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Preliminary Note

Synthesis and reactions of *N*,*N*-dichloroperfluoroalkanesulfonylamides

Shi-zheng Zhu*, Cheng-ming Zhou, Ai-wen Li and Bin Xu

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032 (China)

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Abstract

Reactions of *N*,*N*-dichloroperfluoroalkanesulfonylamides with alkenes, benzene, dimethyl sulfide and dimethyl sulfoxide in the presence of zinc dust gave addition or insertion products via the fluoroalkanesulfonylnitrene intermediate. On heating $R_fSO_2NCl_2$ in the presence of alkene without zinc, 1:1 addition products were formed via a free-radical mechanism.

N,*N*-Dichlorotrifluoromethanesulfonylamide, $CF_3SO_2NCl_2$, was first prepared in 1974 [1]. Its chemistry, however, has received little study. Recently, Yagupol'skii *et al.* reported its reactions with diphenyl sulfide [2] and trifluoromethylphenyl sulfide [3].

Here, we report the preparation of some *N*,*N*-dichlorofluoroalkanesulfonylamides and their reactions with benzene, dimethyl sulfide, dimethyl sulfoxide and alkenes. The title compounds were conveniently prepared by the one-pot reaction of fluoroalkanesulfonylamides with KOH(aq.) and chlorine gas:

$$\underset{(\mathbf{1})}{R_fSO_2NH_2} \xrightarrow[0\ ^\circ C\text{–}20\ ^\circ C,\ 24\ h,\ 52\%\text{–}63\%]{KOH(aq.),\ Cl_2} \underset{(\mathbf{2})}{R_fSO_2NCl_2}$$

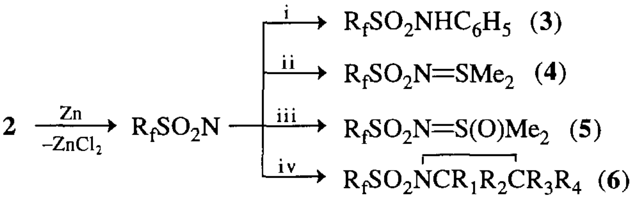
$R_f = I(CF_2)_2O(CF_2)_2$, **2a**

$R_f = Cl(CF_2)_2O(CF_2)_2$, **2b**

$R_f = H(CF_2)_2O(CF_2)_2$, **2c**

Compounds **2** were obtained as yellowish liquids. They are unstable, for example, after storage for 1 week in a flask at room temperature with nearly 50% of **2** decomposing to the corresponding fluoroalkanesulfonylamides (detected by ^{19}F NMR spectroscopy: the chemical shifts of $-CF_2S$ in compounds **1** and **2** were 40 ppm and 29 ppm, respectively; TFA external standard; upfield positive). Heating **2** with benzene in the presence of zinc dust afforded 70% of $R_fSO_2NHC_6H_5$ (**3**). Similarly, treatment of **2** with dimethyl sulfide or dimethyl sulfoxide gave the sulfonium ylid $R_fSO_2N{=}SMe_2$ (**4**) and the sulfoxonium ylid $R_fSO_2N{=}S(O)Me_2$ (**5**), respectively. The *N*-fluoroalkanesulfonylaziridines **6** were obtained by refluxing **2** with styrene or 1,4-dimethyl-but-2-ene in CH_2Cl_2. In these two reactions, $R_fSO_2NH_2$ was also formed in *c.* 15% yield.

These results appear to indicate that fluoroalkanesulfonylnitrene intermediates are involved in all the above questions [4, 5]. This is similar to the reactions of fluoroalkanesulfonylazides [6] (see Scheme 1).



[$R_1 = R_2 = R_3 = H$, $R_4 = C_6H_5$ (**6a**); $R_1 = R_2 = R_3 = R_4 = CH_3$ (**6b**)]

Reagents, conditions and yields: i, C_6H_6, reflux, 8 h, 70%; ii, Me_2S, r.t., 8 h, 68%; iii, DMSO, 60 °C, 8 h, 65%; iv, $PhCH{=}CH_2$, CH_2Cl_2, r.t., 8 h, 62%, $Me_2C{=}CMe_2$, r.t., 8 h, 64%.

Scheme 1.

It was noteworthy that the reaction of **2** with styrene occurred rapidly without zinc powder, and gave 1:1 addition products:

$$2 + \underset{(\mathbf{7})}{R_1CH{=}CHR_2} \xrightarrow[reflux,\ 8\ h]{CH_2Cl_2} \underset{(\mathbf{8})}{R_fSO_2NClCHR_1CHClR_2}$$

[$R_1 = H$; $R_2 = C_6H_5$]

This reaction was demonstrated to be a free-radical reaction process since the radical intermediate $R_fSO_2NClCH_2CHPh$ could be captured by Bu^{t}NO. The ESR spectrum showed triplet–doublet peaks ($a_N = 15.18$ G, $a_H = 3.04$ G, $g = 2.0052$).

Reduction of **8** by $NaHSO_3$, followed by elimination of HCl with alcoholic NaOH gave *N*-fluoroalkanesulfonylaziridine (**6a**) [7]:

$$8 \xrightarrow{NaHSO_3} R_fSO_2NHCH_2CHClPh \xrightarrow[-HCl]{NaOH/EtOH} \underset{(\mathbf{6a})}{R_fSO_2\overline{NCH_2C}HPh}$$

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*Author to whom correspondence should be addressed.

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All the new compounds were fully characterized by their IR, ^{1}H NMR, ^{19}F NMR, MS spectra and by elemental analysis.

Further studies on the chemistry of **2** are in progress.

Experimental

General procedure for the preparation of N,N-dichloroperfluoroalkanesulfonylamides 2

Perfluoroalkanesulfonylamides **1a** (6.3 g, 15 mmol), KOH (1.7 g, 30 mmol) and water (15 ml) were placed in a 50 ml three-necked flask and the mixture stirred at room temperature for 2 h. The flask was cooled down via an ice bath, then chlorine gas (4.1 g, 60 mmol) was introduced during which time the reaction temperature was kept at 0–5 °C. The reaction mixture was then stirred for another 2 h at 20 °C. A yellowish oil separated which was dried over Na_2SO_4 and distilled under vacuum to give **2a** (3.8 g, 52%), b.p. 42–44 °C/2 mmHg. IR (film) (ν_{max}, cm^{-1}): 1605 (w); 1420 (m); 1380 (s); 1320 (vs); 1292 (s); 1220–1120 (vs); 1092 (s); 990 (s); 713 (s); 600 (m); 530 (m). ^{19}F NMR (neat) (TFA external, upfield positive) δ: −11.8 (s, ICF_2); 5.20 (m, CF_2); 8.5 (m, CF_2O); 29.3 (s, CF_2S) ppm. MS *m/z%*: 492 (MH$^+$, 0.62); 424 ($M^+ - F - SO$, 1.90); 364 ($M^+ - I$, 0.96); 343 ($M^+ - SO - C_2F_4$, 5.52); 329 ($M^+ - SON - C_2F_4$, 4.82); 227 ($IC_2F_4^+$, 100); 205 (ISO_2N^+, 15.7). Analysis: Calc. for $C_4Cl_2F_8INO_3S$: C, 9.76; N, 2.85; F, 30.89%. Found: C, 10.04; N, 2.99; F, 31.30%.

Typical reaction of 2 in the presence of zinc powder

A mixture of **2b** (2 g, 5 mmol), DMSO (10 ml) and zinc powder (1 g, 15 mmol) was stirred for 8 h at 60 °C. After filtration, the filtrate was fractionally distilled under reduced pressure giving **5b** (1.3 g, 64%); b.p. 98–100 °C/2 mmHg. IR (film) (ν_{max}, cm^{-1}): 2971 (s); 2892 (s); 1580 (m); 1443 (m); 1380 (s); 1370 (s); 1277 (s); 1210–1100 (vs); 1005 (vs); 980 (s); 881 (m); 700 (m); 653 (s); 517 (s). ^{1}H NMR δ: 3.50 (s, $2CH_3$) ppm. ^{19}F NMR δ: −1.0 (s, $ClCF_2$); 6.5 (m, OCF_2); 11.6 (m, CF_2O); 42.3 (s, CF_2S) ppm. MS *m/z %*: 408/410 (MH$^+$, 0.75/0.37); 392/394 ($M^+H - O$, 25.96/16.09); 372 ($M^+ - Cl$, 2.64); 344/346 ($M^+H - SO_2$, 4.34/2.72); 332/334 ($M^+H - SMe_2 - N$, 20.22/8.40); 156 ($M^+ - R_f$, 11.09); 141 ($M^+ - R_f - Me$, 4.99); 140 ($M^+ - R_f - O$, 17.32); 135/137 ($ClC_2F_4^+$, 15.39/7.45); 85/87 ($ClCF_2^+$, 14.72/6.37); 80 (SOS^+, 100); 78 (Me_2SO^+, 5.74); 64 (SO_2^+, 85.47); 61 ($MeSN^+$, 12.90); 47 (MeS^+, 5.14). Analysis: Calc. for $C_6H_6F_8ClNO_4S_2$: C, 17.67; H, 1.47; N, 3.44; F, 37.30%. Found: C, 18.03; H, 1.80; N, 3.13; F, 37.00%.

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