





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

Shi-Zheng Zhu*, Jie Zhang, Bin Xu

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China Received 24 January 1994; accepted 8 May 1994

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 welldeveloped 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, CF₃SO₂N=SMe₂, was prepared from N-sulfinyltrifluoromethanesulfonyl amide, CF₃SO₂NSO, or N-trifluoromethanesulfonyl isocyanate, CF₃SO₂NCO, 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_fSO₂N:, which is formed from the decomposition of R_fSO₂N₃ or R_fSO₂NCl₂, 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_rSO₂NH₂, which are readily obtained from the reaction of perfluoroal-

kanesulfonyl 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.

$$\begin{array}{ccc} R_{r}SO_{2}NH_{2} + R_{1}R_{2}S \xrightarrow[r.t., 1 \text{ h, } 72\%-88\%]{\text{Pb(OAc)_4/Py}} & R_{r}SO_{2}N = SR_{1}R_{2} \\ \text{(1)} & \text{(2)} & \text{(3)} \end{array}$$

$$\begin{array}{ll} [R_f\!=\!I(CF_2)_2O(CF_2)_2 & (\textbf{1a}), & Cl(CF_2)_2O(CF_2)_2 & (\textbf{1b}), \\ H(CF_2)_2O(CF_2)_2 & (\textbf{1c}), & n\text{-}C_4F_9 & (\textbf{1d}); & R_1\!=\!R_2\!=\!CH_3 & (\textbf{2a}), \\ R_1R_2\!=\!-(CH_2)_4\!-& (\textbf{2b})] \end{array}$$

In contrast to a similar compound N-perfluoroalkanesulfonyl imine, R_fSO₂N=CR₁R₂, (e.g. ICF₂CF₂OCF₂CF₂SO₂N=CHC₆H₅ [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.

$$1 + R_1 R_2 S = O \xrightarrow{\text{Pb(OAc)}_4/\text{Py}} R_t SO_2 N = S(O)R_1 R_2$$
(4) (5)

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

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

^{*} Corresponding author.

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
1a 1b	2a 2a	or	4a	3b a	72	47	5b ^a	54	98-100/1
10 1c	2a 2a	or	4a	3c	88	46–48	5c ^a	46	96-98/1
1d	2a 2a	or	4a	3d	76	104–105	5d	53	90–91
la	2b	01		3e a	72	120-122/1		-	_
1b	2b			3f a	75	122-124/1		_	_
1c	2b	or	4b	3g	77	118-120/1	5 g	57	125-127/1
1d	4b	01		-8			5h	57	107-110

^a Known compounds identical with authentic samples prepared from R_fSO₂N₃ and the corresponding sulfides or sulfoxides [8].

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

In both above reactions the intermediate nitrene R_rSO₂N: 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.

¹H NMR and ¹⁹F NMR spectra were recorded on a Varian 360L instrument using TMS and TFA ($\delta_{\text{CFCl}_3} = 77.0 + \delta_{\text{TFA}}$, and upfield as positive) as internal or external standards, respectively. CDCl₃ 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-C₄F₉SO₂NH₂ (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 Na₂SO₄. The crude product was obtained after removing the solvent. Recrystallization from ether/CH₂Cl₂ 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, $H(CF_2)_2O(CF_2)_2SO_2N=SMe_2$: ¹H NMR δ : 5.60 (t, ² J_{HF} =54.0 Hz); 2.82 (s, CH₃) ppm. ¹⁹F NMR δ : 5.2 (m, OCF₂); 12.6 (m, CF₂O); 40.8 (s, CF₂S); 62.4 (d, HCF₂) ppm. MS m/z (%): 357 (M⁺, 50.63); 140 (⁺SO₂N=SMe₂, 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 C₆H₇F₈NO₃S₂: 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-C₄F₉SO₂N=SMe₂: ¹H NMR δ : 2.43 (s, CH₃) ppm. ¹⁹F NMR δ : 4.5 (s, 3F); 36.6 (s, CF₂S); 44.5 (m, 2F); 49.3 (m, 2F) ppm. MS m/z (%): 360 (M⁺H, 10.02); 140 (⁺SO₂N=SMe₂, 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 C₆H₆F₈NO₂S₂: 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(CF₂)₂O(CF₂)₂SO₂N= $\overline{S}(\overline{CH_2})_3$ CH₂:
¹H NMR δ : 5.61 (t, 1H); 2.70 (m, 4H); 1.98 (m, 4H) ppm.
¹⁹F NMR δ : 5.3 (m, OCF₂); 12.7 (m, CF₂O); 41.0 (s, CF₂S); 62.4 (d, HCF₂) ppm. MS m/z (%): 384 (M⁺H, 1.53); 383 (M⁺, 1.49); 209 (HCF₂CF₂SONSCH₂⁺, 41.17); 106 (SONSC⁺, 100.0); 88 (C₄H₈S⁺, 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 C₈H₉F₈NO₃S₂: C, 25.07;

^b Isolated yields based on 1.

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-C₄F₉SO₂NH₂ (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 Na₂SO₄. The solvent was removed. Recrystallization from acetone/CH₂Cl₂ 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(CF₂)₂O(CF₂)₂SO₂N=S(O)Me₂: 1 H NMR δ : 3.43 (s, CH₃) ppm. 19 F NMR δ : -10.0 (s, ICF₂); 2.8 (m, CF₂O); 7.3 (m, CF₂O); 39.0 (s, CF₂S) ppm. MS m/z (%): 500 (M⁺H, 4.27); 372 (M⁺ – I, 8.56); 156 (M⁺ – I(CF₂)₂O(CF₂)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 C₆H₆F₈INO₄S₂: 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-C₄F₉SO₂N=S(O)Me₂: ¹H NMR δ : 3.47 (s, CH₃) ppm. ¹⁹F NMR δ : 2.8 (s, 3F); 35.0 (s, CF₂S); 43.3 (m, 2F); 48.0 (m, 2F) ppm. MS m/z (%): 376 (M⁺H, 7.01); 156 (M⁺ - C₄F₉, 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 C₆H₆F₉NO₃S₂: 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**, $H(CF_2)_2O(CF_2)_2SO_2N = \overline{S(O)(CH_2)_3}$ - $\overline{C}H_2$: ¹H NMR δ : 5.63 (t, ¹H); 3.46 (m, 4H); 1.13 (m, 4H) ppm. ¹⁹F 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 (SO₂, 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-C₄F₉SO₂N= $\overline{S(O)(CH_2)_3}CH_2$: ¹H NMR δ : 3.60 (m, 4H); 2.47 (m, 4H) ppm. ¹⁹F NMR δ : 2.9 (s, 3F); 36.0 (s, CF₂S); 44.1 (m, 2F); 48.7 (m, 2F) ppm. MS m/z (%): 402 (M⁺H, 12.34); 182 (M⁺ - C₄F₉, 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 C₈H₈F₉NO₃S₂: 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%.

Acknowledgements

The authors thank the National Natural Science Foundation of China (NNSFC. No. 29472071) for financial support.

References

- H.S. Raper, Report to British Chemical Warfare Department, 1917; [Chem. Abs., 16 (1922) 28 559].
- [2] T.L. Gilchrist and J.C. Moody, Chem. Rev., 77 (1977) 409.
- [3] P.D. Kennewell and J.B. Taylor, Chem. Soc. Rev., 4 (1975) 189.
- [4] I.V. Koval, Russ. Chem. Rev., 59 (1990) 819.
- [5] E. Behrend and A. Hass, J. Fluorine Chem., 4 (1974) 83.
- [6] H.W. Roesky and G. Holtschreider, Z. Anorg. Allg. Chem., B378 (1970) 168.
- [7] S.Z. Zhu and Q.Y. Chen, J. Chem. Soc., Chem. Commun., (1991) 732.
- [8] S.Z. Zhu, Tetrahedron Lett., 33 (1992) 6503.
- [9] S.Z. Zhu, C.M. Zhou, A.W. Li and Bin Xu, J. Fluorine Chem., 67 (1994) 7.
- [10] S.Z. Zhu, A.W. Li, Y.H. Zhu, J.N. Dai, X.M. Chen and X.W. Yuan, J. Fluorine Chem., 60 (1993) 283.
- [11] M. Okahara, K. Matsunaga and S. Komori, Synthesis, (1972) 203.
- [12] D.J. Anderson, T.L. Gilchrist, D.C. Horwell and C.W. Rees, J. Chem. Soc. C, (1970) 576.
- [13] C.R. Johnson and R.A. Kirchhoff, J. Org. Chem., 44 (1979) 2280.