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Reactions of *N*-sulfinylfluoroalkanesulfonylamides with alkene oxides

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Abstract

Reactions of *N*-sulfinylfluoroalkanesulfonylamides, R_fSO_2NSO (**1**), with alkene oxides **2** at room temperature gave the cyclo condensation products 2-oxa-3-fluoroalkanesulfonyl-1,2,3-oxathiazolidines, $R_fSO_2\overline{NCH(R)CH_2OS}(O)$ (**3**). When R was phenyl, the compound decomposed at 160 °C to give *N*-fluoroalkanesulfonylaziridine, $R_fSO_2\overline{NCH_2CH}(C_6H_5)$, with elimination of SO_2. Acidic hydrolysis of **3c** [$R_f = I(CF_2)_2O(CF_2)_2$, R = Ph] gave $R_fSO_2NHCH(Ph)CH_2OH$ (**5**) which was identified by X-ray diffraction analysis.

Keywords: *N*-Sulfinylfluoroalkanesulfonylamides; Alkene oxides; Cyclo condensation; 2-Oxa-3-fluoroalkanesulfonyl-1,2,3-oxathiazolidines; X-ray diffraction; NMR spectroscopy; IR spectroscopy; Mass spectrometry

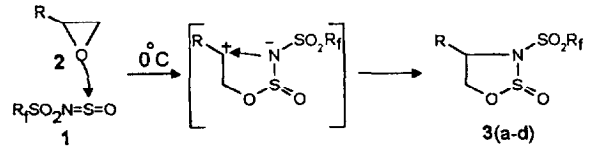
1. Introduction

The reaction of *N*-sulfinylamine, ArNSO, with alkene oxides was well studied many years ago [1–4]. For example, Etlis *et al.* [1] reported that in the presence of Et_4NBr, ArNSO reacted with oxirane at 95–100 °C in a sealed ampoule to give 2-oxa-3-aryl-1,2,3-oxathiazolidine, $Ar\overline{NCH_2CH_2OS}(O)$. Yamada *et al.* [2,3] found that ArNSO reacted with ethylene oxide without solvent and catalyst to form mainly resinous products, which decomposed to *N,N'*-diarylhexahydro-1,4-diazines, $Ar\overline{NCH_2CH_2N(Ar)CH_2CH_2}$, with evolution of SO_2 when heated up to 160 °C.

During the study of the chemistry of *N*-sulfinylfluoroalkanesulfonylamides, R_fSO_2NSO (**1**), it was found that the polar N=S double bond is very sensitive to nucleophilic attack [5,6] and is also subjected to a Diels–Adler reaction with dienes [7]. In this paper, the cyclo condensation between **1** and alkene oxides is reported and the decomposition of the corresponding heterocyclo products is studied in detail.

2. Results and discussion

Reaction of *N*-sulfinylaniline with oxirane in the presence of catalysts such as Et_4NBr, LiCl or LiBr at 60–90 °C gave a cyclo condensation product. In the case of R_fSO_2NSO (**1**),



Scheme 1. $R_f = I(CF_2)_2O(CF_2)_2$, (**1a**); R = H, (**2a**); $R_f = H(CF_2)_2O(CF_2)_2$, (**1b**); $R = C_6H_5$ (**2b**)].

the strong electron-withdrawing group R_fSO_2 makes the nitrogen sulfur double bond more reactive and easy to react with nucleophiles. The reaction of **1** with alkene oxides **2** occurred smoothly at 0 °C and without catalyst.

In contrast to the reaction of Ar–N=S=O with alkene oxide, Etlis has reported that two regioisomers, (3-aryl-4-alkyl)- and (3-aryl-5-alkyl)-2-oxa-1,2,3-oxathiazolidine, were obtained, the latter being the major product [1]. However, reaction of **1** with styrene oxide **2b** gave only 3-fluoroalkanesulfonyl-4-phenyl-2-oxa-1,2,3-oxathiazolidine (**3c, d**). The reaction results are summarised in Table 1. The structure of product **3c** was characterised by ^1H NMR and ^{13}C NMR spectra, and by elemental analyses, and was further confirmed by X-ray analysis of its hydrolysis product **5** (Fig. 1). In the reactions a small amount of the by-product $R_fSO_2NH_2$ is also formed.

The cyclo condensation products **3a** and **3b**, $R_fSO_2\overline{NCH_2CH_2OS}(O)$, are high boiling point oils which can be purified by vacuum fractional distillation without decomposition at 160–170 °C. Compound **3c**, $R_fSO_2\overline{NCH(Ph)CH_2OS}(O)$, is a solid which decomposed at 160 °C to *N*-fluoroalkanesulfonylaziridine, R_fSO_2-

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Table 1

Reactants	Solvent	Products	B.p. (°C/mmHg) or m.p. (°C)	Yield [a] (%)
1a + **2a**	ether	**3a**	136–138/2	62
1b + **2a**	ether	**3b**	130–132/2	68
1a + **2b**	benzene	**3c**	94–95	77
1b + **2b**	benzene	**3d**	87–89	56

[a] Isolated yields based on **1**.

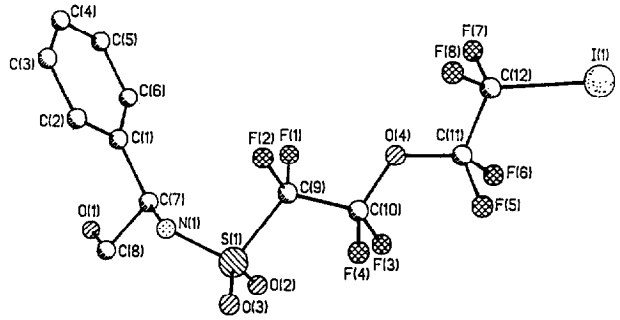


Fig. 1.

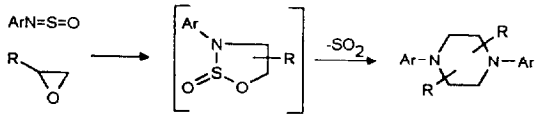
$\overline{NCH_2CHPh}$ (**4**), through the elimination of SO_2 (see Scheme 3 below).

It should be noted that both Yamada *et al.* [2] and Tsuge and Mataka [4] have reported that $ArN\overline{CH(R)CH_2OS}(O)$ (R = H, Ph) decomposed on heating and gave the *N,N'*-diarylhexahydro-1,4-diazine derivatives via coupling of the two intermediates (Scheme 2).

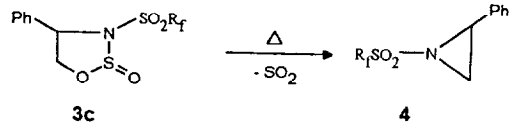
In our case, no corresponding 1,4-diazine derivatives could be detected during the decomposition of **3c**. The sole product was **4** which was a high boiling point oil characterised by comparison with an authentic sample which was prepared from the reaction of $R_fSO_2N_3$ with styrene [8].

The hydrolysis of **3c** under acidic conditions gave a pale yellow solid **5**. Recrystallisation from CH_3CN–CH_3OH gave colourless crystals. Their structure was determined by X-ray crystal structure analysis and is as shown in Fig. 1, the bond angles and bond lengths being listed in Tables 2 and 3. The proposed mechanism for the hydrolysis is that **3c** is first protonated at the nitrogen atom, followed by N–S bond scission and evolution of SO_2 (Scheme 4).

In conclusion, the cyclo condensation of *N*-sulfinyl-fluoroalkanesulfonylamides with alkene oxides have been



Scheme 2.



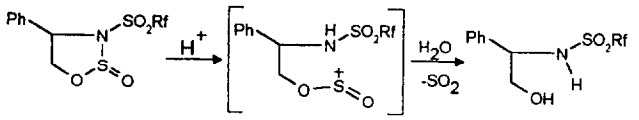
Scheme 3.

Table 2
Selected bond lengths (Å) for compound **5**

C(1)–C(7)	1.502(12)	N(1)–S(1)	1.579(8)
C(7)–N(1)	1.499(12)	S(1)–C(9)	1.829(10)
C(7)–C(8)	1.538(13)	S(1)–O(2)	1.410(7)
C(8)–O(1)	1.436(11)	S(1)–O(3)	1.430(7)

Table 3
Selected bond angles (∞) for compound **5**

O(2)–S(1)–O(3)	122.4(4)	O(2)–S(1)–N(1)	111.7(4)
O(3)–S(1)–N(1)	107.5(4)	O(2)–S(1)–C(9)	104.8(5)
O(3)–S(1)–C(9)	104.7(4)	N(1)–S(1)–C(9)	104.9(4)
N(1)–C(7)–C(1)	110.6(7)	S(1)–N(1)–C(7)	123.1(6)
O(1)–C(8)–C(7)	110.4(7)	N(1)–C(7)–C(8)	106.0(7)



Scheme 4.

studied and the products were 2-oxa-3-fluoroalkanesulfonyl-(4-phenyl-)-1,2,3-oxathiazolidines.

3. Experimental details

Melting points were measured on a Thiele apparatus. Both melting points and boiling points are reported uncorrected. Solvents were purified and dried before use. ^1H NMR (60 MHz) and ^{19}F NMR (54.6 MHz) spectra were recorded on a Varian-360L instrument with TMS and TFA ($\delta_{CFCl_3} = \delta_{TFA} + 77.8$, and with upfield as positive) as internal and external standards, respectively. ^1H NMR and ^{13}C NMR (300 MHz) spectra were recorded on a Bruker AM-300 instrument. Elemental analysis were performed at this Institute. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low resolution mass spectra were obtained on a Finnigan GC–MS 4021 instrument.

Reactants **1** were synthesized by refluxing the corresponding sulfonylamines with $SOCl_2$ [9].

3.1. Reaction of 1 with 2a

Ethylene oxide (5 ml, excess) was bubbled into a 50 ml flask containing a solution of **1a** (4.7 g, 10 mmol) and dry ether (15 ml) at 0 °C for 2 h. The reaction mixture was then stirred for another 2 h at room temperature. The solvent and excess ethylene oxide were evaporated and the residue distilled under vacuum to give $I(CF_2)_2O(CF_2)_2SO_2NH_2$ (b.p. 88–90 °C/2 mmHg, 0.5 g, 12%), which was identified with an authentic sample [9], and $I(CF_2)_2O(CF_2)_2SO_2\text{-}\overline{NCH_2CH_2OS}(O)$ (**3a**) (3.2 g, b.p. 139 °C/2 mmHg, 62%).

Compound **3a**: IR (film, ν, cm^{-1}): 2984 (m); 2880 (w, CH_2); 1378 (s, SO_2); 1188 (m, S=O); 1220–1080 (vs, C–

F). ^{1}H NMR ($CDCl_3$) δ: 5.00 (m, CH_2O); 3.60 (m, NCH_2) ppm. ^{19}F NMR δ: −12.5 (s, ICF_2); 3.9 (m, OCF_2); 7.8 (m, CF_2O); 37.7 (s, CF_2S) ppm. MS *m/e*, %): 514 (M^+H, 1.6); 466 (M^+H-SO, 37.7); 450 (M^+H-SO_2, 100.0); 227 ($ICF_2CF_2^+$, 90.6). Analysis: Calc. for $C_6H_4F_8INO_5S_2$: C, 14.04; H, 0.78; N, 2.73; F, 29.63%. Found: C, 14.34; H, 0.55; N, 2.77; F, 29.64%.

Similar treatment of $H(CF_2)_2O(CF_2)_2SO_2NSO$ (**1b**) (3.4 g, 10 mmol) with **2a** (5 ml) gave $H(CF_2)_2O(CF_2)_2SO_2NCH_2CH_2OS(O)$ (**3b**) (2.6 g, b.p. 130 °C/2 mmHg, 68%).

Compound **3b**: IR (film, ν, cm^{-1}): 2980 (m); 2880 (w, CH_2); 1380 (vs, SO_2); 1190 (s, S=O); 1200–1080 (vs, C–F). ^{1}H NMR ($CDCl_3$) δ: 6.33 (t, HCF_2, $^2J_{HF}=54$ Hz); 5.03 (m, CH_2O); 3.53 (m, NCH_2) ppm. ^{19}F NMR δ: 8.6 (m, OCF_2); 15.3 (m, CF_2O); 43.3 (s, CF_2S); 65.3 (d, HCF_2) ppm. MS (*m/e*, %): 388 (M^+H, 2.3); 368 (M^+-F, 40.2); 352 (M^+-F-O, 90.0); 324 (M^+H-SO_2, 24.9); 101 ($HCF_2CF_2^+$, 57.2); 90 (NCH_2CH_2OS, 73.2); 42 ($CH_2CH_2N^+$, 100.0); Analysis: Calc. for $C_6H_5F_8NO_5S_2$: C, 18.61; H, 1.29; N, 3.62; F, 39.28%. Found: C, 18.50; H, 1.44; N, 3.79; F, 39.00%).

3.2. Reaction of *1* with styrene oxide (*2b*)

Styrene oxide (**2b**) (1.2 g, 10 mmol) was added dropwise into a 25 ml flask containing a solution of **1a** (4.7 g, 10 mmol) and dry benzene (10 ml) at 0 °C. After addition, the reaction mixture was stirred for another 4 h at room temperature. Column chromatography on silica gel [using petroleum ether/ethyl acetate (9:1) as eluent] gave $I(CF_2)_2O(CF_2)_2SO_2\overline{NCH(C_6H_5)CH_2OS}(O)$ (**3c**) (4.5 g, 77%) and $I(CF_2)_2O(CF_2)_2SO_2NH_2$ (0.3 g, 8%), respectively.

Compound **3c**: M.p. 94–95 °C. IR (KBr, ν, cm^{-1} −: 2990 (m); 2887 (w); 1380 (s, SO_2); 1190 (s, S=O); 1210–1100 (vs, C–F); 730 (s); 700 (s). ^{1}H NMR ($CDCl_3$) δ: 7.31 (m, 5H); 4.89 (d–d, $J_1=4.1$ Hz, $J_2=5.5$ Hz, 1H); 4.13 (d–d, $J_1=4.1$ Hz, $J_3=11.7$ Hz, 1H); 3.94 (d–d, $J_2=5.5$ Hz, $J_3=11.7$ Hz, 1H) ppm. ^{19}F NMR δ: −11.5 (s, ICF_2); 5.0 (m, OCF_2); 8.5 (m, CF_2O); 39.5 (s, CF_2S) ppm. ^{13}C NMR ($CDCl_3$) δ: 137.3 (Ar–C); 129.0 (Ar–C); 128.5 (Ar–C); 126.5 (Ar–C); 66.1 (O–C); 60.6 (N–C) ppm. MS (*m/e*, %): 512 (M^+-SO_2-CH, 100.0); 462 (M^+-I, 1.4); 227 ($ICF_2CF_2^+$, 24.5); 104 ($M^+-C_6H_6-R_f$, 72.3). Analysis: Calc. for $C_{12}H_8F_8INO_5S_2$: C, 24.45; H, 1.36; N, 2.38; F, 25.81%. Found: C, 24.40; H, 1.52; N, 2.40; F, 25.66%.

$H(CF_2)_2O(CF_2)_2SO_2NCH(C_6H_5)CH_2OS(O)$ (**3d**) was obtained similarly (56%).

Compound **3d**: IR (KBr, ν, cm^{-1}): 2995 (m); 2880 (w, CH_2); 1375 (s, SO_2); 1200 (s, S=O); 1200–1100 (vs, C–F); 725 (s); 700 (s). ^{1}H NMR ($CDCl_3$) δ: 7.27 (m, 5H); 6.50 (t, HCF_2, $^2J_{HF}=54$ Hz); 6.29 (m, 1H); 4.56 (m, 1H); 3.90 (m, 1H) ppm. ^{19}F NMR δ: 8.5 (m, OCF_2); 15.3 (m, CF_2O); 42.9 (s, CF_2S); 66.8 (d, HCF_2) ppm. MS (*m/e*, %): 464 (M^+H, 1.5); 386 (M^+-SO_2-CH, 100.0); 101 ($HCF_2CF_2^+$, 50.1). Analysis: Calc. for $C_{12}H_9F_8NO_5S_2$: C, 31.10; H, 1.94; N, 3.02; F, 32.83%. Found: C, 29.95; H, 1.77; N, 3.13; F, 32.68%.

3.3. Thermolysis of *3c*

Compound **3c** (4.0 g, 6.8 mmol) was heated to 160 °C to eliminate a large amount of gas which was identified as SO_2. The residue was distilled under vacuum to give $ICF_2CF_2OCF_2CF_2SO_2\overline{NCH_2CH}(Ph)$ (**4**) (2.1 g, b.p. 133–135 °C, 58%).

Compound **4**: ^{1}H NMR ($CDCl_3$) δ: 7.33 (m, 5H); 4.83 (m, 1H); 2.95 (m, 2H) ppm. ^{19}F NMR δ: −10.9 (s, ICF_2); 5.5 (m, OCF_2); 9.5 (m, CF_2O); 40.0 (s, CF_2S) ppm. MS (*m/z*, %): 526 (M^+H, 1.0); 525 (M^+, 1.7); 449 ($M^+H-C_6H_5$, 22.1); 227 (ICF_2CF_2, 100.0).

3.4. Hydrolysis of **3c**

A mixture of **4c** (4.0 g, 6.8 mmol) and hydrochloric acid (10%, 10 ml) was stirred for 2 h at room temperature and then extracted with Et_2O (3×10 ml). After removing the ether, the residual solid was recrystallised from CH_3CN–CH_3OH to give $I(CF_2)_2O(CF_2)_2SO_2NHCH(Ph)CH_2OH$ (**5**) (3.4 g, 91%).

Compound **5**: M.p. 103–104 °C. IR (KBr, ν, cm^{-1}): 3200 (m); 3030 (m); 2883 (w); 1370 (s, SO_2); 1200–1100 (vs, C–F); 730 (s). ^{1}H NMR ($CDCl_3$) δ: 7.55 (m, 5H); 6.72 (d, NH); 4.78 (m, 1H); 3.94 (m, 1H); 3.83 (m, 1H); 2.62 (broad, OH) ppm. ^{19}F NMR δ: −11.2 (s, ICF_2); 4.8 (m, OCF_2); 8.7 (m, CF_2O); 41.3 (s, CF_2S) ppm. MS (*m/e*, %): 512 (M^+-H_2O-CH, 100.0); 227 ($ICF_2CF_2^+$, 34.0).

3.5. Crystal structure data

$C_{12}H_{10}F_8INO_4S$: $M=542.2$, monoclinic, space group $P2_1/C$, $a=5.6200(10)$, $b=30.557(6)$, $c=10.396(2)$ Å, $\beta=91.90(3)°$, $V=1784.5(6)$ Å^3, $Z=4$, $D_c=2.018$ g cm^{-3}. Absorption coefficient = 1.982 mm^{-1}, $F(000)=1044$. Radiation, Mo Kα ($\lambda=0.71073$ Å). Crystal dimensions, 0.3×0.3×0.4 mm. Intensity data were collected at 23 °C with a Siemens R3 M/V diffractometer using graphite-monochromated Mo Kα radiation. A total of 3142 independent reflections were measured in the range $4°<2\theta<50°$ with $0<h<6$, $0<k<36$, $-12<l<12$. The structure was solved via a direct method using a Siemens SHELXTL PLUS (VMS) system. The position of all H atoms was obtained by theoretical calculations. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by means of a full-matrix least-squares technique. The final R and R_w values were 0.0689 and 0.0678, respectively, for 2002 observed reflections [$F>4.0\sigma(F)$]. All calculations were performed on a MICRO VAXII computer with SDP, MULTAN 82 and ORTEP programs.

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