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Reactions of fluorine-containing N-sulfinylamides with carboxylic acids and acid anhydrides

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Abstract

Heating *N*-sulfinylperfluoroalkane sulfonylamides, R_fSO_2NSO , or *N*-sulfinylpentafluoroaniline, C_6F_5NSO , with carboxylic acids in the presence of catalytic amounts of SOCl₂ gave *N*-perfluoroalkane sulfonylamides, R_fSO_2NHCOR , or *N*-pentafluorophenylamides, C_6F_5NHCOR , respectively. Acid anhydrides reacted similarly with R_fSO_2NSO or C_6F_5NSO to form *N*-perfluoroalkane sulfonylimides or *N*-pentafluorophenylimides.

Keywords: N-sulfinylamides; Carboxylic acids; Acid anhydrides

1. Introduction

Fluorine-containing heterocumylenes such as $R_fSO_2N=$ S=O, $C_6F_5N=$ S=O, $R_fSO_2N=$ C=O, are very reactive compounds. Since the first *N*-sulfinylperfluoroalkane sulfonylamide, CF₃SO₂NSO, was synthesized by Roesky et al. [1], their chemistry is attracting much attention. Many chemical reactions of these compounds have been reported [2–4]. This paper reports the reactions of fluorine-containing *N*-sulfinylamides, Y-NSO (1) (Y = R_fSO_2 , C_6F_5 , 4-FC₆H₄), with carboxylic acids and acid anhydrides.

2. Results and discussion

Heating N-sulfinylperfluoroalkane sulfonylamides or Nsulfinylpentafluoroaniline with carboxylic acids in the presence of a catalytic amount of SOCl₂ gave N-perfluoroalkane sulfonylamides, R_rSO_2NHCOR , or N-pentafluorophenylamides, C_6F_5NHCOR , respectively, with the elimination of sulfur dioxide. These reactions can be carried out without solvents or in an inert dry solvent such as xylene according to:

$$\begin{array}{c} Y-NSO + RCOOH \xrightarrow{SOCl_2 (cat.)} \\ (1) \quad (2) \end{array} \xrightarrow{A, 70\%-81\%} RCONHY + SO_2 \\ (3) \end{array}$$

 $\begin{array}{ll} Y = CF_3SO_2 \ (1a) & R = C_6H_5 \ (2a) \\ I(CF_2)_2O(CF_2)_2SO_2 \ (1b) & 4 - IC_6H_4 \ (2b) \\ Cl_2(CF_2)_2O(CF_2)_2SO_2 \ (1c) & CH_3 \ (2c) \\ C_6F_5 \ (1d) \\ 4 - FC_6H_4 \ (1e) \end{array}$

The reaction of 1 with 2a or 2b takes place at 150 °C; however with 2c, it occurred smoothly at 60 °C. The product, $CF_3SO_2NHCOCH_3$ (3d), is a known compound which was first prepared by treatment of CF_3SO_2NCO with CH_3COOH [5] or by reaction of CF_3SO_2NHM (M = Na, K) with CH_3COCI [6]. However it was found that the yield was less than 45% because the more acidic product which is formed reacts with the starting material, CF_3SO_2NHM .

Acid anhydrides such as phthalic and maleic anhydrides reacted similarly with 1 to give the corresponding imides 5:

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Table 1	
Compounds 3, 5 and 7:	preparation conditions

Reactants 1 + 2, 4 or 6	Conditions			Products	Yields ^a	M.p.
	Solvent	Temp. (°C)	Time (h)	3, 5 01 7	(70)	(C)
1b+2a	xylene	150	10	3a	70	92–95
1e + 2a	xylene	160	10	3b ^b [9]	81	186-188
1b+2b	-	160	10	3c	70	97-99
1a + 2c	-	60	8	3d ^b [5,6]	76	subl.
1b+2c	_	60	8	3e	71	8486
1b + 4a	xylene	150	10	5a	81	94-96
1c + 4a	xylene	150	10	5b	70	98-101
1d + 4a	xylene	150	10	5c	68	128-130
1b + 4b	-	160	8	5d	82	90-93
1e + 4b	-	160	8	5e ^b [10]	72	150-152
1b+6	-	160	8	7b	70	150-152

^a Isolated yield based on 1.

^b Known compound; cf. Refs. [5], [6], [9] and [10].

When acetic acid anhydride was refluxed with **1b** or **1d**, no SO_2 was released and no expected product $(CH_3CO)_2NY$ obtained.

Recently, Amarasekara and Pathmasiri have reported a

2+2 reaction between N-sulfinglaniline and
$$(1)$$
 [7]. In

our case, however, on stirring **1b** or **1d** with **4b** for 1 week at 20–40 °C, no reaction took place.

When tosyl-OH was reacted with **1b**, *N*-perfluoroalkane sulfonyltoluenesulfonamides, tosyl-NHSO₂R_f (**7b**), were obtained in 70% yield. However, attempted preparation of bis(perfluoroalkanesulfonyl)imine, $(R_fSO_2)_2NH$ [8], by treating **1a** with CF₃SO₃H or **1b** with I(CF₂)₂O(CF₂)₂SO₃H failed. The only product detected was $R_fSO_2NH_2$.

$$1b + 4-CH_{3}C_{6}H_{4}SO_{3}H \xrightarrow[160 \ °C, 8 \ h]{}$$

$$(6) \qquad \qquad I(CF_{2})_{2}O(CF_{2})_{2}SO_{2}NHSO_{2}C_{6}H_{4}CH_{3}-4$$

$$(7b)$$

The reaction results are summarized in Table 1.

3. Experimental details

Melting points were measured on a Thiele apparatus and are reported uncorrected. ¹H NMR and ¹⁹F NMR spectra were recorded on a Varian 360L instrument using TMS and TFA ($\delta_{CFCI_3} = 77.0 + \delta_{TFA}$, and upfield as positive) as internal or external standards, respectively. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Mass spectra were obtained on a Finnigan GC–MS 4021 instrument. Microanalysis was performed by the analysis department of this institute. Solvent and reagents were dried before use.

3.1. Reaction of compound 1 with carboxylic acids

A typical procedure was as follows. A mixture of **1b** (1.1 g, 2.3 mmol), **2a** (0.3 g, 2.5 mmol), $SOCl_2$ (0.1 ml) and dry xylene (5 ml) in a 25 ml flask equipped with a reflux condenser, magnetic stirring bar and drying tube was heated for 8 h at 150 °C. After removing the solvent, the residue was sublimed under vacuum giving $I(CF_2)_2O(CF_2)_2SO_2$ -NHCOC₆H₅ (**3a**) (0.85 g). Yields and melting points are shown in Table 1.

Compound **3a**: IR (KBr, ν , cm⁻¹): 3250 (w, N–H); 1690 (m, C=O); 1350 (s, SO₂); 1140–1220 (vs, C–F). ¹H NMR [(CD₃)₂CO)] δ : 6.93 (s, NH); 7.50 (m, 2H); 7.23 (m, 2H); 7.13 (s, 1H) ppm. ¹⁹F NMR δ : –12.3 (s, ICF₂); 2.3 (m, OCF₂); 9.0 (m, CF₂O); 38.3 (s, CF₂S) ppm. MS (*m*/*z*, %): 527 (M⁺, 14.16); 400 (M⁺ – I, 14.20); 105 (C₆H₅CO⁺, 100.00). Analysis: Calc. for C₁₁H₆F₈INO₄S: C, 25.05; H, 1.14; F, 28.84; N, 2.66%. Found: C, 24.79; H, 1.38; F, 29.10; N, 2.46%.

Similar treatment of **1e** (1.6 g, 10 mmol) with **2a** (1.2 g, 10 mmol) gave 4-FC₆H₄NHCOC₆H₅ (**3b**) (1.7 g) [9].

Compound **3b**: IR (KBr, ν , cm⁻¹): 3225 (s, N–H); 1650 (s, C=O); 1610–1500 (m, C₆H₅). ¹H NMR (DMSO-*d*₆) δ : 10.13 (s, NH); 7.76–7.43 (m, 4H); 7.30–6.83 (m, 5H) ppm. ¹⁹F NMR δ : 40.0 (s, 1F) ppm. MS (*m*/*z*, %): 216 (M⁺H, 3.30); 215 (M⁺, 17.40); 105 (C₆H₅CO⁺, 100.00).

Heating **1b** (1.1 g, 2.3 mmol), **2b** (0.57 g, 2.3 mmol) and SOCl₂ (0.1 ml) without solvent gave $I(CF_2)_2O(CF_2)_2$ -SO₂NHCOC₆H₄I-4 (**3c**) (1.1 g).

Compound 3c: IR (KBr, ν , cm⁻¹): 3250 (w, N–H); 1690 (m, C=O); 1350 (s, SO₂); 1140–1220 (vs, C–F). ¹H NMR [(CD₃)₂CO] δ : 7.03 (s, NH); 7.43 (AB, 2H); 7.66 (AB, 2H) ppm. ¹⁹F NMR δ : – 12.7 (s, ICF₂); 2.3 (m, OCF₂); 9.2 (m, CF₂O); 38.0 (s, CF₂S) ppm. MS (*m*/*z*, %): 654 (M⁺H, 12.30); 653 (M⁺, 6.21); 526 (M⁺ – I, 10.43); 231 (IC₆H₄CO⁺, 100.00). Analysis: Calc. for C₁₁H₅F₈I₂NO₄S:

C, 20.21; H, 0.77; F, 23.28; N, 2.14%. Found: C, 19.83; H, 0.75; F, 23.44; N, 2.50%.

Treatment of **1a** (1.5 g, 10 mmol) with **2c** (0.6 g, 10 mmol) gave $CF_3SO_2NHCOCH_3$ (**3d**) (1.5 g) [5].

Compound **3d**: IR (KBr, ν , cm⁻¹): 3090 (w, NH); 1720 (s, C=O); 1387 (s, SO₂); 1190 (s); 1120 (s). ¹H NMR [(CD₃)₂CO] δ : 7.13 (s, NH); 2,03 (s, CH₃) ppm. ¹⁹F NMR δ : -1.3 (s, CF₃) ppm. MS (m/z, %): 191 (M⁺, 1.07); 80 (SO₂NH₂⁺, 100.00).

 $I(CF_2)_2O(CF_2)_2SO_2NHCOCH_3$ (3e) was prepared similarly.

Compound **3e**: IR (KBr, ν , Cm⁻¹): 3100 (w, NH); 1725 (s, C=O); 1390 (s, SO₂); 1100–1240 (vs, C–F); ¹H NMR [(CD₃)₂CO] δ : 7.60 (s, NH); 1.76 (s, CH₃) ppm. ¹⁹F NMR δ : – 12.5 (s, ICF₂); 2.4 (m, OCF₂); 9.0 (m, CF₂O); 38.0 (s, CF₂S) ppm. MS (*m*/*z*, %): 466 (M⁺H, 7.24); 43 (CH₃CO⁺, 100.00). Analysis: Calc. for C₆H₄F₈INO₄S: C, 15.48; H, 0.86; F, 32.69; N, 3.01%. Found: C, 15.52; H, 0.95; F, 32.74; N, 3.00%.

3.2. Reaction of compound 1 with carboxylic acid anhydrides

A typical procedure was as follows. A mixture of **1b** (1.3 g, 2.7 mmol), phthalic anhydride (**4a**) (0.4 g, 2.7 mmol), SOCl₂ (0.1 ml) and 5 ml of xylene in a 10 ml flask equipped with a magnetic stirring bar, reflux condenser and dry tube was heated at 150 °C for 10 h. After removing the solvent, the reaction product was sublimed under vacuum to give

Compound **5a**: IR (KBr, ν , cm⁻¹): 3055 (w, C–H); 1850 (m); 1760 (m, C=O); 1370 (s, SO₂); 1100–1200 (vs, C–F). ¹H NMR [(CD₃)₂CO] &: 7.50–7.73 (m, 4H) ppm. ¹⁹F NMR δ : –12.7 (s, ICF₂); 2.3 (m, OCF₂); 9.2 (m, CF₂O); 34.2 (s, CF₂S) ppm. MS (m/z, %): 553 (M⁺, 12.41); 426 (M⁺ – I, 47.48); 210 (M⁺ – IC₂F₄OC₂F₄, 100.00). Analysis: Calc. for C₁₂H₄F₈INO₅S: C, 26.04; H, 0.72; F, 27.49; N, 2.53%. Found: C, 26.33; H, 0.97; F, 27.08; N, 2.08%.

Similar treatment of 1c (4.4 g, 11 mmol) with 4a (1.7 g,

11 mmol) gave $Cl_2CFCF_2O(CF_2)_2SO_2 \bigvee_{i=0}^{i}$ (5b) (3.7 g).

Compound **5b**: IR (KBr, ν , cm⁻¹): 1858 (s); 1770 (s, C=O); 1380 (s, SO₂); 1100–1200 (vs, C–F). ¹H NMR [(CD₃)₂CO] δ : 7.53 (m, 4H) ppm. ¹⁹F NMR δ : 0.2 (s, Cl₂CF); 5.5 (m, OCF₂); 8.0 (m, CF₂O); 33.3 (s, CF₂S) ppm. MS (*m*/*z*, %): 348 (M⁺ – Cl₂CF – CO, 5.12); 104 (C₆H₄CO⁺, 100.00). Analysis: Calc. for C₁₂H₄Cl₂F₇NO₅S: C, 30.13; H, 0.84; F, 27.82; N, 2.93%. Found: C, 29.87 H, 1.05; F, 27.51; N, 2.76%. Reaction of **1d** (2.3 g, 10 mmol) with **4a** (1.5 g, 10 mmol) 0

Compound **5c**: IR (KBr, ν , cm⁻¹): 3020 (m, C–H); 1880 (m); 1750 (m, C=O); 1610 (m); 1500 (m, ArH). ¹H NMR [(CD₃)₂CO] δ : 7.50 (m, 4H) ppm. ¹⁹F NMR δ : 64.3 (m, 2F); 78.0 (m, 1F); 84.6 (m, 2F) ppm. MS (m/z, %): 313 (M⁺, 1.80); 196 (C₆F₅COH⁺, 100.00); 181 (C₆F₅N⁺, 6.70); 169 (C₅F₅N⁺, 21.70). Analysis: Calc. for C₁₄H₄F₅NO₂: C, 53.67; H, 1.28; F, 30.35; N, 4.47%. Found: C, 53.58; H, 1.51; F, 30.02; N, 4.08%.

$$I(CF_2)_2O(CF_2)_2SO_2 \xrightarrow[n]{1}{10}$$
 (5d) was prepared similarly.

0

Compound **5d**: IR (KBr, ν , cm⁻¹): 3050 (w, C–H); 1705 (s, C=O); 1635 (s, C=C); ; 1330 (s, SO₂); 1220–1130 (vs, C–F). ¹H NMR [(CD₃)₂CO] δ : 7.17 (s, 2H) ppm. ¹⁹F NMR δ : -12.5 (s, ICF₂); 2.1 (m, OCF₂); 9.4 (m, CF₂O); 34.5 (s, CF₂S) ppm. MS (m/z, %): 504 (M⁺H, 3.95); 296 (M⁺ - I - SO₂O, 16.62); 97 (M⁺H - IC₂F₄OC₂F₄SO₂, 22.41); 64 (SO₂, 100.00). Analysis: Calc. for C₈H₂F₈INO₅S: C, 19.09; H, 0.40; F, 30.22; N, 2.78%. Found: C, 18.88; H, 0.61; F, 30.21; N, 2.86%.

Heating a mixture of 1e (1.6 g, 10 mmol), 4b (1.0 g, 10 mmol) and a catalytic amount of SOCl₂ (0.1 ml) gave a

4-FC₆H₄
$$(1.4 g)$$
 [11].

Compound **5e**: IR (KBr, ν , cm⁻¹): 3050 (m, ArH); 3030 (m, =CH); 1730 (s); 1710 (s, C=O); 1632 (m, C=C); 1600 (m); 1517 (m, *p*-C₆H₄). ¹H NMR [(CD₃)₂CO] δ : 7.20 (s, 2H); 7.33 (AB, 2ArH); 7.76 (AB, 2ArH) ppm. ¹⁹F NMR δ : 40.3 (s, 1F) ppm. MS (*m*./*z*, %): 191 (M⁺, 100.00); 109 (F-C₆H₄N⁺, 26.7).

3.3. Reaction of tosyl-OH with compound 1b

A mixture of anhydrous tosyl-OH (6) (1.1 g, 6.4 mmol), 1b (3.0 g, 6.4 mmol) and 0.1 ml of SOCl₂ was heated at 150 °C for 8 h. The pure $I(CF_2)_2O(CF_2)_2SO_2NHSO_2C_6H_4CH_3$ -4 (7b) (2.6 g) was obtained by distillation under vacuum. Compound 7b solidified on cooling.

Compound **7b**: IR (film, ν , cm⁻¹): 3300 (w, N–H); 1600 (s, C=C); 1410 (s, SO₂); 1100–1210 (vs, C–F). ¹H NMR (CDCl₃) δ : 9.06 (s, NH); 7.2–7.7 (AA'BB', 4H); 2.33 (s, 3H) ppm. ¹⁹F NMR δ : –12.6 (s, ICF₂); 2.6 (m, OCF₂); 8.8 (m, CF₂O); 38.5 (s, CF₂S) ppm. MS (*m*/*z*, %): 560 (M⁺-O-H, 0.64); 543 (M⁺-F-CH₃, 0.51); 498 (M⁺H-SO₂-O, 3.63); 227 (ICF₂CF₂⁺, 6.07); 155 (CH₃C₆H₄SO₂⁺, 100.00). Analysis: Calc. for C₁₁H₈F₈INO₅S₂: C, 22.87; H, 1.39; F, 26.34; N, 2.43%. Found: C, 22.85; H, 1.47; F, 26.30; N, 2.28%.

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