Reactions of Per- and Polyfluorinated Amines with Sulfur Compounds

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There are four classes of fluorine-containing compounds with double and triple bonds between sulfur(IV) and nitrogen,[1] i.e., N≡SX, RN=S=O, RN=S=NR, and RN=SX_2. Of the first type, only N≡SF and N≡SCl are known. A wide variety of *N*-sulfinyl compounds, RN=S=O, and sulfur diimides, RN=S=NR,[1-7] as well as numerous compounds of the type RN=SX_2 (X = Cl, F or organic substituent) are in the literature. While several methods for synthesis are available, the most common one is the reaction of compounds containing the primary amino group (NH_2) with SF_4,[1-5] *viz.*,

$$R_fNH_2 + SF_4 \xrightarrow{MF} R_fN{=}SF_2$$

R_f = CF_3, C_2F_5, C_6F_5, SF_5, CF_3SO_2, CF_3S; MF = CsF, NaF

Alternate methods involve reactions of cyanides, cyanates, thiocyanates or $RN(TMS)_2$ with SF_4.[8,9] The reactive sulfur-fluorine bond in $-N{=}SF_2$ gives rise to a large number of derivatives, e.g., sulfur diimides.[3,10]

$$RN{=}SF_2 + RNH_2 \xrightarrow{MF} RN{=}S{=}NR + MF{\cdot}HF$$

R, R = CF_3S, CF_3S;[1] C_6F_5, C_6F_5[8]

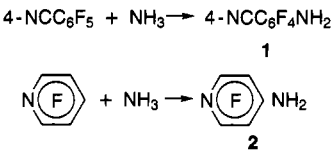
Similarly, N-sulfinyl compounds are obtained when primary amines are treated with thionyl chloride.[11,12] Primary amines can be alkyl or aryl.

$$RNH_2 + SOCl_2 \rightarrow RN{=}S{=}O$$

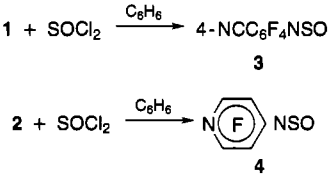
In the work described here, we have extended the reaction chemistry of perfluoroaromatic, perfluoroheterocyclic and aliphatic amines with simple sulfur-containing compounds.

Results and Discussion

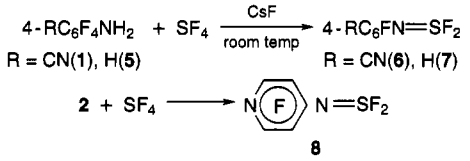
A large number of sulfur difluoride imides ($RN{=}SF_2$) are useful as precursors to other nitrogen-sulfur compounds. Their syntheses continue to be of interest. Following literature methods,[13,14] the two aromatic amines **1** and **2** are synthesized.



These primary amines react with thionyl chloride to give the respective *N*-sulfinyl compounds in essentially quantitative yield.



When amines **1**, **2**, and 4-$HC_6F_4NH_2$ (**5**) are treated with SF_4 in the presence of CsF at 25 °C, the respective sulfur difluoride imides are formed



The sulfur difluorides **6**, **7**, and **8** are not stable at 25 °C but are stable at −78 °C for long periods of time. On standing, SF_4 is eliminated to give sulfur diimides essentially quantitatively.

$$2\,\mathbf{6}\text{−}\mathbf{8} \xrightarrow[-SF_4]{25\ ^\circ C} R_fN{=}S{=}NR_f \quad \mathbf{9}\text{−}\mathbf{11}$$

R_f = 4-NCC_6F_4 (**9**), 4-HC_6F_4 (**10**), NC_5F_4 (**11**)

When primary amine **1** is treated with SOF_4, the corresponding sulfur oxide difluoroimide is obtained.

$$\mathbf{1} + SOF_4 \xrightarrow[25\ ^\circ C]{CsF} 4\text{-}NCC_6F_4N{=}S(O)F_2 \quad \mathbf{12}$$

When compound **1** is treated with 30% H_2O_2 in CH_3COOH at 25 °C for 2 days, a high yield of the azoxy compound **13** is obtained.

$$\mathbf{1} \xrightarrow[CH_3COOH]{30\%\ H_2O_2} 4\text{-}NCC_6F_4N(O){=}NC_6F_4\text{-}4\text{-}CN \quad \mathbf{13}$$

The ^{19}F NMR spectrum of **13** shows only two fluorine signals at δ −135.2 (4 F) and δ −160.4 (4 F), both of which are complex multiplets. The mass spectrum shows a base peak at 393 (MH^+) 100 and the molecular ion peak at 392 (M^+) 9.5%, which supports the formula assigned to **13**. The infrared spectrum shows aromatic and azoxy absorbances between 1642

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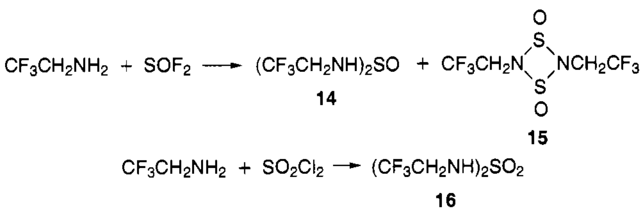
and 1436 cm^{-1} and the nitrile band at 2239 cm^{-1}. Elemental analysis of the product obtained also supports the formula as written.

When aliphatic amines, such as 2,2,2-trifluoroethylamine, are treated with SOF_2, cyclic and acyclic sulfoxides are obtained. With SO_2Cl_2 only an acyclic sulfone is found. In both cases, the acyclic derivatives are the major products



Compound **15**, a very minor product, is obtained in a cold trap at −78 °C while **14** and **16** are obtained as white solids by extracting the reaction products with ether.

When perfluoroazapropenes are treated with ammonia a different class of compound is obtained.

$$C_2F_5N{=}CF_2 + NH_3 \rightarrow CF_3C(NH_2){=}NCN \quad \mathbf{17}$$

$$C_3F_7N{=}CF_2 + NH_3 \rightarrow C_2F_5C(NH_2){=}NCN \quad \mathbf{18}$$

Both compounds **17** and **18** are white solids. Ammonia reacts with azaalkenes with evolution of HF which in turn reacts with ammonia to form ammonium fluoride. The organic product can be easily extracted in ether, leaving the ammonium fluoride behind. With SOF_2, **17** and **18** give $CF_3C(NSO){=}NCN$ (**19**) and $C_2F_5C(NSO){=}NCN$ (**20**), respectively.

Experimental Section

Materials. The starting materials, i.e., NH_3, CsF, $AlCl_3$ (Aldrich), $CF_3CH_2NH_2$, SF_4, 4-$HC_6F_4NH_2$ (PCR), SO_2Cl_2, $SOCl_2$ (MCB), 30% H_2O_2 (J. T. Baker) are purchased and used as received. The starting materials 4-$NCC_6F_4NH_2$ (**1**), NC_5F_4-NH_2 (**2**), $C_2F_5N{=}CF_2$, $C_3F_7N{=}CF_2$, are prepared via literature methods.

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

The preparation of **3** and **4** is as follows: A mixture of 4-$NCC_6F_4NH_2$ (5 mmol) or 4-aminotetrafluoropyridine (5 mmol) and thionyl chloride (7 mmol) in benzene (15 mL) is refluxed for 10−12 h in a 250 mL round-bottomed flask fitted with a reflux condenser attached to a calcium chloride guard tube. The solvents are removed under vacuum, leaving the involatile product **3** or **4**.

Product **3**, 4-NCC_6F_4NSO, is a yellow solid (mp 43−44 °C). Infrared (KBr): 2248 m, 1667 m, 1646 m, 1516 s, 1500 vs, 1482 s, 1433 m, 1393 w, 1366 w, 1331 m, 1316 m, 1254 s, 1200 m, 1171 m, 1126 m, 999 s, 972 s, 910 s, 736 s, 651 m cm^{-1}. ^{19}F NMR: δ −131.2 (2 F, complex), −138.3 (2 F, complex). MS (EI) [*m/e* (species) intensity]: 236 (M^+) 75.8; 220 ($M^+ - O$) 2.2; 217 ($M^+ - F$) 3.1; 210 ($M^+ - CN$) 4.3; 208 ($C_7F_4OS^+$) 100; 188 ($M^+ - SO$) 5; 176 ($C_6F_4N_2$+) 5.6; 169 ($M^+ - SOF$) 3.7; 162 ($M^+ - CNSO$) 12.5; 150 ($M^+ - SOF_2$) 11.8; 143 ($C_6F_3N^+$) 24.3; 138 ($C_4F_4N^+$) 29.3; 124 ($C_6F_2N^+$) 23.7; 119 ($C_4F_3N^+$)7.9; 112 (C_3F_4+) 9.7; 100 ($C_4F_2N^+$) 26.1; 93 ($C_3F_3^+$) 17.5; 74 ($C_3F_2^+$) 8.7; 62 (NSO^+) 6.2. Anal. Calcd for $C_7F_4N_2OS$: C, 35.6; F, 32.2. Found: C, 37.9; F, 34.9.

The compound NC_5F_4NSO (**4**) stops in a trap at −15 °C. Infrared (gas): 1665 s, 1639 s, 1581 w, 1535 m, 1417 m, 1333 m, 1304 s, 1281 s, 1238 vs, 1199 m, 1144 s, 1105 m, 1037 w, 1007 w, 972 vs, 917 s, 751 w, 740 w, 683 s, 633 w, 580 m, 530 m cm^{-1}. ^{19}F NMR: δ −88.1 (2 F, complex), −143.6 (2 F, complex). MS (CI) [*m/e* (species) intensity]: 213 ($M^+ + 1$) 3; 212 (M^+) 4.8; 181 ($M^+ - CF$) 4.7; 166 ($M^+ - CFO$ or $MH^+ - SO$) 100; 147 ($MH^+ - SOF$) 13.2; 138 ($C_4F_4N^+$) 4.1; 119 ($C_4F_3N^+$) 7.2; 100 ($C_4F_2N^+$) 3.8; 93 ($C_3F_3^+$) 5.8; 77 ($C_2F_2NH^+$) 3.2; 75 ($C_3F_2H^+$) 3.8; 74 ($C_3F_2^+$) 3.5. Anal. Calcd for $C_5F_4N_2OS$: C, 28.3; F, 35.8. Found: C, 28.0; F, 35.3.

The preparation of **6**, **7**, and **8** is as follows: Cesium fluoride (25 mmol) and 4-$RC_6F_4NH_2$ (R = CN or H) or $NC_5F_4NH_2$ are placed in a 100-mL Pyrex reactor fitted with a Teflon stopcock. The flask is evacuated and cooled to −196 °C, and 12 mmol of SF_4 is added. The flask is warmed to 25 °C and stirred overnight. The products are then separated by trap-to-trap distillation.

Product **6**, 4-$CNC_6F_4N{=}SF_2$, stops in a trap at −25 °C. Infrared (gas): 2248 s, 1650 s, 1505 vs, 1452 s, 1394 m, 1363 s, 1284 s, 1046 m, 999 s, 899 s, 732 s, 669 s cm^{-1}. ^{19}F NMR: δ 65.4 (SF_2, t, $J_{N(CF)_2}$ = 11.58 Hz), −132.1 (2 F, complex), −143.1 (2 F, complex). MS (CI) [*m/e* (species) intensity]: 259 ($M^+ + 1$) 1.1; 258 (M^+) 0.8; 221 ($MH^+ - 2$ F) 0.6; 190 ($MH^+ - C_3NF$) 16.3; 159 ($MH^+ - C_2F_4$) 1.6; 143 ($C_6F_3N^+$) 1.5; 119 ($C_4F_3N^+$) 15.9; 111 ($C_6F_2H^+$) 2.8; 94 ($C_3F_3H^+$) 8.9; 87 ($C_4F_2H^+$) 74; 86 ($C_4F_2^+$) 32.1; 85 (SF_2NH^+) 45.3; 84 (NSF_2^+) 50; 83 (C_3HNS^+) 100; 70 (SF_2^+) 8.8.

The compound 4-$HC_6F_4N{=}SF_2$ (**7**) stops in a trap at −35 °C. Infrared (gas): 3090 m, 1641 s, 1629 m, 1513 vs, 1419 w, 1385 w, 1357 s, 1240 s, 1180 s, 1135 w, 974 w, 948 s, 845 s, 716 s, 653 s, 567 w, 514 m, 445 m cm^{-1}. ^{19}F NMR: δ 68.1 (SF_2, t, $J_{N(CF)_2}$ = 11.6 Hz), −138.7 (2 F, complex), −146.3 (2 F, complex). MS (CI) [*m/e* (species) intensity]: 234 (MH^+) 18.7; 233 (M^+) 100; 214 ($M^+ - F$) 84.6; 195 ($M^+ - 2F$) 2.9; 183 ($M^+ - CF_2$) 10.4; 182 ($M^+ - CF_2H$) 6.6; 165 ($MH^+ - CF_3$) 34; 163 ($M^+ - SF_2$) 12.6; 149 ($M^+ - NSF_2$) 5.4; 137 ($C_5F_4H^+$) 8; 132 ($M^+ - CFSF_3$) 1.4; 118 ($C_5HF_3^+$) 5.4; 113 ($C_5HF_2N^+$) 18.3; 99 ($C_5HF_2^+$) 14.3; 94 ($C_3F_3H^+$) 4.0; 88 ($C_3F_2N^+$) 1.2; 75 ($C_3HF_2^+$) 5.4.

The sulfur difluoride imide $NC_5F_4N{=}SF_2$ (**8**) stops in a trap at −30 °C. Infrared (gas): 1636 s, 1581 w, 1525 vs, 1490 vs, 1473 s, 1425 m, 1355 s, 1277 m, 1239 s, 1154 w, 1012 w, 974 vs, 739 s, 671 s, 567 w, 531 m, 446 m cm^{-1}. ^{19}F NMR: δ 64.9 (SF_2, t, $J_{SF-NC(CF_3)_2}$ = 11.3 Hz), −88.9 (2 F, complex), −147.4 (2 F, complex). MS (CI) [*m/e* (species) intensity]: 249 ($M^+ + 15$) 8.9; 235 (MH^+) 59.7; 234 (M^+) 100; 215 ($M^+ - F$) 55.2; 189 ($M^+ - NCF$) 1.8; 184 ($M^+ - CF_2$) 7.8; 166 ($MH^+ - CF_3$) 22.5; 150 ($M^+ - NSF_2$) 4.8; 138 ($C_4F_4N^+$) 7; 133 ($M^+ - CFSF_2$) 2.9; 119 ($C_4F_3N^+$) 11.4; 100 ($C_4F_2N^+$) 15.6; 93 ($C_3F_3^+$) 3.2; 88 ($C_3F_2N^+$) 2.3; 83 ($C_3FN_2^+$) 1.2; 70 (SF_2^+) 5.2; 69 (C_3FN^+) 9.8.

The preparation of 4-$RC_6F_4N{=}S{=}NC_6F_4R$-4 [where R = CN (**9**) or H (**10**)] and $NC_5F_4N{=}S{=}NC_5F_4N$ (**11**) is as follows. When 5 mmol of 4-$RC_6F_4N{=}SF_2$ (R = CN or H) or $NC_5F_6N{=}SF_2$ are allowed to stand at 25 °C under vacuum for

2−3 days, complete decomposition occurs to give the corresponding −N=S=N− derivative and SF_4 as the byproduct.

The sulfur diimide 4-NCC_6F_4N=S=NC_6F_4CN-4 (**9**) is a yellow solid (mp 90−92 °C). Infrared (KBr): 2263 s, 1669 w, 1645 m, 1501 vs, 1481 m, 1431 w, 1315 w, 1221 m, 1034 m, 996 s, 833 m cm^{-1}. ^{19}F NMR: δ −134.1 (4 F, m), −142.1 (4 F, m). MS (EI) [*m/e* (species) intensity]: 408 (M^+) 94.3; 389 ($M^+ - F$) 100; 358 ($M^+ - CF_2$) 3.6; 232 ($C_8F_4N_2S^+$) 24.7; 220 ($M^+ - NC_6F_4CN$) 92.3; 208 ($M^+ - CNC_8F_4N_2$) 70.4; 162 ($C_5F_4CN^+$) 15.2; 150 ($C_7F_2N_2^+$) 5.3; 138 ($C_6F_2N_2^+$) 13.1; 124 ($C_6F_2N^+$) 27; 100 ($C_4F_2N^+$) 22; 81 (C_4FN^+) 8.4; 69 (C_3FN^+) 22.5. Anal. Calcd for $C_{14}F_8N_4S$: C, 41.18; F, 37.25. Found: C, 41.0; F, 36.9.

Product **10**, 4-HC_6F_4N=S=NC_6F_4H-4, stops in a trap at −25 °C. Infrared (gas): 3064 m, 1662 m, 1638 m, 1514 s, 1465 m, 1402 w, 1385 w, 1300 m, 1263 s, 1180 s, 1139 s, 1090 w, 951 s, 911 s, 844 m, 739 s, 651 m cm^{-1}. ^{19}F NMR: δ −138 (4 F, complex), −140.5 (4 F, complex). MS (CI) [*m/e* (species) intensity]: 359 (MH^+) 16.4; 358 (M^+) 83.5; 357 ($M^+ - H$) 100; 339 ($M^+ - F$) 55.4; 308 ($M^+ - CF_2$) 0.8; 288 ($M^+ - CF_3H$) 1.0; 209 ($M^+ - C_6F_4H$) 1.7; 195 ($C_6HF_4NS^+$) 46.4; 183 ($C_5HF_4NS^+$) 14.2; 149 ($C_6HF_4^+$) 3.5; 137 ($C_5HF_4^+$) 3.9; 125 ($C_6HF_2N^+$) 1.2; 113 ($C_5HF_2N^+$) 6.1; 99 ($C_5HF_2^+$) 8.0; 87 ($C_4HF_2^+$) 0.4; 75 ($C_3HF_2^+$) 4.4; 63 ($C_2HF_2^+$) 2.7.

Product **11**, NC_5F_4N=S=NC_5F_4N, stops in a trap at −30 °C. Infrared (gas): 1666 s, 1633 s, 1536 m, 1475 vs, 1416 m, 1336 w, 1285 m, 1239 w, 1189 s, 1141 m, 1120 s, 971 s, 911 s, 756 w, 733 w, 697 w, 633 w, 607 w cm^{-1}. ^{19}F NMR: δ −88.5 (4 F, complex), −145.1 (4 F, complex). MS (CI) [*m/e* (species) intensity]: 362 ($M^+ + 2$) 1.1; 313 ($M^+ - N_2F$) 87.9; 285 ($MH^+ - C_2F_2N$) 6.3; 266 ($MH^+ - C_2F_3N$) 7.3; 246 ($M^+ - C_2F_4N$) 2.8; 241 ($M^+ - C_2F_5$) 6.6; 197 ($C_5HF_4N_2S^+$) 20.4; 196 ($C_5F_4N_2S^+$) 5.8; 179 ($M^+ - NC_6F_5$) 16.7; 163 ($C_5F_3NS^+$) 10.0; 154 ($C_5HFN_3S^+$) 26.8; 150 ($C_5F_4N^+$) 3.4; 138 ($C_4F_4N^+$) 81.9; 119 ($C_4F_3N^+$) 15.3; 107 ($C_3F_3N^+$) 4; 101 ($C_4HF_2N^+$) 82.1; 100 ($C_4F_2N^+$) 93.2; 93 ($C_3F_3^+$) 10.1; 89 (C_2FNS^+) 37.4; 74 ($C_3F_2^+$) 65.9; 69 (C_3FN^+) 100.

Reaction of 4-cyanotetrafluoroaniline with SOF_4 to give 4-CNC_6F_4N=S(O)F_2 (**12**) is performed as follows. CsF (20 mmol) and 4-cyanotetrafluoroaniline (5 mmol) are placed in a 250-mL Pyrex reactor fitted with a Teflon stopcock. The flask is evacuated and cooled to −196 °C, and SOF_4 (12 mmol) is added. The reaction mixture is warmed to 25 °C and stirred for 12−14 h. The volatile material is removed and the residue extracted with ether. Evaporation of ether gives the product **12**. Infrared (KBr): 2237 m, 1667 s, 1517 vs, 1454 m, 1438 m, 1417 m, 1395 w, 1341 m, 1316 s, 1254 s, 1166 s, 1123 m, 1056 m, 997 s, 944 m, 910 vs, 736 vs, 651 m cm^{-1}. ^{19}F NMR: δ 49.6 (SF_2, t, $J_{N(CF)_2}$ = 7.6 Hz), −131.7 (2 F, m), −145.2 (2 F, m). MS (CI) [*m/e* (species) intensity]: 275 (MH^+) 1.6; 205 ($M^+ - CF_3$) 50.8; 191 ($M^+ - CNF_3$) 100; 144 ($C_6HF_3N^+$) 6.2; 124 ($C_6F_2N^+$) 13.8; 93 ($C_3F_3^+$) 7.4; 70 (SF_2^+) 4.6. Anal. Calcd for $C_7F_6N_2OS$: C, 30.7; F, 41.61. Found: C, 31.1; F, 41.1.

Reaction of 4-cyanotetrafluoroaniline with H_2O_2 and acetic acid to give the azoxy derivative 4-$NCC_6F_4N(O)$=NC_6F_4CN (**13**). First, 4-cyanotetrafluoroaniline (5 mmol), 30% H_2O_2 (10 mL), and acetic acid (15 mL) are placed in a 250-mL Pyrex glass reaction vessel equipped with a Teflon stopcock. The flask is cooled to -196 °C and evacuated. The reaction mixture is allowed to warm to 25 °C and stirred for 2 days. The resulting mixture is poured into 100 mL of water and extracted with ether (4 × 15 mL). The extract is washed with water (2 × 10 mL) and dried over Na_2SO_4. The ether is removed on a rotary evaporator and **13** is obtained as a pale yellow solid (mp 90 °C). Infrared (KBr): 2239 s, 1642 s, 1620 m, 1597 w, 1532 s, 1436 m, 1318 s, 1169 m, 1115 w, 965 m, 945 s, 805 w, 736 s cm^{-1}. ^{19}F NMR: δ −135.2 (4 F, complex), −160.4 (4 F, complex). MS (CI) [*m/e* (species) intensity]: 393 (MH^+) 100; 392 (M^+) 9.5; 377 ($MH^+ - O$) 7.1; 218 ($M^+ - C_6F_4CN$) 4.2; 205 ($NCC_6F_4NOH^+$) 5.4; 202 ($M^+ - C_7F_4NO$) 18.1; 191 ($C_7HF_4NO^+$) 25.5; 174 ($C_6F_4CN^+$) 9.8; 162 ($C_6F_4N^+$) 5.3; 149 ($C_6F_4H^+$) 21.3; 138 ($C_4F_4N^+$) 4.8; 124 ($C_4F_4^+$) 10.9; 100 ($C_4F_2N^+$) 2.4; 93 ($C_3F_3^+$) 2.1; 69 (C_3FN^+) 2.9. Anal. Calcd for $C_{14}F_8N_4O$: C, 42.86; F, 38.8. Found: C, 43.36; F, 38.4.

Reaction of $CF_3CH_2NH_2$ with SOF_2 to give $(CF_3CH_2NH)_2SO$ (**14**) and $(CF_3CH_2NSO)_2$ (**15**). Into an evacuated 100-mL Pyrex flask at −196 °C are condensed $CF_3CH_2NH_2$ (10 mmol) and SOF_2 (5 mmol). The reaction mixture is warmed to 25 °C and stirred overnight. The products are separated by trap-to-trap distillation and the residue is extracted with ether. Compound **14** is a white solid (mp 47−48 °C). Infrared (KBr): 3050 br, m, 1619 m, 1543 m, 1428 m, 1321 s, 1273 s, 1191 s, 1155 s, 1078 s, 1035 s, 1009 s, 916 m, 835 m, 736 s, 668 s, 638 s, 590 m, 551 m cm^{-1}. ^{19}F NMR: δ −71.0 (CF_3, t, J = 9.0 Hz). ^1H NMR δ 3.8 (CH_2, q). MS (CI) [*m/e* (species) intensity]: 194 ($C_3F_4H_6N_2SO$) 4.0; 180 ($C_3F_4H_6NSO^+$) 68.7; 160 ($M^+ - C_2F_3H_3$) 69.7; 144 ($M^+ - C_2F_3H_5N$) 2.9; 128 ($C_2HF_3NS^+$) 1.0; 110 ($C_2H_2F_2NS^+$) 50.9; 100 ($C_2F_4^+$) 22.9; 84 ($C_2H_3F_3^+$) 8.1; 80 ($C_2H_4F_2N^+$) 55.8; 69 (CF_3^+) 60.5; 57 (C_2FN^+) 100. Anal. Calcd for $C_4H_6F_6N_2OS$: C, 19.67; F, 46.72. Found: C, 20.21; F, 47.5. Product **15** stops in a trap at −78 °C. Infrared (gas): 1433 w, 1374 s, 1360 s, 1351 m, 1293 s, 1260 vs, 1180 vs, 948 m, 849 m, 735 m, 721 m, 672 m, 578 m, 525 w cm^{-1}. ^{19}F NMR: δ −71.5 (CF_3, t, J_{CF-CH} = 7.4 Hz). ^1H NMR δ 4.47 (CH_2, q). MS (CI) [*m/e* (species) intensity]: 223 ($M^+ - SOF$) 0.8; 202 ($M^+ - CF_3 - F$) 0.8; 195 ($C_2F_3H_4NO_2S_2^+$) 7.4; 182 ($C_3H_3FN_2O_2S_2^+$) 2.3; 180 ($C_3HFN_2O_2S_2^+$) 23.4; 146 ($CF_3CH_2NSOH^+$) 48; 145 ($C_2F_3H_2NSO^+$) 1.6; 126 ($C_2H_2F_2NOS^+$) 97.4; 119 ($C_2F_5^+$) 3.5; 110 ($CF_2CH_2NS^+$) 15; 107 ($CFCH_2NOS^+$) 6.6; 106 ($CFCHNOS^+$) 10.8; 69 (CF_3^+) 100.

Reaction of $CF_3CH_2NH_2$ with SO_2Cl_2 to give $(CF_3CH_2NH)_2SO_2$ (**16**) occurs as follows. Into an evacuated 100-mL Pyrex flask at −196 °C are condensed $CF_3CH_2NH_2$ (10 mmol) and SO_2Cl_2 (5 mmol). The reaction mixture is allowed to warm to 25 °C and stirred overnight. After the reaction is complete, all of the volatile materials are removed, the residue is extracted with ether, and the ether extract is dried over Na_2SO_4. The solvent is removed on a rotary evaporator to give a white solid, **16** (mp 58−60 °C). Infrared (KBr): 3298 br, m, 3022 m, 2967 m, 1479 s, 1434 s, 1390 s, 1343 s, 1310 s, 1292 s, 1157 vs, 979 s, 879 s, 837 m, 821 m, 671 s, 660 s, 572 m cm^{-1}. ^{19}F NMR: δ −72.2 (CF_3, t, J_{CF-CH} = 8.6 Hz). ^1H NMR δ 3.5 (CH_2, m), 6.1 (NH, br). MS (CI) [*m/e* (species) intensity]: 261 (MH^+) 10.4; 241 ($M^+ - F$) 8.0; 203 ($M^+ - 3F$) 11.2; 201 ($M^+ - H_2F_3$) 17.7; 191 ($M^+ - CF_3$) 11.1; 163 ($MH^+ - C_2H_3F_3N$) 5.4; 162 ($M^+ - C_2H_3F_3N$) 2.2; 151 ($C_4H_5F_2N_2S^+$) 22.5; 131 ($C_2H_4F_3NS^+$) 28.2; 110 ($C_2H_2F_2NS^+$) 3.2; 100 ($C_2H_5F_3N^+$) 15.5; 85 ($C_2H_4F_3^+$) 100; 80 ($SO_2NH_2^+$) 13.9; 69 (CF_3^+) 6.6; 64 (SO_2^+) 5.6. Anal. Calcd for $C_4H_6F_6N_2O_2S$: C, 18.46; F, 43.9; H, 2.3. Found: C, 18.77; F, 42.9, H 2.15.

Reaction of C_2F_5N=CF_2 or C_3F_7N=CF_2 with ammonia to give $CF_3C(NH_2)$=NCN (**17**) or $C_2F_5C(NH_2)$=NCN (**18**). Into an evacuated 100-mL Pyrex flask at −196 °C are condensed azaalkene (5 mmol) and ammonia (25 mmol). The reaction mixture is allowed to warm to 25 °C and to remain at that temperature for 12 h. After the reaction is complete, the volatile materials are removed, and the residue is extracted with ether and dried over Na_2SO_4. Removal of solvent under vacuum gives the product. Product **17** is a white solid (mp 97 °C). Infrared (KBr): 3345 s, 3329 m, 3102 s, 2229 s, 2195 m, 1692

s, 1611 s, 1526 m, 1468 m, 1402 w, 1218 s, 983 m, 838 m, 771 m, 726 m, 672 w, 595 w cm^{-1}. ^{19}F NMR: δ −73.1 (CF_3, s). ^1H NMR δ 7.73 (NH_2, br). MS (CI) [*m/e* (species) intensity]: 139 ($M^+ + 2$) 3.4; 138 ($M^+ + 1$) 100; 137 (M^+) 10.8; 110 ($M^+ - HCN$) 0.5; 69 (CF_3^+) 2.8; 68 ($M^+ - CF_3$) 12.0; 57 ($CN_3H_3^+$) 9.7. Anal. Calcd for $C_3H_2F_3N_3$: C, 26.3; F, 41.6; H 1.46. Found: C, 26.8; F, 40.8; H, 1.72. Compound **18** is a white solid (mp 60 °C). Infrared (KBr): 3421 m, 3359 m, 3200 m, 1670 s, 1595 s, 1535 s, 1333 s, 1231 s, 1191 vs, 1126 s, 1101 s, 1061 m, 1023 m, 998 m, 986 m, 973 m, 926 m, 905 w, 831 s, 823 m, 814 m, 752 s, 732 s, 705 m, 606 m cm^{-1}. ^{19}F NMR: δ −82.4 (CF_3, s), −120.4 (CF_2, s). ^1H NMR δ 6.5 (NH_2, br). MS (CI) [*m/e* (species) intensity]: 187 (M^+) 4.1; 185 ($M^+ - 2H$) 7.8; 167 ($M^+ - HF$) 1.1; 153 ($MH^+ - FNH_2$) 28.1; 131 ($C_3F_5^+$) 20.1; 119 ($C_2F_5^+$) 7.7; 116 ($M^+ - CH_2F_3$) 8.1; 103 ($C_3HF_2N_2^+$) 23.1; 101 ($C_2HF_4^+$) 34.7; 85 ($C_2FN_3^+$) 100; 69 (CF_3^+) 17.8. Anal. Calcd for $C_4H_2F_5N_3$: C, 25.67; F, 50.8. Found: C, 25.0; F, 51.1.

Reaction of $CF_3C(NH_2)$=NCN (**17**) and $C_2F_5C(NH_2)$=NCN (**18**) with SOF_2 to give $CF_3C(NSO)$=NCN (**19**) and $C_2F_5C(NSO)$=NCN (**20**) occurs as follows. The procedure is the same as the one used for the preparation of **14**. Compound **19** is a liquid found in a trap at −85 °C. Infrared (KBr): 2221 m, 1629 m, 1581 s, 1546 m, 1480 m, 1330 m, 1229 s, 1203 s, 1166 s, 1037 w, 1013 w, 972 w, 912 m, 865 w, 839 w, 813 m, 742 s, 709 m, 677 s cm^{-1}. ^{19}F NMR: δ −72.2 (CF_3, s). MS (CI) [*m/e* (species intensity]: 185 ($M^+ + 2$) 2.7; 165 ($MH^+ - F$) 3.7; 164 ($M^+ - F$) 1.7; 143 ($M^+ - NCN$) 13.5; 135 ($M^+ - SO$) 17.8; 121 ($M^+ - NSO$) 26.3; 116 ($M^+ - SOF$) 7.5; 103 ($MH^+ - NSO - F$) 16.9; 69 (CF_3^+) 100. Compound **20** is a liquid found in a trap at -30 °C. Infrared (KBr): 2211 m, 1627 m, 1588 s, 1537 w, 1479 m, 1396 m, 1334 s, 1223 s, 1192 s, 1125 s, 1037 m, 973 w, 901 w, 838 m, 750 m, 674 s cm^{-1}. ^{19}F NMR: δ −82.9 (CF_3, s), −120.8 (CF_2, s). MS (CI) [*m/e* (species) intensity]: 215 ($MH^+ - F$) 3.9; 185 ($M^+ - SO$) 9.5; 165 ($MH^+ - CF_3$) 5.3; 153 ($MH^+ - NSO - F$) 22.9; 147 ($M^+ - SOF_2$) 14.1; 135 ($C_3F_3N_3^+$) 41.2; 131 ($C_2F_5C^+$) 15.6; 119 ($C_2F_5^+$) 2.5; 116 ($M^+ - CF_3 - SO$) 7.4; 101 ($C_2F_4H^+$) 30.9; 85 ($C_2N_2SH^+$) 100; 69 (CF_3^+) 14.1.

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