Journal of Fluorine Chemistry 74 (1995) 203–206

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

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Received 16 November 1994; accepted 25 March 1995

Abstract

Heating *N*-sulfinylperfluoroalkane sulfonylamides, R_fSO_2NSO, or *N*-sulfinylpentafluoroaniline, C_6F_5NSO, with carboxylic acids in the presence of catalytic amounts of $SOCl_2$ 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, CF_3SO_2NSO, 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**) ($Y = R_fSO_2, C_6F_5, 4\text{-}FC_6H_4$), with carboxylic acids and acid anhydrides.

2. Results and discussion

Heating *N*-sulfinylperfluoroalkane sulfonylamides or *N*-sulfinylpentafluoroaniline with carboxylic acids in the presence of a catalytic amount of $SOCl_2$ gave *N*-perfluoroalkane sulfonylamides, R_fSO_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:

$$\underset{(\mathbf{1})}{\text{Y-NSO}} + \underset{(\mathbf{2})}{\text{RCOOH}} \xrightarrow[\Delta,\ 70\%-81\%]{SOCl_2\ (cat.)} \underset{(\mathbf{3})}{\text{RCONHY}} + SO_2$$

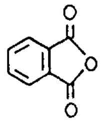
$Y = CF_3SO_2$ (**1a**)
$I(CF_2)_2O(CF_2)_2SO_2$ (**1b**)
$Cl_2(CF_2)_2O(CF_2)_2SO_2$ (**1c**)
C_6F_5 (**1d**)
$4\text{-}FC_6H_4$ (**1e**)

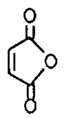
$R = C_6H_5$ (**2a**)
$4\text{-}IC_6H_4$ (**2b**)
CH_3 (**2c**)

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_3COCl [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**:

$$\mathbf{1} + \mathbf{4} \xrightarrow[\Delta,\ 68\%-82\%]{SOCl_2\ (cat.)} \mathbf{5} + SO_2$$

4a =


4b =


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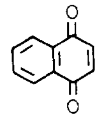
SSDI 0022-1139(95)03282-7

Table 1
Compounds **3**, **5** and **7**: preparation conditions

Reactants **1** + **2**, **4** or **6**	Conditions			Products **3**, **5** or **7**	Yields [a] (%)	M.p. (°C)
	Solvent	Temp. (°C)	Time (h)			
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	84–86
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*-sulfinylaniline and  [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-$NHSO_2R_f$ (**7b**), were obtained in 70% yield. However, attempted preparation of bis(perfluoroalkanesulfonyl)imine, $(R_fSO_2)_2NH$ [8], by treating **1a** with CF_3SO_3H or **1b** with $I(CF_2)_2O(CF_2)_2SO_3H$ failed. The only product detected was $R_fSO_2NH_2$.

$$\underset{\textbf{(6)}}{\textbf{1b} + 4\text{-}CH_3C_6H_4SO_3H} \xrightarrow[160\ ^{\circ}C,\ 8\ h]{SOCl_2\ (cat.)} \underset{\textbf{(7b)}}{I(CF_2)_2O(CF_2)_2SO_2NHSO_2C_6H_4CH_3\text{-}4}$$

The reaction results are summarized in Table 1.

3. Experimental details

Melting points were measured on a Thiele apparatus and 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. 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 $I(CF_2)_2O(CF_2)_2SO_2NHCOC_6H_5$ (**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, SO_2); 1140–1220 (vs, C–F). ^{1}H NMR [$(CD_3)_2CO$)] δ: 6.93 (s, NH); 7.50 (m, 2H); 7.23 (m, 2H); 7.13 (s, 1H) ppm. ^{19}F NMR δ: −12.3 (s, ICF_2); 2.3 (m, OCF_2); 9.0 (m, CF_2O); 38.3 (s, CF_2S) ppm. MS (*m*/*z*, %): 527 (M^+, 14.16); 400 ($M^+ - I$, 14.20); 105 ($C_6H_5CO^+$, 100.00). Analysis: Calc. for $C_{11}H_6F_8INO_4S$: 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 $4\text{-}FC_6H_4NHCOC_6H_5$ (**3b**) (1.7 g) [9].

Compound **3b**: IR (KBr, ν, cm^{-1}): 3225 (s, N–H); 1650 (s, C=O); 1610–1500 (m, C_6H_5). ^{1}H NMR (DMSO-d_6) δ: 10.13 (s, NH); 7.76–7.43 (m, 4H); 7.30–6.83 (m, 5H) ppm. ^{19}F NMR δ: 40.0 (s, 1F) ppm. MS (*m*/*z*, %): 216 (M^+H, 3.30); 215 (M^+, 17.40); 105 ($C_6H_5CO^+$, 100.00).

Heating **1b** (1.1 g, 2.3 mmol), **2b** (0.57 g, 2.3 mmol) and $SOCl_2$ (0.1 ml) without solvent gave $I(CF_2)_2O(CF_2)_2SO_2NHCOC_6H_4I\text{-}4$ (**3c**) (1.1 g).

Compound **3c**: IR (KBr, ν, cm^{-1}): 3250 (w, N–H); 1690 (m, C=O); 1350 (s, SO_2); 1140–1220 (vs, C–F). ^{1}H NMR [$(CD_3)_2CO$] δ: 7.03 (s, NH); 7.43 (AB, 2H); 7.66 (AB, 2H) ppm. ^{19}F NMR δ: − 12.7 (s, ICF_2); 2.3 (m, OCF_2); 9.2 (m, CF_2O); 38.0 (s, CF_2S) ppm. MS (*m*/*z*, %): 654 (M^+H, 12.30); 653 (M^+, 6.21); 526 ($M^+ - I$, 10.43); 231 ($IC_6H_4CO^+$, 100.00). Analysis: Calc. for $C_{11}H_5F_8I_2NO_4S$:

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].

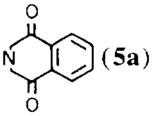
Compound **3d**: IR (KBr, ν, cm^{-1}): 3090 (w, NH); 1720 (s, C=O); 1387 (s, SO_2); 1190 (s); 1120 (s). ^1H NMR [$(CD_3)_2CO$] δ: 7.13 (s, NH); 2,03 (s, CH_3) ppm. ^{19}F NMR δ: −1.3 (s, CF_3) ppm. MS (*m/z*, %): 191 (M^+, 1.07); 80 ($SO_2NH_2^+$, 100.00).

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

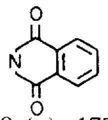
Compound **3e**: IR (KBr, ν, Cm^{-1}): 3100 (w, NH); 1725 (s, C=O); 1390 (s, SO_2); 1100–1240 (vs, C–F); ^1H NMR [$(CD_3)_2CO$] δ: 7.60 (s, NH); 1.76 (s, CH_3) ppm. ^{19}F NMR δ: −12.5 (s, ICF_2); 2.4 (m, OCF_2); 9.0 (m, CF_2O); 38.0 (s, CF_2S) ppm. MS (*m/z*, %): 466 (M^+H, 7.24); 43 (CH_3CO^+, 100.00). Analysis: Calc. for $C_6H_4F_8INO_4S$: 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

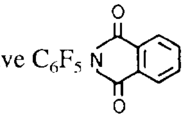
A typical procedure was as follows. A mixture of **1b** (1.3 g, 2.7 mmol), phthalic anhydride (**4a**) (0.4 g, 2.7 mmol), $SOCl_2$ (0.1 ml) and 5 ml of xylene in a 10 ml flask equipped with a magnetic stirring bar, reflux condenser and dry tube was heated at 150 °C for 10 h. After removing the solvent, the reaction product was sublimed under vacuum to give

$I(CF_2)_2O(CF_2)_2SO_2$  (**5a**) (1.2 g).

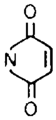
Compound **5a**: IR (KBr, ν, cm^{-1}): 3055 (w, C–H); 1850 (m); 1760 (m, C=O); 1370 (s, SO_2); 1100–1200 (vs, C–F). ^1H NMR [$(CD_3)_2CO$] δ: 7.50–7.73 (m, 4H) ppm. ^{19}F NMR δ: −12.7 (s, ICF_2); 2.3 (m, OCF_2); 9.2 (m, CF_2O); 34.2 (s, CF_2S) ppm. MS (*m/z*, %): 553 (M^+, 12.41); 426 (M^+-I, 47.48); 210 ($M^+-IC_2F_4OC_2F_4$, 100.00). Analysis: Calc. for $C_{12}H_4F_8INO_5S$: 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 $Cl_2CFCF_2O(CF_2)_2SO_2$  (**5b**) (3.7 g).

Compound **5b**: IR (KBr, ν, cm^{-1}): 1858 (s); 1770 (s, C=O); 1380 (s, SO_2); 1100–1200 (vs, C–F). ^1H NMR [$(CD_3)_2CO$] δ: 7.53 (m, 4H) ppm. ^{19}F NMR δ: 0.2 (s, Cl_2CF); 5.5 (m, OCF_2); 8.0 (m, CF_2O); 33.3 (s, CF_2S) ppm. MS (*m/z*, %): 348 (M^+-Cl_2CF-CO, 5.12); 104 ($C_6H_4CO^+$, 100.00). Analysis: Calc. for $C_{12}H_4Cl_2F_7NO_5S$: 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%.

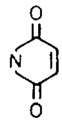
Reaction of **1d** (2.3 g, 10 mmol) with **4a** (1.5 g, 10 mmol) gave C_6F_5  (**5c**) (2.5 g).

Compound **5c**: IR (KBr, ν, cm^{-1}): 3020 (m, C–H); 1880 (m); 1750 (m, C=O); 1610 (m); 1500 (m, ArH). ^1H NMR [$(CD_3)_2CO$] δ: 7.50 (m, 4H) ppm. ^{19}F NMR δ: 64.3 (m, 2F); 78.0 (m, 1F); 84.6 (m, 2F) ppm. MS (*m/z*, %): 313 (M^+, 1.80); 196 ($C_6F_5COH^+$, 100.00); 181 ($C_6F_5N^+$, 6.70); 169 ($C_5F_5N^+$, 21.70). Analysis: Calc. for $C_{14}H_4F_5NO_2$: 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%.

$I(CF_2)_2O(CF_2)_2SO_2$  (**5d**) was prepared similarly.

Compound **5d**: IR (KBr, ν, cm^{-1}): 3050 (w, C–H); 1705 (s, C=O); 1635 (s, C=C); ; 1330 (s, SO_2); 1220–1130 (vs, C–F). ^1H NMR [$(CD_3)_2CO$] δ: 7.17 (s, 2H) ppm. ^{19}F NMR δ: −12.5 (s, ICF_2); 2.1 (m, OCF_2); 9.4 (m, CF_2O); 34.5 (s, CF_2S) ppm. MS (*m/z*, %): 504 (M^+H, 3.95); 296 (M^+-I-SO_2O, 16.62); 97 ($M^+H-IC_2F_4OC_2F_4SO_2$, 22.41); 64 (SO_2, 100.00). Analysis: Calc. for $C_8H_2F_8INO_5S$: 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 $SOCl_2$ (0.1 ml) gave a

$4\text{-}FC_6H_4$  (**5e**) (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*-C_6H_4). ^1H NMR [$(CD_3)_2CO$] δ: 7.20 (s, 2H); 7.33 (AB, 2ArH); 7.76 (AB, 2ArH) ppm. ^{19}F NMR δ: 40.3 (s, 1F) ppm. MS (*m./z*, %): 191 (M^+, 100.00); 109 ($F\text{–}C_6H_4N^+$, 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 $SOCl_2$ 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, SO_2); 1100–1210 (vs, C–F). ^1H NMR ($CDCl_3$) δ: 9.06 (s, NH); 7.2–7.7 (AA'BB', 4H); 2.33 (s, 3H) ppm. ^{19}F NMR δ: −12.6 (s, ICF_2); 2.6 (m, OCF_2); 8.8 (m, CF_2O); 38.5 (s, CF_2S) ppm. MS (*m/z*, %): 560 (M^+-O-H, 0.64); 543 (M^+-F-CH_3, 0.51); 498 (M^+H-SO_2-O, 3.63); 227 ($ICF_2CF_2^+$, 6.07); 155 ($CH_3C_6H_4SO_2^+$, 100.00). Analysis: Calc. for $C_{11}H_8F_8INO_5S_2$: 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%.

Acknowledgement

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

References

[1] H.W. Roesky, G. Holtschenider and H.H. Giere, *Z. Naturforsch., 25b* (1970) 4, 252.

[2] H.W. Roesky and G. Holtschenider, *Z. Anorg. Allg. Chem., 378* (1970) 168.

[3] Shi-Zheng Zhu and Qin-Yun Chen, *J. Chem. Soc., Chem. Commun.,* (1991) 732.

[4] Shi-Zheng Zhu, Ai-Wen Li, Yue-Hua Zhu, Jia-Nin Dai, Xian-Ming Chen and Xin-Wen Yuan, *J. Fluorine Chem., 60* (1993) 283.

[5] E. Behrend and A. Haas, *J. Fluorine Chem., 4* (1974) 83.

[6] G.G.I. Moore and A.C Conway, US Pat. 3 637 845; [*Chem. Abs., 76* (1972) 71 557s; US Pat. 3 705 185; [*Chem. Abs., 78* (1974) P58 095m].

[7] A.S. Amarasekara and W.W. Pathmasiri, *Tetrahedron Lett., 34* (1993) 7965.

[8] D.D. DesMarteau and J. Foropoulos, *Inorg. Chem., 23* (1984) 3720.

[9] A. Roe and W.P. Tucker, *J. Heterocycl. Chem., 2* (1965) 148.

[10] J.M. Barrales-Rienda, J. Gonzalez Ramos and M. Sanchez Chaves, *J. Fluorine Chem., 9* (1977) 293.