Heteroatom Chemistry
Volume 10, Number 1, 1999

Syntheses and Reactions of N-Perfluoroalkanesulfonylimino Sulfurous Dichlorides

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Received 8 April 1998; revised 18 June 1998.

ABSTRACT: *Treatment of N,N-dichloroperfluoroalkanesulfonylamines with sulfur powder at room temperature gave the title products $R_fSO_2N{=}SCl_2$ in good yields. They reacted readily with dimethyl sulfoxide, chloral, DMF, benzophenone, and similar compounds to form to corresponding imines $R_fSO_2N{=}YR^1R^2$ (Y: S, C). A reaction mechanism, one involving formation of a four-membered intermediate, is proposed.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 41–48, 1999

INTRODUCTION

Compounds having the polar N=E double bond, $RN{=}ECl_2$ (E: S, Se), such as $RCON{=}SCl_2$, $ArSO_2N{=}SCl_2$, $R_fN{=}SCl_2$, etc., are very reactive and have attracted much attention. Several research articals concerned with their preparation and chemical transformations have been reported [1–4]. The imino sulfurous compounds $RN{=}SCl_2$ are generally prepared from the corresponding amine. Examples are shown in the following:

$$RNH_2 + SCl_2 \longrightarrow RN{=}SCl_2$$

$$RNH_2 + SOCl_2 \longrightarrow RNSO \xrightarrow{PCl_5} RN{=}SCl_2$$

$$RNH_2 \longrightarrow RNCl_2 \xrightarrow{SCl_2} RN{=}SCl_2$$

$$R = RCO,\ RSO_2,\ ArSO_2,\ (RO)_2P(O)$$

Markovskii and Fedyuk [5] reported an improved method to prepare sulfonylimino sulfurous dichlorides by the direct reaction of N,N-dichloroalkanesulfonylamine with sulfur powder in the presence of catalysts such as I_2, $FeCl_3$, or $AlCl_3$.

$$RSO_2NCl_2 + S \xrightarrow[r.\,t.]{cat} RSO_2N{=}SCl_2\ (64\text{-}90\%)$$

The fluorinated analogues $R_fSO_2N{=}SCl_2$ have been studied rarely until now. Recently, we have reported some research work about the chemical transformation of N,N-dichloroperfluoroalkanesulfonylamines $R_fSO_2NCl_2$ (**1**). Compounds **1** added readily to unsuturated compounds giving a 1:1 adducts via a free radical process [6]. In the presence of zinc powder, they decomposed to form perfluoroalkanesulfonyl nitrene intermediates that were captured by many organic reagents [7,8].

As an extention of this research work, we report now on the preparation and reactions of $R_fSO_2N = SCl_2$.

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Contract grant sponsor; National Natural Science Foundation of China

CCC 1042-7163/99/010041-08

RESULTS AND DISCUSSION

N,N-dichloroperfluoroalkanesulfonylamines $R_fSO_2NCl_2$, prepared by the reaction of $R_fSO_2NH_2$ with chlorine gas in the presence of KOH, have been found to react exothermally with sulfur powder without any catalysis:

$$\underset{\mathbf{1(a\text{-}e)}}{R_fSO_2NCl_2} + S \xrightarrow[89\text{-}92\%]{r.t.,0.5h} \underset{\mathbf{2(a\text{-}e)}}{R_fSO_2N{=}SCl_2}$$

Rf: $I(CF_2)_2O(CF_2)_2$, **a**; $H(CF_2)_2O(CF_2)_2$, **b**; C_4F_9, **c**; C_6F_{13}, **d**; C_8F_{17}, **e**

This reaction occurred readily without solvent at room temperature. If the reaction were carried out in CH_2Cl_2 or CCl_4, however, the reaction rate would be considerably slower. After having been stirred for 2 hours, the reaction mixture contained the starting material **1** (~20%). This was determined by ^{19}F NMR spectroscopy: the chemical shift of $-CF_2SO_2$ in compound **1** is around 30.2. In product **2**, it is shifted upfield and is at 40.0. Compound **2** can be distilled from the reaction mixture as a yellowish liquid. It is very moisture sensitive, and, when exposed to air, it decomposed rapidly.

$$R_fSO_2N{=}SCl_2 \xrightarrow{\text{moisture}} R_fSO_2NH_2 + HCl + SO_2$$

This reaction indicates the high reactivity of **1**.

During study on N-sulfonylperfluoroalkanesulfonylamines R_fSO_2NSO, we found that they condensed smoothly with many carbonyl compounds, such as aldehydes, carboxylic acids, and acid anhydrides. However, these types of compound did not react with some reactive carbonyl reagents such as $CCl_3C(O)H$ and CF_3COCF_3.

Refluxing of compounds **2** with excess $CCl_3C(O)H$ for 20 hours gave the corresponding N-perfluoroalkanesulfonyl trichloro methyl aldimines $R_fSO_2N{=}CHCCl_3$ **4**.

$$\underset{\mathbf{2(a\text{-}d)}}{R_fSO_2N{=}SCl_2} + \underset{\mathbf{3}}{CCl_3C(O)H} \xrightarrow{100^oC} \underset{\mathbf{4(a\text{-}d)}}{R_fSO_2N{=}CHCCl_3}$$

The yields of products **4** are around 45–50%. They are very moisture-sensitive, colorless liquids. Pure samples could be obtained only by several vacuum distillations. Their structures were fully characterized by spectroscopic methods and HRMS. The IR spectrum shows the strong C=N absorption peak at 1644 cm^{-1} (**4a**) or 1650 cm^{-1} (**4c**). In ^{13}C NMR spectra, the chemical shifts of the *C*=N double bond and the *C*Cl_3 are 172.6 and 90.6, respectively, for the compound **4c**. The special M^+ (2 × ^{37}Cl) + 1 (430)/M^+ (^{37}Cl) + 1 (428)/M^+ (^{35}Cl) + 1 (426) peaks with intensities of 1:3:3 in the MS spectrum of **4c** confirmed the presence of the CCl_3 group.

Heating of compounds **2** with aromatic aldehydes without solvent gave the corresponding N-perfluoroalkanesulfonyl arylimines in high yields:

$$\underset{\mathbf{2}}{R_fSO_2N{=}SCl_2} + \underset{\mathbf{5(a\text{-}e)}}{ArCHO} \xrightarrow[6h]{110^oC} \underset{\mathbf{6(a\text{-}e)}}{R_fSO_2N{=}CHAr}$$

Ar : C_6H_5 (**a**); p-$CH_3C_6H_4$ (**b**); 4-$CH_3OC_6H_4$ (**c**); 4-$O_2NC_6H_4$ (**d**); 3-$O_2NC_6H_4$ (**e**)

Benzophenone reacted similarly with compounds **2** to give diphenyl N-perfluoroalkanesulfonylimines:

$$\underset{\mathbf{2(a,e)}}{R_fSO_2N{=}SCl_2} + \underset{\mathbf{7}}{Ph_2C{=}O} \xrightarrow[8h]{130^oC} \underset{\mathbf{8(a,e)}}{R_fSO_2N{=}CPh_2}$$

Products **8** are not moisture sensitive as are the compounds **4** and **6**. They are stable when exposed to the air; however, in an acidic aqueous solution, compounds **8** are decomposed to the corresponding $R_fSO_2NH_2$ and **7**.

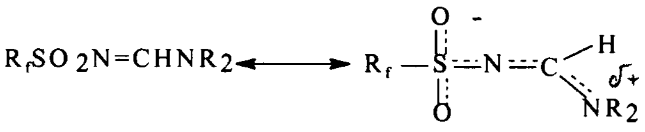
It was notable that relatively unreactive carbonyl compounds, DMF or DEF, reacted more easily with compounds **2** at room temperature. For example, stirring of a mixture of each **2** with DMF or DEF for 3 hours gave the respective N,N-dialkylperfluoroalkanesulfonylformimine **10** in good yield.

$$\underset{\mathbf{2(a\text{-}c)}}{R_fSO_2N{=}SCl_2} + \underset{\mathbf{9}}{HC(O)NR_2} \xrightarrow[3h]{r.t.} \underset{\mathbf{10,11(a\text{-}c)}}{R_fSO_2N{=}CHNR_2}$$

R : Me, (**10**); Et, (**11**)

In sharp contrast to other imines **4**, **6**, and **8**, compounds **10** and **11** are very stable, both under basic or acidic conditions, **10** and **11** not being hydrolyzed. Their stability should be attributed to the electron-donation properties of the R_2N- group resulting in electron delocalization in the molecules **10** and **11** (see Scheme 1).

X-ray diffraction analysis supported this point. The bond length of C-NR_2 (1.287 Å) is shorter than that of N=CH (1.336 Å), and both are shorter than the normal N–C single bond (1.47 Å) but longer than the normal N=C double bond (1.28 Å). The molec-



SCHEME 1

ular structure is shown in Figure 1, and the data of selected bond lengths and bond angles are shown in Tables 1 and 2.

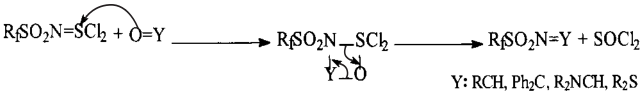
In this reaction, we also found a small amount of a by-product: $[Me_2N^+=CHOS(O)Cl]$. It is surprising that CH_3CONMe_2 has not reacted with **2**; even when heated to 80°C for 4 hours, no expected product, $R_fSO_2N=C(CH_3)NMe_2$, could be detected in the reaction mixture. Similar to the previous carbonyl reagents, dimethyl sulfoxide, having a polar $S=O$ bond, reacted readily with **2** at room temperature to form sulfilimines. In this reaction, a small amount of CH_3SCH_2Cl (20%) was also detected.

$$R_fSO_2N=SCl_2 + Me_2S=O \xrightarrow[5h\ CH_2Cl_2]{r.t.} R_fSO_2N=SMe_2 \quad (61\text{-}73\%)$$

2(a,c) **12** **13(a,c)**

Compounds **13** were obtained as colorless solids; recrystallation from CH_3CN gave stable crystalline materials. Similar to the formamidines **10**, the electron delocalization between the four-valent sulfur atom ($Me_2S=$) and the six-valent sulfur atom (R_fSO_2-) makes these compounds stable also.

We have suggested a four-membered ring intermediate for the condensation of N-sulfinyl perfluoroalkanesulfoneamines with compounds of type $Y=O$ [9]. By analogy with $R_fSO_2N=S=O$, the reaction of **2** with carbonyl reagents or DMSO would follow the same type of pathway:



It is well known that DMF reacts with $SOCl_2$ to give $[Me_2N^+=CHOS(O)Cl]^-$ [10]. By way of contrast, we found that CH_3SCH_2Cl was readily formed in the reaction of $SOCl_2$ with DMSO. The above-suggested reaction mechanism, that is, the formation of the four-membered intermediate and the elimination of $SOCl_2$, could explain the formation of the by-products, $[Me_2N^+=CHOS(O)Cl]^-$ and CH_3SCH_2Cl, in the reaction of **2** with DMF and DMSO.

TABLE 1 Selected Bond Lengths (Å) of Compound **10a**

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
I	C(1)	2.122(6)	S	O(1)	1.436(4)
S	O(2)	1.423(4)	S	N(2)	1.569(4)
S	C(4)	1.851(5)	F(1)	C(1)	1.337(6)
F(2)	C(1)	1.336(7)	F(3)	C(2)	1.336(7)
F(4)	C(2)	1.338(7)	F(5)	C(3)	1.324(7)
F(6)	C(3)	1.318(7)	F(7)	C(4)	1.344(6)
F(8)	C(4)	1.34(1)	O(3)	C(2)	1.375(7)
O(3)	C(3)	1.381(7)	N(1)	C(5)	1.287(7)
N(1)	C(6)	1.453(8)	N(1)	C(7)	1.460(8)
N(2)	C(5)	1.336(8)	C(1)	C(2)	1.519(8)

EXPERIMENTAL

Melting points and boiling points reported are uncorrected. Solvents were purified and dried before use. ^1H NMR (60 MHz), ^{13}C NMR (75.3 MHz), and ^{19}F NMR (54.6 MHz) spectra were recorded on a Varian-360L instrument or a Bruker AM-300 spectrometer with TMS and TFA ($\delta_{CFCl3} = \delta_{TFA} + 78.6$ ppm, and with upfield positive) as an internal and external standard, respectively. X-ray diffraction analyses were performed with a Rigaku AFC 7R Diffractometer. IR spectra were obtained with an IR-440 Shimadzu or Perkin-Elmen 983G spectrophotometer. Lower-resolution mass spectra and high-resolution mass spectra (HRMS) were obtained on a Finnigan GC-MS 4021 and Finnigan MAT-8430 instrument, respectively. Elemental analyses were performed by SIOC.

N,N-Dichloroperfluoroalkanesulfonylamines $R_fSO_2NCl_2$ (**1**) are prepared according to the literature method [11].

Preparation of $R_fSO_2N=SCl_2$ (**2**)

General Procedure. **1a** (1.7 g, 4.6 mmol) was injected slowly into a 25 mL flask containing sulfur powder (0.15 g, 4.6 mmol) and a magnetic stirring bar. An exothermal reaction occurred. After having been stirred at room temperature for 30 minutes this reaction mixture became homogenous and transparent. Vacuum distillation gave the product **2a** (2.0 g, 85%). Similarly, **2(b–e)** are prepared.

$ICF_2CF_2OCF_2CF_2SO_2N=SCl_2$ **2a.** ^{19}F NMR ($CDCl_3$) δ: -12.0 (ICF_2, s), 3.8 (OCF_2, t), 8.3 (CF_2O, m), 38.3 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 1390 (vs), 1340 (s), 1300 (s), 1240–1090 (vs), 990 (m), 920 (s), 770 (s), 690 (m), 610 (s). MS (m/e, %): 528/526/524 (M^+ $(2 \times {}^{37})d) + 1/M^+({}^{37}d) + 1/M^+({}^{35}d) + 1$),2.44/10.75/14.49), 488 ($M^+ - Cl$, 12.92), 404 ($M^+ - C_2F_5$, 4.64), 343 ($M^+ - SO_2NSCl_2$, 10.42), 296 ($M^+ - IC_2F_4$, 88.17), 227 ($ICF_2CF_2^+$, 100.00), 180 ($^+SO_2NSCl_2$, 16.61), 177 (ICF_2^+, 48.21), 102 (SCl_2^+, 1.26). Elemental analysis for $C_4F_8NO_3S_2Cl_2I$: calcd: C, 9.18; N, 2.68; F, 29.06%; found: C, 9.43; N, 2.92; F, 29.41%.

$HCF_2CF_2OCF_2CF_2SO_2N=SCl_2$ **2b.** ^1H NMR ($CDCl_3$) δ: 5.78 (HCF_2,t-t,$J_{HF}=51.6$ Hz). ^{19}F NMR ($CDCl_3$) δ (ppm): 4.0 (OCF_2, t), 12.0 (CF_2O, s), 38.7 (SO_2CF_2, s), 61.5 (HCF_2, d). IR (ν_{max}, cm^{-1}): 1420 (vs), 1360 (s), 1330 (s), 1260–1120 (vs), 1000 (s), 860 (m),

TABLE 2 Selected Bond Angles of Compound **10a**

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O(1)	S	O(2)	117.7(3)	O(1)	S	N(2)	115.2(3)
O(1)	S	C(4)	102.9(2)	O(2)	S	N(2)	109.9(3)
O(2)	S	C(4)	105.0(3)	N(2)	S	C(4)	104.4(2)
C(2)	O(3)	C(3)	121.4(4)	C(5)	N(1)	C(6)	121.7(5)
C(5)	N(1)	C(7)	121.0(5)	C(6)	N(1)	C(7)	117.3(5)
S	N(2)	C(5)	117.6(4)	I	C(1)	F(1)	109.9(4)
I	C(1)	F(2)	109.2(4)	I	C(1)	C(2)	114.7(4)
F(1)	C(1)	F(2)	107.4(5)	F(1)	C(1)	C(2)	107.4(5)
F(2)	C(1)	C(2)	108.0(5)	F(3)	C(2)	F(4)	106.7(5)
F(3)	C(2)	O(3)	11.6(5)	F(3)	C(2)	C(1)	109.7(5)
F(4)	C(2)	O(3)	110.5(5)	F(4)	C(2)	C(1)	109.2(5)
O(3)	C(2)	C(1)	109.1(5)	F(5)	C(3)	F(6)	108.4(5)
F(5)	C(3)	O(3)	110.1(5)	F(5)	C(3)	C(4)	109.3(5)
F(6)	C(3)	O(3)	112.2(5)	F(6)	C(3)	C(4)	110.6(5)
O(3)	C(3)	C(4)	106.1(5)	S	C(4)	F(7)	106.8(3)
S	C(4)	F(8)	107.6(4)	S	C(4)	C(3)	117.7(4)
F(7)	C(4)	F(8)	107.8(4)	F(7)	C(4)	C(3)	107.5(5)
F(8)	C(4)	C(3)	108.9(4)	N(1)	C(5)	N(2)	122.7(5)

770 (s), 710 (s), 650 (s). MS (m/e, %): 402/400/398 [$M^+(2 \times {}^{37}Cl) + 1/M^+({}^{37}Cl) + 1/M^+ ({}^{35}Cl) + 1$,2.03/10.21/22.14], 362 ($M^+ - Cl$, 20.3), 298 ($M^+H - C_2F_4$, 6.08), 281 ($HCF_2CF_2OCF_2CF_2SO_2^+$, 2.95), 198 ($M^+ - HC_4F_8$, 13.25), 180 ($SO_2NSCl_2^+$, 24.8), 167 ($HCF_2CF_2OCF_2^+$, 51.8), 101 ($HC_2F_4^+$, 86.9), 46 (NS^+, 100.00). HRMS for $C_4HF_8NS_2O_3Cl_2$: calcd: 361.8958; found: 361.8923.

$C_4F_9SO_2N{=}SCl_2$ **2c.** ^{19}F NMR ($CDCl_3$) δ: 3.7 (CF_3, t), 36.0 (SO_2CF_2, t), 43.7 (CF_2, s), 48.7 (CF_2, t). IR (ν_{max}, cm^{-1}): 1540 (m), 1392 (s), 1207–1152 (vs), 989 (m), 746 (m), 710 (m), 606 (m). MS (m/e, %): 364 ($M^+ - Cl$, 0.35), 219 ($C_4F_9^+$, 7.67), 180 ($^+SO_2N{=}SCl_2$, 2.85), 100 ($C_2F_4^+$, 40.38), 80 (SO_3^+, 100.00), 69 (CF_3^+, 87.01), 64 (SO_2^+, 48.20). Elemental analysis for $C_4F_9NO_2S_2Cl_2$: calcd: C, 12.03; N, 3.51; F, 42.86%; found: C, 12.33; N, 3.62; F, 42.61%.

$C_6F_{13}SO_2N{=}SCl_2$ **2d.** ^{19}F NMR ($CDCl_3$) δ: 3.7 (CF_3, t), 36.0 (SO_2CF_2, t), 43.7 (CF_2, s), 44.0 (m, 3 × CF_2). IR (ν_{max}, cm^{-1}): 1543 (m), 1402 (s), 1217–1132 (vs), 736 (m), 701 (m), 616 (m). MS (m/e, %): 499 (M^+, 3.35), 464 ($M^+ - Cl$, 7.67), 383 ($C_6F_{13}SO_2^+$, 100.00), 180 ($^+SO_2N{=}SCl_2$, 12.85), 69 (CF_3^+, 75.01), 64 (SO_2^+, 28.30). Elemental analysis for $C_6F_{13}NO_2S_2Cl_2$: calcd: C, 14.43; N, 2.81; F, 49.50%; found: C, 14.33; N, 2.62; F, 49.61%.

$C_8F_{17}SO_2N{=}SCl_2$ **2e.** ^{19}F NMR: 3.3 (s, CF_3), 36.2 (s, SCF_2), 33.0 (s, CF_2), 42.0 (s, CF_2), 44.0 (m, 3 × CF_2), 48.7 (s, CF_2). IR (ν_{max}, cm^{-1}): 1545 (w), 1414 (s), 1260–1103 (vs), 744 (s), 705 (s), 663 (s). MS (m/e, %): 600 (M^+H, 0.65), 500 ($M^+H - C_2F_4$, 5.60), 180 ($^+SO_2N{=}SCl_2$, 15.44), 169 ($C_3F_7^+$, 29.40), 131 ($C_3F_5^+$, 100.00), 119($C_2F_5^+$, 30.25), 116 ($^+N{=}SCl_2$, 1.30), 100 ($C_2F_4^+$, 54.75), 80 (SO_3^+, 41.50), 64 (SO_2^+, 29.88). Elemental analysis for $C_8F_{17}NO_2S_2Cl_2$: calcd: C, 16.03; N, 2.34; F, 53.92%; found: C, 16.35; N, 2.45; F, 53.73%.

Reaction of $R_fSO_2N{=}SCl_2$ **2** *with Chloral*

At room temperature, chloral (4 mL, 6.1 g) was injected into a 25 mL three-necked round-bottom flask containing $R_fSO_2N{=}SCl_2$ **2a** (2.6 g, 5 mmol) and equipped with a reflux condensor, drying tube, and magnetic stirring bar. After injection, the homogenous reaction mixture was heated to 100–110°C (oil bath) and stirred for 20 hours. Excess chloral was distilled, and the residue was then distilled under vacuum to give the crude product $I(CF_2)_2O(CF_2)_2$-SO_2 $N{=}CHCCl_3$ **4a** (1.2 g, 43%). Double distillation gave the pure sample for analysis. Compounds **4b** and **4c** were prepared similarly.

$I\ CF_2CF_2OCF_2CF_2SO_2N{=}CHCCl_3$ **4a.** ^1H NMR ($CDCl_3$): δ 8.30 (s, N=CH). ^{19}F NMR: δ −12.3 (s, ICF_2), 4.0 (s, OCF_2), 8.2 (s, CF_2O), 38.0 (s, SCF_2). IR (film)(ν_{max}/cm^{-1}): 1640 (m), 1445 (m), 1390 (s), 1340 (m), 1300 (m), 1230–1090 (vs), 990 (m), 910 (m), 870 (m), 800 (m). MS (m/e, %): 521/519/517 ($M^+(2 \times {}^{37}Cl) + 1 - Cl/M^+({}^{37}Cl) + 1 - Cl/M^+ ({}^{35}Cl) + 1 - Cl$, 6.61/33.39/46.84), 485/483 [$M^+(2 \times {}^{37}Cl) - 2 \times Cl/M^+({}^{37}Cl) - 2 \times Cl$, 1.17/3.20], 227 ($IC_2F_4^+$, 85.25), 210/208/206 [$M^+({}^{37}Cl)) - IR_f/M^+ - IR_f/M^+ - 2 -$

TABLE 3 Reaction Result of **2** with Carbonyl Compounds

Entry	*Reactants*	*Reaction Condition* T (°C)	t (h)	*Products*	*M.p. or B.p.* (°C)	*Yield* (%)
1	**2a** + 3	100	20	**4a**	93/2 torr	43
2	**2b** + 3	100	20	**4b**	55/2 torr	42
3	**2c** + 3	110	24	**4c**	60/2 torr	45
4	**2d** + 3	110	24	**4d**	75/2 torr	45
5	**2a** + **5a**	110	5	**6a**	142/2 torr	77
6	**2a** + **5b**	110	5	**6b**	45	77
7	**2a** + **5c**	110	6	**6c**	160	83
8	**2a** + **5d**	110	6	**6d**	125	73
9	**2a** + **5e**	140	6	**6e**	162/2 torr	78
10	**2a** + **7**	130	8	**8a**	170/2 torr	71
11	**2e** + **7**	130	8	**8e**	124/2 torr	69
12	**2a** + DMF[a]	15	3	**10a**	78–80	81
13	**2b** + DMF	15	3	**10b**	76	78
14	**2c** + DMF	15	3	**10c**	75	83
15	**2b** + DEF	15	3	**11b**	oil[b]	76
16	**2c** + DEF	15	3	**11c**	oil[b]	73
17	**2a** + DMSO	10	5	**13a**	54	73
18	**2c** + DMSO	10	5	**13c**	104	61

[a] Reaction **2** with DMF and DMSO were carried out in CH_2Cl_2.
[b] Purified by column chromatography and gave stick oil.

IR_f, 0.68/0.97/1.91), 177 (ICF_2^+, 42.25), 144/142/140 [$M^+(3 \times {}^{37}Cl) - IR_f - 2 \times Cl/M^+(2 \times {}^{37}Cl) - IR_f - 2 \times Cl/M^+({}^{37}Cl) - IR_f - 2 \times Cl$, 1.05/1.06/2.07], 144 ($^+N{=}CHCCl_3$, 1.05), 130 ($^+CHCCl_3$, 2.18), 117 ($^+C\ Cl_3$, 3.11), 114/112/110 [$M^+(2 \times {}^{37}Cl) + 1 - IR_fSO_2 - Cl/M^+({}^{37}Cl) + 1 - IR_fSO_2 - Cl/M^+ + 1 - IR_fSO_2 - Cl$, 11.82/68.52/100.00], 83 ($^+SO_2F$ or $HCCl_2^+$, 42.25), 64 (SO_2^+, 11.27). Elemental analysis for $C_6HCl_3F_8INO_3S$: calcd: C, 13.07; N, 2.53; F, 27.59%; found: C, 13.23; N, 2.25; F, 27.32%.

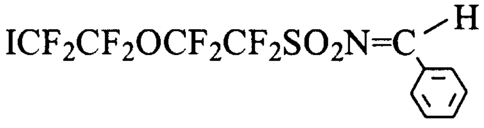
H $CF_2CF_2OCF_2CF_2SO_2N{=}CHCCl_3$ **4b.** ^1H NMR ($CDCl_3$) δ 8.40 (s, N=CH), 5.60 (t-t, $^2J_{H\text{-}F} = 54.0$ Hz). ^{19}F NMR: δ 4.0 (t, OCF_2), 11.5 (s, CF_2O), 38.3 (s, SCF_2), 61.0 (d, HCF_2, $^2J_{H\text{-}F} = 54.0$ Hz). ^{13}C NMR ($CDCl_3$) δ 172.642 (N=*C*H), 116.803 (t-t, SCF_2, $^1J_{C\text{-}F} = 284.93$ Hz, $^2J_{C\text{-}F} = 30.12$ Hz), 115.830 (t-t, CF_2, $^1J_{C\text{-}F} = 288.64$ Hz, $^2J_{C\text{-}F} = 30.27$ Hz), 113.028 (t-t, CF_2, $^1J_{C\text{-}F} = 301.54$ Hz, $^2J_{C\text{-}F} = 37.97$ Hz), 107.015 (t-t, HCF_2, $^1J_{C\text{-}F} = 253.43$ Hz, $^2J_{C\text{-}F} = 38.50$ Hz), 90.657 (*C*Cl_3). IR (film)(ν_{max}, cm^{-1}): 1644 (s), 1440 (s), 1394 (s), 1334 (m), 1292 (s), 1240–1137 (vs), 1064 (m), 1010 (m), 870 (m), 836 (m), 702 (m). MS (m/e, %): 430/428/426 [$M^+(2 \times {}^{37}Cl) + 1/M^+({}^{37}Cl) + 1/M^+({}^{35}Cl) + 1$, 4.78/13.65/13.65], 393/391 [$M^+({}^{37}Cl) + 1 - Cl/M^+ + 1 - Cl$, 1.04/1.51], 217 ($HR_f^+$, 3.98), 194/192 [$M^+({}^{37}Cl) + 1 - HC_2F_4O\text{-}CCl_3/M^+ + 1 - HC_2F_4O\text{-}CCl_3$, 18.31/14.87], 149/147($^+SO_2N{=}CHCCl + 2/{}^+SO_2N = CHCCl$, 2.37/1.25), 146/144 ($M^+ + 2 - HR_fSO_2/M^+ - HR_fSO_2$, 16.31/1.19), 130 ($^+CHCCl_3$, 2.39), 119 ($C_2F_5^+$, 100.00), 117 ($^+C\ Cl_3$, 19.16), 101 ($HC_2F_4^+$, 72.90), 84($^+N{=}CHCCl$, 16.01), 82 ($CCl_2^+$, 30.68). HRMS for $C_6H_2NO_3Cl_2F_8S$: Calcd: 389.9005; found: 389.8963.

$C_4F_9SO_2N{=}CHCCl_3$ **4c.** ^{1H} NMR ($CDCl_3$) ν 8.65 (s, N=CH). ^{19}F NMR: δ 4.0 (t, CF_3), 33.2 (t, SCF_2), 43.0 (s, CF_2) 48.2 (s, CF_2). IR (film)(ν_{max}, cm^{-1}): 1640 (s), 1460 (s), 1420 (s), 1360 (m), 1250–1180 (vs), 1140 (s), 1120 (m), 1030 (m), 1000 (m), 980 (w), 870 (m), 690 (m). MS (m/e, %): 432/430/428 [$M^+(2 \times {}^{37}Cl) + 1/M^+({}^{37}Cl) + 1/M^+ ({}^{35}Cl) + 1$, 4.77/13.45/13.32], 395/393 [$M^+({}^{37}Cl) + 1 - Cl/M^+ 1 - Cl$, 1.39/2.05], 246 ($M^+ - 1 - CF_2 - CHCCl_3$, 21.97), 219 ($C_4F_9^+$, 100.00), 169 ($C_3F_7^+$, 4.27), 131 ($M^+ + 1 - C_4F_9SO_2N$, 51.93), 119 ($C_2F_5^+$, 32.17), 117 ($^+CCl_3$, 17.52), 83 ($^+SO_2F$ or $HCCl_2^+$, 14.55), 64 (SO_2^+, 21.91). Elemental analysis for $C_6HF_9NO_2SCl_3$: calcd: C, 16.86; N, 3.28; F, 40.05%; found: C, 16.54; N, 3.30; F, 40.08%.

$C_6F_{13}SO_2N{=}CHCCl_3$ **4d.** ^1H NMR ($CDCl_3$) δ 8.20 (s, N=CH). ^{19}F NMR: δ 4.0 (t, CF_3), 33.8 (t, SCF_2), 42.6 (s, CF_2), 44.6 (s, CF_2), 45.8 (s, CF_2), 49.3 (s, CF_2). IR (film)(ν_{max}, cm^{-1}): 1650 (s), 1460 (s), 1390 (s), 1370 (m), 1250–1170 (vs), 1150 (s), 1060 (m), 790 (m), 690 (m). MS (m/e, %): 532/530/528 [$M^+(2 \times {}^{37}Cl) + 1/M^+({}^{37}Cl) + 1/M^+({}^{35}Cl) + 1$, 2.95/8.51/8.40], 495/493 [$M^+({}^{37}Cl) + 1 - Cl/M^+ + 1 - Cl$, 0.53/0.75], 402/400 [$M^+(2 \times {}^{37}Cl) + 1 - CHCCl_3/M^+({}^{37}Cl) + 1 - CHCCl_3$, 4.58/88.68], 319 ($C_6F_{13}^+$, 6.58), 169 ($C_3F_7^+$, 4.27), 131 ($M^+ + 1 - C_6F_{13}SO_2N$, 41.58), 119 ($C_2F_5^+$, 39.59), 117 ($^+CCl_3$, 7.02), 83 ($HCCl_2^+$, 14.55), 111 ($M^+ + 2 - C_6F_{13}SO_2 - Cl$, 24.46), 82 ($CCl_2^+$, 24.59), 80 ($SO_3^+$, 100.00), 69 ($CF_3^+$, 48.85), 64 ($SO_2^+$, 21.91). HRMS for $C_8H_2NO_2Cl_2Cl^*F_{13}S$: calcd: 529.8634; found: 529.8646.

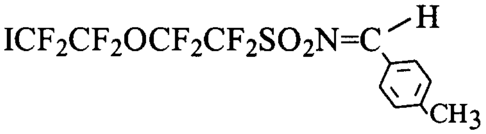
Reaction of $R_fSO_2N{=}SCl_2$ **2** *with Aromatic Aldehydes* **5** *and Benzophenone* **7**

Typical Reaction Process. Benzaldehyde (0.54 g, 5 mmol) was mixed with **2a** (2.62 g, 5 mmol) at room temperature. After having been stirred for 6 hours at 110°C, this reaction mixture was distilled under reduced pressure to give the product **6a** (2.0 g, 77%). The distillate became solid in the receiving flask at room temperature. Column chromatography tended to decompose this product. The pure product was obtained only by vacuum distillation.



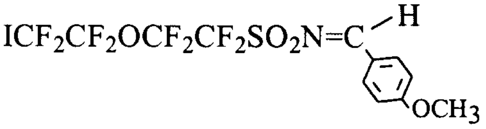
6a

^{1}H NMR($CDCl_3$) δ(ppm): 8.83 (1H, s), 7.62–7.70 (2ArH, m), 7.37–7.07 (3ArH, m). ^{19}F NMR ($CDCl_3$)δ(ppm): -11.5 (ICF_2, s), 4.5 (OCF_2, t), 8.5 (CF_2O, s), 40.0 (SO_2CF_2, s). IR (ν_{max}/cm^{-1}): 3030 (w), 1600 (s), 1560 (s), 1450 (m), 1360 (s), 1220–1120 (vs), 910 (m), 800 (s), 760 (m), 710 (w), 640 (m). MS (m/e, %): 512 (M^+H, 15.47), 384 ($M^+ - I$, 8.81), 320 ($M^+ - I - SO_2$, 0.56), 227 ($IC_2F_4^+$, 19.80), 168 ($^+SO_2N{=}CHC_6H_5$, 100.00), 104 ($^+N{=}CH\ C_6H_5$, 79.76), 77 ($C_6H_5^+$, 86.01), 64 (SO_2^+, 2.20). Elemental analysis for $C_{11}H_6F_8NO_3SI$: calcd: C, 25.83; H, 1.17; N, 2.74; F, 29.75%; found: C, 25.65; H, 1.42; N, 2.70; F, 29.41%.



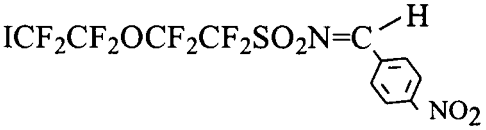
6b

^{1}H NMR: 2.46 (3H, s), 7.60 (AA′BB′, J_{AB} = 9 Hz, 4H), 9.05 (1H, s). ^{19}F NMR: -14.0 (ICF_2, s), 2.0 (OCF_2, t), 6.3 (CF_2O, s), 37.0 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 3030 (w), 2950 (m), 1680 (s), 1570 (vs), 1450 (m), 1360 (s), 1220–1100 (vs), 990 (m), 900 (s), 820 (s), 620 (m). MS (m/e, %): 526 (M^+H, 7.54), 525 (M^+, 3.66), 398 ($M^+ - I$, 4.18), 334 ($M^+ - I - SO_2$, 7.78), 296 ($IC_3F_7^+$, 1.78), 227 ($IC_2F_4^+$, 14.75), 182 ($^+SO_2N{=}CHC_6H_4CH_3$, 100.00), 118 ($^+N{=}CH\ C_6H_4CH_3$, 87.07), 91 ($C_6H_4CH_3^+$, 90.29). Elemental analysis for $C_{12}H_8F_8NO_3SI$: calcd: C, 27.43; H, 1.52; N, 2.67; F, 28.95%; found: C, 27.35; H, 1.43; N, 2.74; F, 29.04%.



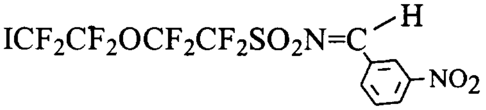
6c

^{1}H NMR: 3.98 (OCH_3, s), 7.48 (AA′BB′, J_{AB} = 9 Hz, 4H), 9.0 (1H, s). ^{19}F NMR: -13.5 (ICF_2, s), 2.5 (OCF_2, t), 7.0 (CF_2O, s), 38.0 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 2960 (m), 1600 (m), 1580 (s), 1550 (s), 1520 (m), 1430 (m), 1360 (s), 1200–1110 (vs), 990 (m), 1020 (m), 900 (s), 820 (s), 770 (m). MS (m/e, %): 542 (M^+H, 34.97), 541 (M^+, 19.62), 414 ($M^+ - I$, 4.84), 296 ($IC_3F_7^+$, 9.40), 227 ($IC_2F_4^+$, 14.42), 198 ($M^+ - IR_f$, 100.00), 134 ($^+N{=}CHC_6H_4OCH_3$, 90.36), 107 ($C_6H_4OCH_3^+$, 28.10), 92 ($C_6H_4O^+$, 22.96), 64 (SO_2^+, 26.25). Elemental analysis for $C_{12}H_8F_8NO_4SI$: calcd: C, 26.62; H, 1.48; N, 2.59; F, 28.10%. found: C, 26.73; H, 1.50; N, 2.53; F, 28.24%.



6d

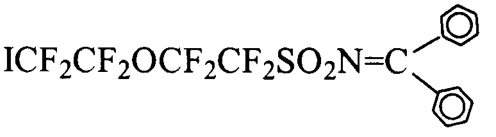
^{1}H NMR: 8.34 (AA′BB′, J_{AB} = 9 Hz, 4H), 9.25 ($N{=}CH$, s). ^{19}F NMR: -12.8 (ICF_2, s), 3.5 (OCF_2, t), 7.5 (CF_2O, s), 38.5 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 1610 (m), 1530 (s), 1380 (s), 1300 (s), 1220–1120 (vs), 1000 (s), 910 (s), 850 (m), 810 (s), 730 (m), 670 (m). MS (m/e, %): 556 (M^+, 6.53), 429 ($M^+ - I$, 100.00), 296 ($IC_3F_7^+$, 8.05), 227 ($IC_2F_4^+$, 46.48), 213 ($M^+ - IR_f$, 96.12), 150 ($M^+H - IR_fSO_2$, 77.28), 149 ($^+N{=}CHC_6H_4NO_2 - p$, 59.13), 135 ($M^+ - IR_fSO_2N$, 5.07), 119 ($C_2F_5^+$, 59.77). Elemental analysis for $C_{11}H_5F_8N_2O_5SI$: calcd: C, 23.74; N, 5.04; F, 27.34%. found: C, 23.79; N, 5.32; F, 27.41%.



6e

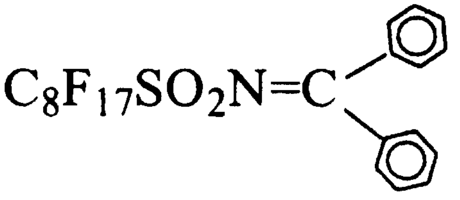
^{1}H NMR: 7.82 (1ArH, s), 8.32 ~ 8.60 (2ArH, s), 8.8 (1ArH, s), 9.22 ($N{=}CH$, s). ^{19}F NMR: -12.5 (ICF_2, s), 3.6 (OCF_2, t), 7.6 (CF_2O, s), 38.3 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 3030 (m), 1603 (s), 1571 (s), 1433 (m), 1356 (s), 1297–1202 (vs), 1097 (s), 806 (s), 736 (m), 690 (m). MS (m/e, %): 557 (M^+H, 38.69), 540

(M^+-O, 32.09), 429 (M^+-I, 67.03), 227 ($IC_2F_4^+$, 32.65), 213 (M^+-IR_f, 100.00), 149 ($^+N{=}CH$ $C_6H_4NO_2$ − m, 50.02), 135 ($M^+-IR_fSO_2N$, 6.44), 127 (I^+, 7.87), 122 ($^+C_6H_4NO_2$ − m, 6.71), 64 (SO_2^+, 30.20). HRMS (M^+) for $C_{11}H_5F_8IN_2O_5S$: calcd: 555.8835; found: 555.8875.



8a

^1H NMR: 7.48 (m, 10ArH). ^{19}F NMR: −12.6 (ICF_2, s), 3.0 (OCF_2, t), 8.0 (CF_2O, s), 39.0 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 3050 (w), 1580 (s), 1545 (vs), 1430 (s), 1360 (s), 1220–1110 (vs), 990 (m), 910 (s), 830 (s), 790 (m), 760 (m), 700 (s), 660 (m). MS (m/e, %): 588 (M^+H, 9.07), 522 ($M^+-C_5H_5$, 0.50), 460 (M^+-I, 0.55), 244 ($^+SO_2N{=}CPh_2$, 30.35), 227 ($IC_2F_4^+$, 4.70), 180 ($^+N{=}CPh_2$, 100.00), 177 ($IC_2F_4^+$, 4.20), 167 ($^+SO_2N{=}CPh$, 0.66), 166 ($^+CPh_2$, 0.68), 103 ($^+N{=}CPh$, 2.51), 77 (Ph^+, 36.32), 64 (SO_2^+, 2.42), 51 ($C_4H_3^+$, 13.05). HRMS (M^+) for $C_{17}H_{10}F_8INO_3S$: calcd: 586.9297; found: 586.9306.



8e

^1H NMR: 7.03 ~ 7.25 (m, 6ArH), 7.30 ~ 7.53 (m, 4ArH). ^{19}F NMR: 3.7 (CF_3, s), 35.0 (SO_2CF_2, t), 42.2 (CF_2, s), 44.4 (4 × CF_2, br), 48.7 (CF_2, s). IR (ν_{max}, cm^{-1}): 3062 (m), 1598 (m), 1578 (m), 1378 (s), 1320 (m), 1280–1154 (vs), 1032 (m), 924 (m), 814 (m), 704 (m). MS (m/e, %): 664 (M^+H, 5.16), 581 ($M^+-C_6H_{10}$, 1.03), 503 ($M^+-C_2F_5-C_3H_5$, 4.49), 219 ($C_4F_9^+$, 1.02), 244 (M^+ − C_8F_{17}, 16.15), 180 ($^+N{=}CPh_2$, 100.00), 167 ($^+SO_2N{=}CPh$, 1.20), 166 ($^+CPh_2$, 1.54), 103 ($^+N{=}CPh$, 2.04), 77 (Ph^+, 34.28), 69 (CF_3^+, 9.88). Elemental analysis for $C_{21}H_{10}F_{17}NO_2S$: calcd: C, 38.01; H, 1.51; N, 2.11; F, 48.72%. found: C, 38.23; H, 1.23; N, 2.34; F, 48.41%.

Reaction of $R_fSO_2N{=}SCl_2$ **2** *with DMF and DEF*

A mixture of **2a** (2.62 g, 5 mmol), DMF (5 mL), and CH_2Cl_2 (5 mL) was stirred at 15°C for 3 hours. After removal of the CH_2Cl_2 and excess DMF, the residue was washed with ice water; the solid was filtered off and dried. Recrystallization from a mixed solvent (CH_2Cl_2:CH_3CN = 1:1) gave fine crystals **10a** (1.9 g, 81%).

$ICF_2CF_2OCF_2CF_2SO_2N{=}CHN(CH_3)_2$ **10a.** ^1H NMR ($CDCl_3$) δ: 8.00 (N=CH, s), 3.27 (CH_3, s), 3.15 (CH_3, s). ^{19}F NMR ($CDCl_3$): −13.0 (ICF_2, s), 3.5 (OCF_2, t), 7.5 (CF_2O, m), 39.0 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 2980 (w), 1630 (s), 1420 (s), 1340 (s), 1220–1100 (vs), 990 (m), 910 (s), 850 (m), 760 (m), 720 (m), 620 (s). MS (m/e, %): 479 (M^+H, 0.63), 395 (M^+-F-SO_2, 0.32), 359 ($M^+-C_2F_5$, 0.22), 351 (M^+-I, 2.18), 227 ($IC_2F_4^+$, 4.04), 177 (ICF_2^+, 4.12), 135 ($^+SO_2N{=}CHNMe_2$, 100.00), 119 ($C_2F_5^+$, 13.49), 100 ($C_2F_4^+$, 8.52), 91 ($^+SO_2N{=}CH$, 0.59), 71 ($^+N{=}CHNMe_2$, 13.83).

$HCF_2CF_2OCF_2CF_2SO_2N{=}CHN(CH_3)_2$ **10b.** ^1H NMR ($CDCl_3$) δ: 7.92 (N=CH, s), 5.85 (HCF_2, t-t, J_{HF} = 54.0 Hz), 3.10 (CH_3, s), 3.0 (CH_3, s). ^{19}F NMR ($CDCl_3$) δ: 4.0 (OCF_2, s), 11.2 (CF_2O, s), 40.0 (SO_2CF_2, s), 60.3 (HCF_2, d). IR (ν_{max}, cm^{-1}): 3022 (s), 1647 (s), 1437 (s), 1429 (s), 1335 (s), 1285 (s), 1200–1131 (vs), 996 (vs), 860 (s), 752 (s), 698 (s). MS (m/e, %): 353 (M^+H, 37.33), 336 (M^+-H-CH_3, 0.70), 333 (M^+-F, 1.43), 269 (M^+-F-SO_2, 2.59), 135 ($^+SO_2N{=}CHMe_2$, 100.00), 119 ($C_2F_5^+$, 21.62), 101 ($HC_2F_4^+$, 8.20), 71 ($^+N{=}CHNMe_2$, 16.53), 44 (NMe_2^+, 32.27). Elemental analysis for $C_7H_8F_8N_2O_3S$: calcd: C, 23.88; H, 2.27; N, 7.96; F, 43.18%. found: C, 23.45; H, 2.23; N, 7.92; F, 43.41%.

$C_4F_9SO_2N{=}CHN(CH_3)_2$ **10c.** ^1H NMR ($CDCl_3$) δ: 8.02 (N=CH, s), 3.15 (CH_3, s), 3.25 (CH_3, s). ^{19}F NMR ($CDCl_3$) δ: 3.0 (CF_3, s), 35.8 (SO_2CF_2, t), 43.5 (CF_2, s), 48.4 (CF_2, t). IR (ν_{max}, cm^{-1}): 2980 (w), 1650 (s), 1480 (w), 1420 (s), 1340 (s), 1240–1160 (vs), 1030 (m), 1010 (m), 940 (s), 860 (m), 820 (m), 800 (m), 720 (m), 660 (m). MS (m/e, %): 296 ($M^+-H-CHNMe_2$, 2.90), 256 (M^+H − CF_3 − 2 × Me, 6.71), 219 ($C_4F_9^+$, 3.45), 135 ($^+SO_2N{=}CHNMe_2$, 100.00), 71 ($^+N{=}CHNMe_2$, 33.08), 69 (CF_3^+, 33.7), 44 (NMe_2^+, 64.59). Elemental analysis for $C_7H_7F_9N_2O_2S$: calcd: C, 23.73; H, 1.98; N, 7.91; F, 48.31%. found: C, 23.82; H, 2.04; N, 7.92; F, 48.41%.

$HCF_2CF_2OCF_2CF_2SO_2N{=}CHN(CH_2CH_3)_2$ **11b.** ^1H NMR ($CDCl_3$) δ: 7.90 (N=CH, s), 5.85 (HCF_2, t−t, J_{HF} = 54.0 Hz), 3.30–3.63 (2 × CH_2, m), 1.0–1.35 (2 × CH_3, m). ^{19}F NMR ($CDCl_3$) δ: 4.0 (OCF_2, s), 11.3 (CF_2O, s), 40.3 (SO_2CF_2, s), 61.0 (HCF_2, d). IR (ν_{max}, cm^{-1}): 2980 (m), 1628 (vs), 1452 (s), 1351 (s), 1340 (vs), 1285–1180 (vs), 997 (s), 963 (s), 895 (s), 861 (m), 797 (s), 774 (s), 752 (s). MS (m/e, %): 381 (M^+H, 58.67, 361 (M^+ − F, 20.3), 337 ($M^+H-CH_3-C_2H_5$, 4.17), 297 (M^+-F-SO_2, 2.36), 163 ($^+SO_2N=CHNEt_2$, 100.00), 119 (C_2F_5+, 8.58), 99 ($^+N=CHNEt_2$, 16.53). Elemental analysis for $C_9H_{12}F_8N_2O_3S$: calcd: C, 28.42; H, 3.18; N, 7.36%. found: C, 28.33; H, 3.08; N, 7.22%.

$C_4F_9SO_2N=CHN(CH_2CH_3)_2$ **10b.** ^1H NMR ($CDCl_3$) δ: 8.0 (N=CH, s), 3.33–3.64 (2 × CH_2, m), 1.1–1.35 (2 × CH_3, m). ^{19}F NMR ($CDCl_3$) δ: 3.7 (CF_3, t), 36.0 (SO_2CF_2, t), 43.7 (CF_2, s), 48.7 (CF_2, t). IR (ν_{max}, cm^{-1}): 2980 (m), 1640 (vs), 1440 (s), 1360 (s), 1240–1110 (vs), 1030 (m), 960 (s), 890 (m), 779 (m), 730 (m). MS (m/e, %): 383 (M^+H, 52.55), 363 (M^+ − F, 2.08), 339 ($M^+H-CH_3-C_2H_5$, 3.32), 299 (M^+-F-SO_2, 4.24), 219 ($C_4F_9^+$, 2.74), 163 ($^+SO_2N=CHNEt_2$, 100.00), 147 ($M^+-C_4F_9-O$, 13.72), 99 ($^+N=CHNEt_2$, 16.53), 72 (NEt_2^+, 50.79), 69 (CF_3^+, 19.97), 64 (SO_2^+, 3.11). Elemental analysis for $C_9H_{11}F_9N_2O_2S$: calcd: C, 28.27; H, 2.88; N, 7.33; F, 44.76%. found: C, 28.35; H, 2.73; N, 7.42; F, 44.41%.

Reaction of $R_fSO_2N=SCl_2$ **2** *with DMSO*

A mixture of **2a** (2.62 g, 5 mmol), CH_2Cl_2 (5 mL) and DMSO (5 mL) in a 25 mL round flask was stirred at 10°C for 5 hours. After removal, the solvent (CH_2Cl_2), ice water (10 mL), was poured into the flask to give the crude product **13a** (1.8 g, 73%). Recrystallation from CH_3CN gave the pure sample.

$ICF_2CF_2OCF_2CF_2SO_2N=SMe_2$ **13a.** ^1H NMR ($CDCl_3$) δ: 2.83 (CH_3, s). ^{19}F NMR ($CDCl_3$) δ: −12.6 (ICF_2, s), 4.0 (OCF_2, s), 8.0 (CF_2O, s), 39.0 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 1300 (vs), 1080–1200 (vs), 1030 (s), 960 (s), 910 (s), 800 (m), 760 (s), 740 (s). MS (m/e, %): 484 (M^+H, 0.93), 356 (M^+-I, 3.08), 227 ($ICF_2CF_2^+$, 7.98), 140 ($^+SO_2N=SME_2$, 100.00), 124 ($^+SON=SMe_2$, 9.97), 76 ($^+N=SMe_2$, 42.95). Elemental analysis for $C_6H_6F_8NO_3S_2I$: calcd: C, 14.91; H, 1.24; N, 2.90; F, 31.47%. found: C, 14.87; H, 1.23; N, 2.92; F, 31.41%.

$C_4F_9SO_2N=SMe_2$ **13c.** ^1H NMR ($CDCl_3$) δ: 2.87 (CH_3, s). ^{19}F NMR ($CDCl_3$) δ: 4.5 (CF_3, s), 36.6 (CF_2, m), 44.5 (CF_2, m), 49.3 (SCF_2, s). IR (ν_{max}, cm^{-1}): 2980 (w), 1420 (w), 1340 (m), 1320 (s), 1240–1120 (vs), 1040 (m), 970 (s), 860 (m), 740 (m), 680 (w), 580 (m). MS (m/e, %): 359 (M^+, 21.18), 225 ($M^+-C_2F_5-CH_3$, 58.73), 213 ($M^+H-CF_3SO_2N$, 14.93), 147 ($CF_3SO_2N^+$, 48.20), 140 ($^+SO_2N=SMe_2$, 13.90), 125 ($^+SO_2N=SMe$, 8.59), 124 ($^+SON=SMe_2$, 18.57), 119 ($C_2F_5^+$, 9.40), 114 ($^+SO_2CF_2$, 1.69), 110 ($SO_2N=S^+$, 5.48), 61 (^+NSMe, 4.39). Elemental analysis for $C_6H_6F_9NO_2S_2$: calcd: C, 20.06; H, 1.67; N, 3.90; F, 47.63%. found: C, 20.35; H, 1.63; N, 3.92; F, 47.41%.

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