Articles

Reactions of Bis(trifluoromethyl)sulfoxydifluoride with Nitrogen or Oxygen Nucleophiles

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The reactions of bis(trifluoromethyl)sulfoxy difluoride with secondary amines give high yields of bis(trifluoromethyl)sulfoxyamines, $(CF_3)_2S(O)(NR_2)_2$ where $R_2N = (CH_3)_2N$, $(C_2H_5)_2N$, $\overline{\mathrm{NCH_2CH_2CH_2CH_2CH_2}}$, and $\overline{\mathrm{CH_2CH_2NCH_2CH_2N}}\mathrm{CH_3}$. With *N*,*N'*-dimethylethylenediamine a 1:2 reaction occurs to form $(CF_3)_2S(O)[N(CH_3)CH_2CH_2N(CH_3)H]_2$ whereas with ethylene glycol the reaction stoichiometry is 1:1 with concomitant cyclization to give $(CF_3)_2\overline{\mathrm{S(O)OCH_2CH_2O}}$. Sulfoximides $(CF_3)_2S(O){=}NR$ [$R = CH_2CF_3$, $C(CH_3)_3$ and CH_2CH_2OH] result from reaction with primary amines. With primary diamines, bis(sulfoximides), $(CF_3)_2S(O){=}N(CH_2)_nN{=}S(O)(CF_3)_2$ ($n = 2, 3$), form. The reaction products of $(CF_3)_2S(O)F_2$ with various nucleophiles are compared with those found for other simple fluorine-containing S(VI) compounds.

Introduction

The complexity of or the number of steps required in the synthesis of a compound very often is the determining factor in the extent to which its reaction chemistry is investigated. Attempts to prepare perfluoroalkyl derivatives of sulfur oxytetrafluoride by fluorination of (trifluoromethyl)sulfinyl fluoride with elemental fluorine result in a variety of products but cleavage of the C–S bond occurs to give CF_4 as a major reaction product.[2,3] However, thionyl fluoride is oxidatively fluorinated to thionyl tetrafluoride with chlorine fluoride.[4] By taking advantage of this methodology, we were able to report the initial synthesis of $(R_f)_2S(O)F_2$ via a high yield, albeit, multistep, synthetic route, *viz.*

$$CCl_3SCl \xrightarrow[\text{NaF}]{\text{TMSO}} CF_3SCl^{5}$$

$$CF_3SCl + AgOC(O)R_f \rightarrow CF_3SOC(O)R_f^{6}$$

$$CF_3SOC(O)R_f \xrightarrow[\text{or } \Delta]{h\nu} CF_3SR_f + CO_2$$

$$CF_3SR_f + 2ClF \xrightarrow{-78\ ^\circ\mathrm{C}} CF_3SF_2R_f$$

$$CF_3SF_2R_f + HCl \xrightarrow{\text{Pyrex}} CF_3S(O)R_f$$

$$CF_3S(O)R_f + 2ClF \xrightarrow{-78\ ^\circ\mathrm{C}} R_f(CF_3)S(O)F_2^{7}$$

$$R_f = CF_3,\ C_2F_5,\ C_3F_7,\ {-}CF_2CF_2CF_2CF_2{-}$$

When the latter reaction is carried out at higher temperature, the yields of the bis(perfluoroalkyl)sulfoxy difluorides decrease with a concomitant increase in the degree of C–S bond cleavage. Further fluorination or chlorofluorination of these oxydifluorides did not occur since addition across the sulfur–oxygen double bond normally requires a catalyst, such as an alkali metal fluoride.[8,9] Elemental fluorine also oxidatively fluorinates RR'SO to $RR'S(O)F_2$ ($R = R' = C_6H_5$; $R = R' = p\text{-}FC_6H_4$) in CCl_3F.[10] Now, by using the methodology of Farnham and others,[11,12] $(CF_3)_2S(O)F_2$ can be readily obtained in a two-step synthesis

$$SOF_2 + 2CF_3SiR_3 \xrightarrow[-2R_3SiF]{F^-} (CF_3)_2SO$$

$$(CF_3)_2SO \xrightarrow[-Cl_2]{2ClF} (CF_3)_2S(O)F_2^{13}$$

As is typical of sulfur–fluorine bonds in sulfur(VI) compounds (except SF_6), $(CF_3)_2S(O)F_2$ is susceptible to nucleophilic attack by a variety of moieties. In particular, much attention has been directed to reactions of sulfoxy(VI) difluorides with ammonia and amines.[14-19] The reactions of bis(perfluoroalkyl)sulfoxy difluorides with ammonia provide a direct route to the synthesis of bis(perfluoroalkyl)sulfoximines

where $R_f = R_f' = CF_3$ or C_2F_5 or where $R_f = CF_3$ and $R_f' = C_2F_5$.[20] Under similar conditions without solvent, sulfur oxytetrafluoride reacts with ammonia to give polymers.[21,22] Since dehydrofluorination can not occur with the bis(perfluoro-

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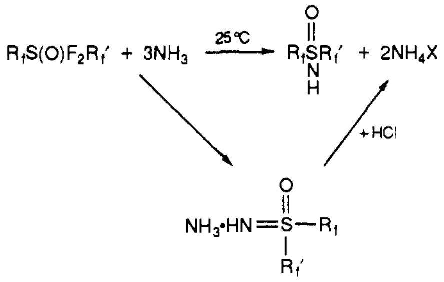


alkyl)sulfoximines, polymerization does not happen. However, in all cases, a white sublimable solid is formed. This solid is believed to have the formula $(R_f)_2S(O)NH{\cdot}NH_3$, analogous to the solid isolated in the reaction of ammonia with sulfur oxytetrafluoride.[20] However, the free bis(perfluoroalkyl)sulfoximines are produced quantitatively when the sublimable solid is treated with anhydrous hydrogen chloride.

The reaction of bis(trifluoromethyl)sulfoximine with labile chlorides proceeds smoothly at -20 °C in the presence of tertiary amines which provide the driving force for the formation of quatenary ammonium chlorides. Reactions with cyanogen chloride, trimethylchlorosilane, and (trifluoromethyl)sulfenyl chloride proceed similarly to yield the appropriate N-substituted bis(trifluoromethyl)sulfoximine.

$$R_fCl + (CF_3)_2S(O)NH \xrightarrow[-20\,^\circ C]{R_3N} R_fN{=}S(O)(CF_3)_2$$

$$R_f = CF_3S,\ CN,\ (CH_3)_3Si$$

With acid fluorides, NaF is used to remove HF. Although trace amounts of products are observed in the reaction without NaF, the presence of a base greatly enhances the yield. Reaction of bis(trifluoromethyl)sulfoximine with (trifluoromethyl)sulfinyl fluoride or acetyl fluoride in the presence of dry NaF proceeds smoothly at room temperature to give the products in high yield.

$$R_fF + (CF_3)_2S(O)NH \xrightarrow{NaF} R_fN{=}S(O)(CF_3)_2$$

$$R_f = CF_3C(O),\ CF_3S(O)$$

Bis(trifluoromethyl)sulfoximine reacts with silver(I) oxide in benzene solution to form the silver salt $AgN{=}S(O)(CF_3)_2$[23,24]

$$2(CF_3)_2S(O)NH + Ag_2O \xrightarrow[25\,^\circ C]{benzene} 2AgN{=}S(O)(CF_3)_2 + H_2O$$

which when reacted with methyl iodide produces *N*-methylbis(trifluoromethyl)sulfoximine. This is identical with a sample produced when bis(trifluoromethyl)sulfoxy difluoride reacts with methylamine. With elemental chlorine at 25 °C, *N*-chlorobis(trifluoromethyl)sulfoximine is formed.

$$AgN{=}S(O)(CF_3)_2 + CH_3I \xrightarrow[25\,^\circ C]{} (CF_3)_2S(O)NCH_3 + AgI$$

$$AgN{=}S(O)(CF_3)_2 + Cl_2 \xrightarrow[25\,^\circ C]{} (CF_3)_2S(O)NCl + AgCl$$

In this paper, we have extended the study of the reactions of $(CF_3)_2S(O)F_2$ to primary and secondary mono- and diamines and alcohols in the presence of a base or, in some cases, as their silylated derivatives.

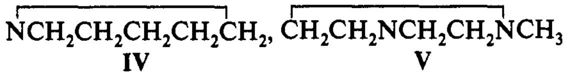
Results and Discussion

Although $(CF_3)_2S(O)F_2$ was prepared 2 decades ago and the reaction chemistry of its imine derivatives has been examined,[7,20] little is available concerning the reactions of the compound itself. We now report further studies based on the susceptibility of $(CF_3)_2S(O)F_2$ to nucleophilic attack to give a variety of products some of which are unexpected.

The reactions of bis(trifluoromethyl)sulfoxy difluoride (I) with secondary amines give bis(trifluoromethyl)sulfoxyamines in essentially quantitative yields in the presence of NaF, *viz.*,

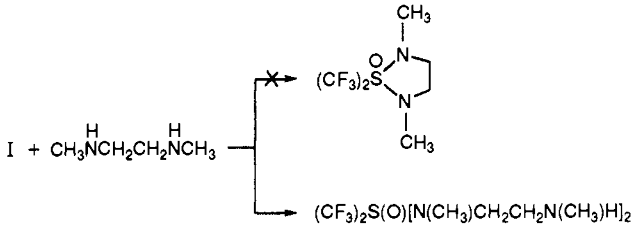
$$\underset{\mathbf{I}}{(CF_3)_2S(O)F_2} + R_2NH \xrightarrow[-HF]{NaF} (CF_3)_2S(O)(NR_2)_2$$

$$R_2N = \underset{\mathbf{II}}{(CH_3)_2N},\ \underset{\mathbf{III}}{(C_2H_5)_2N},$$



IV **V**

Purification is carried out by trap-to-trap distillation. Compounds **II**–**IV** are slightly volatile and are stopped in traps at -20, -20, and -60 °C, respectively, while **V** is nonvolatile and was extracted from the reaction mixture with carbon tetrachloride. In an attempt to obtain a stable cyclic heteroatom compound, we extended our study to a diamine, *N,N'*-dimethylethylenediamine. However, cyclization does not occur under any conditions tried.



VI

Compound **VI** is a nonvolatile, stable yellow liquid whose acyclic structure is confirmed by elemental analysis and spectral data. Steric hindrance by the methyl group may prohibit cyclization in this case. In contrast to this secondary diamine, as will be seen below, primary diols behave quite differently.

A few sulfoximides have been prepared from the reaction of **I** with CH_3NH_2 or from $(CF_3)_2S(O){=}NM$ (M = H, Ag) with compounds that have electropositive centers. In addition, we have also demonstrated that compounds such as $(CF_3)_2(CF_3O)_2S(O)$ with primary amines[25] and $(R_f)_2S{=}NR$ with *m*-chloroperbenzoic acid[26] are routes to sulfoximides. The extension of the reaction of **I** with more highly substituted primary amines allows preparation of mono and bis(sulfoximides), e.g.,

$$\mathbf{I} + H_2NR \xrightarrow{NaF} (CF_3)_2S(O){=}NR$$

$$R = \underset{\mathbf{VII}}{CH_2CF_3},\ \underset{\mathbf{VIII}}{C(CH_3)_3},\ \underset{\mathbf{IX}}{CH_2CH_2OH}$$

In general, the products are formed in rather small yield and when purified via trap-to-trap are retained in the trap at -78 °C.

When the reaction stoichiometry used is two parts of **I** to one part of a diamine, bis(sulfoximides) are obtained.

$$\mathbf{I} + H_2N(CH_2)_nNH_2 \rightarrow (CF_3)_2S(O){=}N(CH_2)_nN{=}S(O)(CF_3)_2$$

$$n = 2\ (\mathbf{X}),\ 3\ (\mathbf{XI})$$

All of the sulfoximides are stable, colorless liquids which may be stored at 25 °C in Pyrex glass indefinitely.

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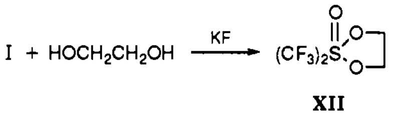
Table I. Reactions of Nucleophiles with Fluorinated S(VI) Compounds

	products from nucleophiles			
reactants	$HNCH_2CH_2CH_2CH_2CH_2$	CF_3CH_2OH	R_3SiCN	R_2NSiR_3
$(CF_3)_2S(O)F_2$	$(CF_3)_2S(O)(NCH_2CH_2CH_2CH_2CH_2)_2$[a] substitution	$(CF_3)_2SO_2$[a] substitution	$(CF_3)_2SO_2$, $(CF_3)_2SO$, $(CF_3)_2S$[a] reduction	$(CF_3)_2S(O)(NR_2)_2$[a] substitution
CF_3SF_4Cl	$CF_3S(NCH_2CH_2CH_2CH_2CH_2)_2Cl$[b] reduction	$CF_3S(OCH_2CF_3)_2Cl$[b] reduction	$CF_3SF_2(CN)_2Cl$[c] substitution	$CF_3S(NR_2)_2Cl$[d] reduction
SF_5Cl		$FS(OCH_2CF_3)_2Cl$[a] reduction	$S(CN)_2$[c] reduction	R_2NSF_4Cl[d] substitution

[a] This work. [b] Reference 28. [c] Kumar, R. C.; Shreeve, J. M. *Z. Naturforsch.* **1981**, *36B*, 1407. [d] Kitazume, T.; Shreeve, J. M. *J. Am. Chem. Soc.*, **1977**, *99*, 3690.

It is particularly interesting to compare the reactions of I under identical conditions with $CH_3N(H)CH_2CH_2N(H)CH_3$ and with $H_2NCH_2CH_2OH$ to form compounds **VI** and **IX**, respectively, with that of I with ethylene glycol where cyclization occurs smoothly.



XII

After extracting the residue with CCl_4 and evaporating the solvent to leave a colorless liquid (fp 17 ± 1 °C), compound **XII** is found in ~57% yield. With $H_2NCH_2CH_2OH$, reaction only occurs at the nitrogen–hydrogen bond. With CF_3CH_2OH (either in the presence of $(C_2H_5)_3N$ or as the lithium derivative), I reacts smoothly to form $(CF_3)_2SO_2$.[27] When SF_5Cl is reacted with CF_3CH_2OH, reduction with concomitant defluorination results to form $FS(OCH_2CF_3)_2Cl$ (**XIII**). This behavior is identical to that observed when CF_3SF_4Cl is reduced and defluorinated in reaction with CF_3CH_2OH.[28]

Various trimethylsilyl compounds have been used as nucleophilic reagents with compounds which contain sulfur–fluorine bonds. For example, in the reaction of I with $(CH_3)_3SiN(CH_3)_2$, **II** is obtained at 25 °C in reasonable yield. However, when I is reacted with $(CH_3)_3SiCF_3$ and $(CH_3)_3SiCN$, only a variety of decomposition products are obtained, e.g., $(CF_3)_2SO_2$, $(CF_3)_2SO$, $(CF_3)_2S$, $(CH_3)_3SiF$, and other unidentified materials.

These results make it worthwhile to point out the very great variability in behavior of polyfluoro- or poly(fluoroalkyl)sulfur(VI) compounds toward common reagents, as given in Table I.

While it might be expected that there would be greater similarity between the reaction chemistry of CF_3SF_4Cl and SF_5Cl, with these limited data for $(CH_3)_3SiX$ (X = CN, NR_2), $(CF_3)_2S(O)F_2$ and SF_5Cl undergo reduction when X = CN and substitution when X = NR_2. With the same reagents and CF_3SF_4Cl, a reversal of the chemistry observed takes place; i.e., when X = CN substitution occurs, and reduction occurs when X = NR_2.

Experimental Section

Materials. The starting materials, i.e., 2,2,2-trifluoroethylamine, 2,2,2-trifluoroethanol, *tert*-butylamine, dimethylamine, diethylamine, *N,N'*-dimethylethylenediamine, *N*-methylpiperazine, ethylenediamine, piperazine, 1,3-diaminopropane, 2-aminoethanol, dimethyl(trimethylsilyl)amine, and sodium fluoride were purchased and used as received. Bis(trifluoromethyl)sulfur oxydifluoride[7] and SF_5Cl[29] were prepared *via* the literature methods.

General Procedures. A Bruker NR200 Fourier transform NMR spectrometer was used to obtain ^{19}F and ^1H NMR spectra with $CFCl_3$ and $(CH_3)_4Si$ as external references, respectively, and $CDCl_3$ as solvent. By using a VG-7070 mass spectrometer, chemical and electron impact ionization mass spectra were recorded. Infrared spectra were obtained by using a Perkin-Elmer Model 1700 Fourier transform infrared spectrometer. Volatile compounds were manipulated in a standard Pyrex glass vacuum line equipped with Heise–Bourdon tube and Televac micron thermocouple gauges.

The preparation of **II–VI** is as follows: Sodium fluoride (12 mmol) and the dialkylamine (5 mmol) are placed in a 500-mL flask equipped with a Teflon stopcock. The flask is cooled to −196 °C, evacuated, and bis(trifluoromethyl)sulfoxy difluoride (5 mmol) is introduced. After 24 h were allowed for a gradual warm up from −78 to +25 °C, the contents of the flask are separated by trap-to-trap distillation or extracted as a pale yellow liquid from the nonvolatile residue with CCl_4, filtered, and the solvent evaporated.

II. $(CF_3)_2S(O)[N(CH_3)_2]_2$ (Stops in a Trap at −20 °C). Spectral data are as follows. Infrared (KBr, capillary film): 2938 s, 2839 m, 1485 sh, 1474 sh, 1461 s, 1439 sh, 1387 m, 1327 s, 1281 s, 1227 s, 1170 s, 1142 s, 1060 w, 966 sh, 870 sh, 767 w, 755 w, 716 w, 686 sh, 613 sh, 594 w cm^{-1}. NMR: ^{19}F δ −73.0 (m) ppm; ^1H δ 2.98 (m) ppm. MS (CI) [*m/e* (species), intensity]: 205 ($M^+ - CF_3$), 1.2; 191 ($CF_3SON_2C_3H_9^+ + 1$), 100; 189 ($CF_3SON_2C_3H_8^+$), 24.3; 162 ($CF_3SONC_2H_6^+ + 1$), 5.1; 161 ($CF_3SONC_2H_6^+$), 1.6; 137 ($SON_2C_4H_{12}^+ + 1$), 1.3; 135 ($SON_2C_4H_{11}^+$), 2.0; 123 ($CFSONC_2H_6^+$), 19.2; 122 ($SON_2C_3H_{10}^+$), 25.7; 121 ($SON_2C_3H_9^+$), 100; 117 (CF_3SO^+), 1.6; 92 ($SONC_2H_6^+$), 100; 76 (N_2SO^+), 7.0; 69 (CF_3^+), 100. Anal. Calcd for $C_6H_{12}F_6N_2OS$: C, 26.27; H, 4.37. Found: C, 25.41; H, 4.65.

III. $(CF_3)_2S(O)(N(C_2H_5)_2)_2$ (Stops in a Trap at −20 °C). Spectral data are as follows. Infrared (KBr, capillary film): 2930 s, 2900 m, 1655 m, 1561 m, 1485 s, 1474 s, 1461 s, 1439 s, 1386 s, 1327 s, 1281 s, 1229 s, 1281 s, 1229 s, 1171 s, 1141 s, 1116 s, 1060 m, 955 s, 870 sh, 787 m, 755 m, 716 m, 686 s, 613 s, 594 m, 547 s cm^{-1}. NMR: ^{19}F δ −73.0 (s) ppm; ^1H δ 2.72 (q, 2H, J = 2.74 Hz) CH_2, 1.15 (t, 3H) CH_3. MS (CI) [*m/e* (species), intensity]: 261 ($M^+ - CF_3$), 1.3; 260 ($M^+ - CF_3H$), 4.7; 246 ($M^+ - C_2F_3H_3^+$), 27.4; 203 [$CF_3S(O)N_2(C_2H_5)_2^+$], 15.3; 189 [$CF_3S(O)N(C_2H_5)_2$], 54.8; 119 [$S(O)NC_4H_9^+$], 45.2; 69 (CF_3^+), 14.3.

IV. $(CF_3)_2S(O)(NCH_2CH_2CH_2CH_2CH_2)_2$ (Stops in a Trap at −60 °C). Spectral data are as follows. Infrared (gas, KBr disks): 3035 m, 2990 m, 1481 m, 1376 s, 1283 m, 1253 s, 1210 m, 1151 s, 1112 s, 1029 w, 950 w, 911 w, 822 m, 721 s, 700 m, 629 s, 405 s, cm^{-1}. NMR: ^{19}F δ −76.1 (s); ^1H δ 3.42 (4H) $(CH_2)_2N$, 1.32 (6H) $(CH_2)_3$. MS (CI) [*m/e* (species), intensity]: 353 ($M^+ - H$), 0.4; 307 ($M^+ - C_2H_4F$), 0.7; 267 ($M^+ - CF_4 + 1$), 1.1; 247 ($M^+ - C_5H_9F_2$), 7.8; 216 ($M^+ - 2CF_3$), 1.0; 203 ($M^+ - C_3F_6H$), 26.2; 201 ($M^+ - C_6H_{10}F_3N$), 1.8; 186 [$(CF_3)_2SO^+$], 2.0; 185 ($C_6H_{10}F_3NS^+$), 2.3.

V. $(CF_3)_2S(O)(CH_2CH_2NCH_2CH_2NCH_3)_2$ (Nonvolatile Liquid). Spectral data are as follows. Infrared (KBr, capillary film): 2924 m, 2846 sh, 2801 m, 1560 m, 1509 m, 1457 sh, 1391 s, 1373 m, 1322 sh, 1289 s, 1002 m, 965 m, 945 m, 853 w, 780 w, 715 w, 590 m cm^{-1}. NMR: ^{19}F δ −74.7 (s); ^1H δ 2.75 (t, 4H) $SNCH_2$, 2.29 (t, 4H) NCH_2, 2.0 (s, 3H) CH_3. MS (CI) [*m/e* (species), intensity]: 257 ($C_8H_{14}F_3N_3OS^+$), 1.2; 217 ($C_6H_{12}F_3N_2OS^+$), 2.9; 147 ($C_5H_{11}N_2OS^+$), 32.5; 117 (CF_3SO^+), 1.9; 101 (CF_3S^+), 11.6; 100 ($C_5H_{12}N_2^+$), 100; 99 ($C_5H_{11}N_2^+$), 100; 84 ($C_4H_8N_2^+$), 4.3; 69 (CF_3^+), 21.4. Anal. Calcd for $C_{12}H_{22}F_6N_4OS$: C, 37.50; H, 5.73. Found: C, 36.17; H, 5.61.

VI. $(CF_3)_2S(O)[N(CH_3)CH_2CH_2N(CH_3)H]_2$ (extracted with CCl_3F). Spectral data are as follows. Infrared (KBr, capillary film): 2948 s, 1474 m, 1459 m, 1387 m, 1322 m, 1227 m, 1181 s, 1160 m, 920 m, 860 w, 592 w cm^{-1}. NMR: ^{19}F δ −73.66 (3F), −75.18 (3F) ppm; ^1H δ 3.50 (2H) $SNCH_2$, 2.93 (3H) $SNCH_3$, 2.63 (2H) NCH_2, 2.48 (3H) CH_2NCH_3, 2.21 (1H) NH. MS (CI) [*m/e* (species), intensity]: 334

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($M^+ - CH_4$), 2.8; 233 [$CF_3SO(N(CH_3)C_2H_4NHCH_3)NCH_3^+$], 26.4; 147 ($CF_3SONCH_3^+ + 1$), 9.8; 117 ($CF_3SO^+$), 6.2; 70 ($N_2C_3H_6^+$), 31.3; 69 ($CF_3^+$), 34.3. Anal. Calcd for $C_{10}H_{22}F_6N_4OS$: C, 33.33; H, 6.11; N, 15.55. Found: C, 33.3; H, 6.0; N, 16.2.

The general procedure for the preparation of bis(trifluoromethyl)sulfoximines **VII**, **VIII**, and **IX** was as follows: Sodium fluoride (12 mmol) was placed in a 500-mL Pyrex reactor fitted with a Teflon stopcock. The flask was evacuated, cooled to –196 °C, and 5 mmol each of $(CF_3)_2S(O)F_2$ and 5 mmol primary amine (2,2,2-trifluoroethylamine, *tert*-butylamine, or 2-aminoethanol) were condensed in. The reaction mixture was allowed to warm from –78 to 25 °C over 24 h. Purfication via trap-to-trap distillation permitted isolation of $(CF_3)_2S(O){=}NCH_2CF_3$ (**VII**, 80%), $(CF_3)_2S(O){=}NC(CH_3)_3$ (**VIII**, 75%), and $(CF_3)_2S(O){=}NCH_2CH_2OH$ (**IX**, 60%) in a trap at –78 °C.

VII. $(CF_3)_2S(O){=}NCH_2CF_3$. Spectral data are as follows. Infrared (gas, KBr disks): 2955 m, 1402 s, 1305 m, 1277 s, 1250 s, 1197 sh, 1174 sh, 1127 s, 952 m, 914 m, 820 m, 755 w, 668 m, 619 sh, 584 m, 517 m, cm^{-1}. NMR: ^{19}F δ –71.73 (q of t, 6F, $J_{F-F} = 0.88$ Hz, $J_{H-F} = 0.76$ Hz) CF_3S, – 73.88 (sept of t, 3F, $J_{H-F} = 8.47$ Hz) CF_3C; ^1H δ 3.89 (q of sept, 2H). MS (CI) [*m/e* (species), intensity]: 284 ($M^+ + 1$), 11.5; 264 ($M^+ - F$), 35.3; 214 ($M^+ - CF_3$), 34.5; 198 ($CF_3SNCH_2CF_3^+$), 13.9; 195 ($M^+ - CF_4$), 8.7; 146 ($CF_3SONCH_2^+ + 1$), 22.1; 128 ($CF_3SNCH_2^+ + 1$), 7.9; 117 (CF_3SO^+), 17.8; 101 (CF_3S^+), 3.3; 76 ($OSNCH_2^+$), 24.1; 69 (CF_3^+) 100. Anal. Calcd for $C_4H_2F_9NOS$: C, 16.96; H, 0.7; N, 4.94. Found: C, 16.06; H, 0.46; N, 5.88.

VIII. $(CF_3)_2S(O){=}NC(CH_3)_3$. Spectral data are as follows. Infrared (gas, KBr disk): 2986 sh, 1402 s, 1374 sh, 1239 s, 1190 s, 1138 sh, 1111 sh, 950 w, 911 w, 822 w, 735 w, 689 w, 617 m, 588 m, 541 w, 515 m cm^{-1}. NMR: ^{19}F δ –73.83 (s) CF_3; ^1H 1.38 (s) CH_3. MS (CI) [*m/e* (species), intensity]: 258 ($M^+ + 1$), 1.8; 242 ($M^+ - CH_3$), 86.3; 216 ($M^+ - H_3F_2$), 1.6; 202 ($M^+ - C_2F_2H_5$), 32.7; 188 ($M^+ - CF_3$), 16.6; 173 ($CF_3SONC_3H_6^+$), 15.1; 147 (CF_3SON), 11.1; 132 ($CF_3SON^+ + 1$), 1.1; 117 (CF_3SO^+), 1.37; 116 ($CF_3SN^+ + 1$), 6.6; 104 ($SNC_4H_9^+ + 1$), 25.8; 101 (CF_3S^+), 1.0; 69 (CF_3^+), 29.9; 57 ($C_4H_9^+$), 100.

IX. $(CF_3)_2S(O){=}NCH_2CH_2OH$. Spectral data are as follows. Infrared (gas, KBr disk): 3660 w, 2982 w, 2964 w, 1480 w, 1392 w, 1352 s, 1316 w, 1243 s, 1192 s, 1136 s, 1073 m, 1050 m, 997 w, 874 w, 736 s, 623 w, 588 w, 517 w, 481 m cm^{-1}. NMR: ^{19}F –71.60 s; ^1H 4.33 (t, 2H, $J = 5.6$ Hz) CH_2N, 3.62 (t, 2H) CH_2O, 3.50 (s, 1H) OH. MS (CI) [*m/e* (species), intensity]: 228 ($M^+ - OH$), 26.1; 214 ($M^+ - CH_2OH$), 44.4; 195 ($M^+ - F - CH_2OH$), 7.8; 178 ($M^+ - CF_3OH$), 62.3; 132 (CF_3SONH^+), 11.5; 117 (CF_3SO^+), 11.5; 101 (CF_3S^+), 3.2; 90 (SNC_2H_4O), 22.6; 76 ($OSNCH_2^+$), 14.0; 69 (CF_3^+), 100; 60 ($SNCH_2^+$), 40.0. Anal. Calcd for $C_4H_5F_6NO_2S$: C, 19.59; H, 2.04; N, 5.72. Found: C, 18.95; H, 1.53; N, 5.45.

The general procedure for the preparation of $(CF_3)_2S(O){=}N(CH_2)_nN{=}S(O)(CF_3)_2$ [$n = 2$ (**X**), $n = 3$ (**XI**)] was to place NaF (12 mmol) into a Pyrex flask, to evacuate the flask, and to add $(CF_3)_2S(O)F_2$ (2.5 mmol) and 1,2-ethylenediamine or 1,3-propylenediamine (1 mmol) at –196 °C. After the mixture was allowed to warm from –78 to +25 °C over 24 h, the volatile products were separated by trap-to-trap distillation with **X** or **XI** stopping at –20 °C.

X. $(CF_3)_2S(O){=}N(CH_2)_2N{=}S(O)(CF_3)_2$. Spectral data are as follows. Infrared (capillary film, KBr): 2965 m, 1636 w, 1559 w, 1541 w, 1471 w, 1361 s, 1337 s, 1303 s, 1225 s, 1184 s, 1127 s, 965 w, 859 w, 812 m, 746 m, 618 m, 584 m, cm^{-1}. NMR: ^{19}F δ –71.86 s, CF_3; ^1H δ 3.53 s, CH_2. MS (CI) [*m/e* (species), intensity]: 429 ($M^+ + 1$), 15.6; 290 ($M^+ - C_2F_6$), 1.5; 228 [$(CF_3)_2SONC_2H_4^+$], 42.5; 214 [$(CF_3)_2SONCH_2^+$], 100; 198 [$(CF_3)_2SNCH_2^+$], 3.0; 145 ($CF_3SONCH_2^+$), 6.0; 117 (CF_3SO^+), 14.2; 101 (CF_3S^+), 1.6; 76 ($OSNCH_2^+$), 11.1; 69 (CF_3^+), 100; 60 ($SNCH_2^+$), 49.0. Anal. Calcd for $C_6H_4F_{12}N_2O_2S_2$: C, 16.82; H, 0.93; N, 6.54. Found: C, 16.57; H, 0.90; N, 6.55.

XI. $(CF_3)_2S(O){=}N(CH_2)_3N{=}S(O)(CF_3)_2$. Spectral data are as follows. Infrared (capillary film, KBr): 2765 m, 1397 s, 1328 s, 1225 s, 1181 s, 1127 s, 1104 s, 901 m, 860 m, 812 s, 772 m, 736 s, 620 s, 586 m, 514 s cm^{-1}. NMR: ^{19}F δ –71.72 s; ^1H δ 3.51 (t, 4H) NCH_2, 1.95 (p, 2H) CCH_2. MS (CI) [*m/e* (species), intensity]: 443 ($M^+ + 1$), 25.2; 373 ($M^+ - CF_3$), 20.1; 242 [$(CF_3)_2SONC_3H_6^+$], 15.1; 214 [$(CF_3)_2SONCH_2^+$], 9.2; 172 ($CF_3SONC_3H_5^+$), 2.8; 145 ($CF_3SONCH_2^+$), 3.4; 131 (CF_3SON^+), 2.0; 101 (CF_3S^+), 1.7; 69 (CF_3^+), 100.

XII. Reaction of $(CF_3)_2S(O)F_2$ with $HOCH_2CH_2OH$ to give $(CF_3)_2\overline{S(O)OCH_2CH_2O}$ (XII). To a 200-mL Pyrex glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added predried KF (46 mmol) and $HOCH_2CH_2OH$ (6.1 mmol). The vessel was evacuated and $(CF_3)_2S(O)F_2$ (6.3 mmol) was added at –196 °C. After the reaction was warmed to 25 °C and allowed to stand for 20 h, the reaction products were extracted with CCl_4 (4 × 5 mL portions). The excess CCl_4 was removed under vacuum to leave a colorless liquid (yield ~57%). Spectral data are as follows. Infrared (KBr, capilary film): 2985 w, 2907 w, 1475 w, 1237 s, 1205 sh, 1156 s, 1100 m, br, 1052 m, 1010 w, 943 m, 905 w, 781 w, 761 w, 725 m, 690 m, 660 w, 604 m, 583 w, 558 w, 524 w, 486 w cm^{-1}. NMR: ^{19}F δ –64.2 (s); ^1H δ 4.25 (s). MS (CI) [*m/e* (species)]: 177 ($M^+ - CF_3$); 133 ($CF_3SO_2^+$); 117 (CF_3SO^+); 98 (CF_3SO^+); 69 (CF_3^+); 44 ($C_2H_4O^+$). Anal. Calcd for $C_4H_4F_6O_3S$: C, 19.52; H, 1.64. Found: C, 19.71; H, 1.73.

XIII. Reaction of SF_5Cl with CF_3CH_2OH to give $FS(OCH_2CF_3)_2Cl$. 2,2,2-Trifluoroethanol (4 mmol), SF_5Cl (2 mmol), $(C_2H_5)_3N$ (4 mmol), and hexane (10 mL) were added to a 250-mL Pyrex glass reaction vessel at –196 °C. The reaction mixture was warmed slowly to 25 °C over 12 h. The mixture was fractionated through a series of traps at –10, –60 and –78 °C. **XIII** was retained in the trap at –78 °C. Spectral data are as follows. Infrared (gas, KBr disks): 2970 s, 2960 s, 2930 s, 1454 s, 1280 s, 1170 s, 1150 s, 1100 m, 1075 m, 1025 m, 950 m, 680 s, 670 s, 625 m cm^{-1}. NMR: ^{19}F δ –72.1 (t, $J_{F-H} = 8.3$ Hz); ^1H δ 3.80 (q). MS (CI) [*m/e* (species), intensity]: 249 ($M^+ - Cl$), 32.5; 231 ($M^+ + 1 - ClF$), 5.2; 230 ($M^+ - ClF$), 6.8; 229/227 ($M^+ - 3F$), 22.0/71.0; 215 ($M^+ - CF_3$), 15.0; 181 ($M^+ + 1 - CF_3Cl$), 93.7; 179/177 ($M^+ - CF_5$), 19.0/56.7; 163 ($M^+ - CF_4Cl + 2H$), 100; 149 ($M^+ - C_2H_3F_3ClO$), 90.0; 147 ($C_2H_2F_3O_2S^+$), 78; 131 ($C_2H_2F_3SO^+$), 41.9; 69 (CF_3^+), 100.

Reaction of $(CF_3)_2S(O)F_2$ with $(CH_3)_3SiN(CH_3)_2$. Into an evacuated 100-mL Pyrex flask at –196 °C were condensed $(CF_3)_2S(O)F_2$ (3 mmol) and $(CH_3)_3SiN(CH_3)_2$ (6 mmol). The reaction mixture was allowed to warm from –78 to +25 °C over 12 h. Purification via trap-to-trap distillation gave rise to **II** in 60% yield in a –20 °C trap.

Reaction of $(CF_3)_2S(O)F_2$ with $(CH_3)_3SiCN$ or $(CH_3)_3SiCF_3$. With or without solvent (benzonitrile) or in the presence or absence of KF, only reduction and/or defluorination occurred to give $(CF_3)_2S$, $(CF_3)_2SO$, and $(CF_3)_2SO_2$ as well as other unidentified materials.

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