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A convenient synthetic method for *N*-perfluoroalkanesulfonyl sulfilimines and sulfoximides

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Abstract

Reaction of perfluoroalkanesulfonyl amides with dialkyl sulfides or sulfoxides in the presence of stoichiometric amounts of lead tetra-acetate gave *N*-perfluoroalkanesulfonyl sulfilimines or *N*-perfluoroalkanesulfonyl sulfoximides, respectively, in moderate to good yield.

Keywords: Synthesis; Perfluoroalkanesulfonyl amides; *N*-perfluoroalkanesulfonyl sulfilimine; Sulfoximide

1. Introduction

The synthesis and chemistry of sulfilimines, $R'N{=}SR_2$, and sulfoximides, $R'N{=}S(O)R_2$, can be traced back to 1917 [1]. Starting from this period, it evolved quite rapidly and at the present time is a well-developed branch of organoelement chemistry. The interest shown in these compounds is mainly due to their synthetic importance. Their preparation and chemical reactions have been covered in several review articles [2–4]. However, syntheses of the fluorine-containing analogues have been rarely reported to date. The only example, *N*-trifluoromethanesulfonyl sulfilimine, $CF_3SO_2N{=}SMe_2$, was prepared from *N*-sulfinyltrifluoromethanesulfonyl amide, CF_3SO_2NSO, or *N*-trifluoromethanesulfonyl isocyanate, CF_3SO_2NCO, and dimethyl sulfoxide [5–7].

Recently, in our laboratory, a series of *N*-perfluoroalkanesulfonyl sulfilimines and sulfoximides have been synthesized by trapping the *N*-perfluoroalkanesulfonyl nitrene, $R_fSO_2N{:}$, which is formed from the decomposition of $R_fSO_2N_3$ or $R_fSO_2NCl_2$, with dialkyl sulfides or DMSO [8,9].

In this paper we describe a new convenient method for preparing such compounds.

2. Results and discussion

Perfluoroalkanesulfonyl amides, $R_fSO_2NH_2$, which are readily obtained from the reaction of perfluoroalkanesulfonyl fluorides with ammonia, were treated with equal molar amounts of lead tetra-acetate followed by excess dialkyl sulfides in pyridine at room temperature. After work-up, the title products, *N*-perfluoroalkanesulfonyl sulfilimines, were obtained in good yield.

$$\underset{(1)}{R_fSO_2NH_2} + \underset{(2)}{R_1R_2S} \xrightarrow[\text{r.t., 1 h, 72\%–88\%}]{\text{Pb(OAc)}_4\text{/Py}} \underset{(3)}{R_fSO_2N{=}SR_1R_2}$$

[$R_f = I(CF_2)_2O(CF_2)_2$ (**1a**), $Cl(CF_2)_2O(CF_2)_2$ (**1b**), $H(CF_2)_2O(CF_2)_2$ (**1c**), n-C_4F_9 (**1d**); $R_1 = R_2 = CH_3$ (**2a**), $R_1R_2 = -(CH_2)_4-$ (**2b**)]

In contrast to a similar compound *N*-perfluoroalkanesulfonyl imine, $R_fSO_2N{=}CR_1R_2$, (e.g. $ICF_2CF_2OCF_2CF_2SO_2N{=}CHC_6H_5$ [10]) which was moisture-sensitive, compounds **3** are stable solids and can be exposed to air for several weeks without decomposition. Even after reflux of **3a** with pyridine for 8 h, it was recovered nearly quantitatively.

Similar treatment of **1** with $Pb(OAc)_4$ and sulfoxides in pyridine gave *N*-perfluoroalkanesulfonyl sulfoximides.

$$\mathbf{1} + \underset{(4)}{R_1R_2S{=}O} \xrightarrow[\text{60 °C, 4 h, 46\%–57\%}]{\text{Pb(OAc)}_4\text{/Py}} \underset{(5)}{R_fSO_2N{=}S(O)R_1R_2}$$

[$R_1 = R_2 = CH_3$ (**4a**), $R_1R_2 = -(CH_2)_4-$ (**4b**)]

Okahara has reported that *N*,*N*-disubstituted sulfamides are oxidized with $Pb(OAc)_4$ in dimethyl sulfide to give the corresponding sulfilimines, while the analogous reaction in DMSO was unsuccessful [11]. In our

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Table 1
Preparation of compounds 3 and 5

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

[a] Known compounds identical with authentic samples prepared from $R_fSO_2N_3$ and the corresponding sulfides or sulfoxides [8].
[b] 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_fSO_2N: 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 $ArSO_2N{=}S(O)Me_2$ may be obtained from the oxidation of $ArSO_2N{=}SMe_2$ by H_2O_2 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. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Varian 360L instrument using TMS and TFA ($\delta_{CFCl_3} = 77.0 + \delta_{TFA}$, and upfield as positive) as internal or external standards, respectively. $CDCl_3$ 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-$C_4F_9SO_2NH_2$ (**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 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_2SO_4. The crude product was obtained after removing the solvent. Recrystallization from ether/CH_2Cl_2 gave pure white crystal **3d** (0.64 g, 76%). Other compounds **3** were prepared similarly. Compounds **3e–g** were purified by distillation under vaccum.

Compounds **3c**, $H(CF_2)_2O(CF_2)_2SO_2N{=}SMe_2$: ^{1}H NMR δ: 5.60 (t, $^2J_{HF}$=54.0 Hz); 2.82 (s, CH_3) ppm. ^{19}F NMR δ: 5.2 (m, OCF_2); 12.6 (m, CF_2O); 40.8 (s, CF_2S); 62.4 (d, HCF_2) ppm. MS *m/z* (%): 357 (M^+, 50.63); 140 ($^+SO_2N{=}SMe_2$, 100.0). IR (KBr) ν (cm^{-1}): 2960 (w); 1560 (m); 1335 (s); 1280 (s); 1220–1110 (vs); 985 (s); 930 (m); 860 (m); 760 (m). Analysis: Calc. for $C_6H_7F_8NO_3S_2$: 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-$C_4F_9SO_2N{=}SMe_2$: ^{1}H NMR δ: 2.43 (s, CH_3) ppm. ^{19}F NMR δ: 4.5 (s, 3F); 36.6 (s, CF_2S); 44.5 (m, 2F); 49.3 (m, 2F) ppm. MS *m/z* (%): 360 (M^+H, 10.02); 140 ($^+SO_2N{=}SMe_2$, 100.0). IR (KBr) ν (cm^{-1}): 1430 (s); 1340 (m); 1320 (m); 1230–1120 (vs); 1040 (s); 960 (s); 865 (m); 740 (s); 580 (s). Analysis. Calc. for $C_6H_6F_8NO_2S_2$: 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**, $H(CF_2)_2O(CF_2)_2SO_2N{=}\overline{S(CH_2)_3CH_2}$: ^{1}H NMR δ: 5.61 (t, 1H); 2.70 (m, 4H); 1.98 (m, 4H) ppm. ^{19}F NMR δ: 5.3 (m, OCF_2); 12.7 (m, CF_2O); 41.0 (s, CF_2S); 62.4 (d, HCF_2) ppm. MS *m/z* (%): 384 (M^+H, 1.53); 383 (M^+, 1.49); 209 ($HCF_2CF_2SONSCH_2^+$, 41.17); 106 ($SONSC^+$, 100.0); 88 ($C_4H_8S^+$, 31.90). IR (film) ν (cm^{-1}): 2940 (m); 1580 (m); 1560 (m); 1450 (m); 1380 (vs); 1330 (s); 1280 (s); 980 (s); 747 (m); 605 (m). Analysis: Calc. for $C_8H_9F_8NO_3S_2$: 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-$C_4F_9SO_2NH_2$ (**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 Na_2SO_4. The solvent was removed. Recrystallization from acetone/CH_2Cl_2 gave pure **5d** (0.46 g, 53%). Other compounds **5** were prepared similarly. Compounds **5b,c,g** were purified by distillation under vaccum.

Compound **5a**, $I(CF_2)_2O(CF_2)_2SO_2N{=}S(O)Me_2$: ^1H NMR δ: 3.43 (s, CH_3) ppm. ^{19}F NMR δ: −10.0 (s, ICF_2); 2.8 (m, CF_2O); 7.3 (m, CF_2O); 39.0 (s, CF_2S) ppm. MS *m/z* (%): 500 (M^+H, 4.27); 372 (M^+-I, 8.56); 156 ($M^+-I(CF_2)_2O(CF_2)_2$, 100.0). IR (film) ν (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 $C_6H_6F_8INO_4S_2$: 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-$C_4F_9SO_2N{=}S(O)Me_2$: ^1H NMR δ: 3.47 (s, CH_3) ppm. ^{19}F NMR δ: 2.8 (s, 3F); 35.0 (s, CF_2S); 43.3 (m, 2F); 48.0 (m, 2F) ppm. MS *m/z* (%): 376 (M^+H, 7.01); 156 ($M^+-C_4F_9$, 100.0). IR (KBr) ν (cm^{-1}): 1240–1140 (vs); 1090 (s); 1030 (s); 950 (s); 820 (s); 730 (s); 645 (s). Analysis: Calc. for $C_6H_6F_9NO_3S_2$: 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**, $H(CF_2)_2O(CF_2)_2SO_2N{=}\overline{S(O)(CH_2)_3CH_2}$: ^1H NMR δ: 5.63 (t, ^1H); 3.46 (m, 4H); 1.13 (m, 4H) ppm. ^{19}F NMR δ: 3.7 (m, CF_2O); 11.0 (m, OCF_2); 39.5 (s, CF_2S); 60.1 (d, HCF_2) ppm. MS *m/z* (%): 400 (M^+H, 68.63); 384 (M^+H-O, 41.43); 182 ($M^+-H(CF_2)_2O(CF_2)_2$, 54.79); 64 (SO_2, 100.0). IR (film) ν (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 $C_8H_9F_8NO_4S_2$: 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-$C_4F_9SO_2N{=}\overline{S(O)(CH_2)_3CH_2}$: ^1H NMR δ: 3.60 (m, 4H); 2.47 (m, 4H) ppm. ^{19}F NMR δ: 2.9 (s, 3F); 36.0 (s, CF_2S); 44.1 (m, 2F); 48.7 (m, 2F) ppm. MS *m/z* (%): 402 (M^+H, 12.34); 182 ($M^+-C_4F_9$, 100.0). IR (KBr) ν (cm^{-1}): 1640 (s); 1390 (m); 1340 (s); 1220–1130 (vs); 1050 (s); 950 (s); 830 (s); 655 (s). Analysis: Calc. for $C_8H_8F_9NO_3S_2$: 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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