\text{OCF}_2$ ); 39.5 (s,  $\text{CF}_2\text{S}$ ); 60.1 (d,  $\text{HCF}_2$ ) ppm. MS  $m/z$  (%): 400 ( $\text{M}^+\text{H}$ , 68.63); 384 ( $\text{M}^+\text{H} - \text{O}$ , 41.43); 182 ( $\text{M}^+ - \text{H}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2$ , 54.79); 64 ( $\text{SO}_2$ , 100.0). IR

(film)  $\nu$  ( $\text{cm}^{-1}$ ): 2980 (s); 1610 (s); 1540 (s); 1390 (s); 1320 (s); 1280 (s); 1220–1100 (vs); 920 (m); 850 (s); 800 (s); 742 (s); 610 (s). Analysis: Calc. for  $\text{C}_8\text{H}_9\text{F}_8\text{NO}_4\text{S}_2$ : C, 24.06; H, 2.26; N, 3.51; F, 38.10%. Found: C, 24.12; H, 2.51; N, 3.54; F, 38.40%.

Compound **5h**,  $n\text{-C}_4\text{F}_9\text{SO}_2\text{N}=\overline{\text{S}(\text{O})(\text{CH}_2)_3}\text{CH}_2$ :  $^1\text{H}$  NMR  $\delta$ : 3.60 (m, 4H); 2.47 (m, 4H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : 2.9 (s, 3F); 36.0 (s,  $\text{CF}_2\text{S}$ ); 44.1 (m, 2F); 48.7 (m, 2F) ppm. MS  $m/z$  (%): 402 ( $\text{M}^+\text{H}$ , 12.34); 182 ( $\text{M}^+ - \text{C}_4\text{F}_9$ , 100.0). IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 1640 (s); 1390 (m); 1340 (s); 1220–1130 (vs); 1050 (s); 950 (s); 830 (s); 655 (s). Analysis: Calc. for  $\text{C}_8\text{H}_8\text{F}_9\text{NO}_3\text{S}_2$ : C, 23.94; H, 2.00; N, 3.49; F, 42.64%. Found: C, 24.10; H, 2.10; N, 3.45; F, 42.45%.

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