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SOME NEW HIGHLY SUBSTITUTED TRIFLUOROMETHYL SULFURANES

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SUMMARY

trans-Chlorotetrafluoro(trifluoromethyl)sulfur(VI), CF_3SF_4Cl, readily undergoes reductive defluorination to sulfur(IV)-containing compounds when it is reacted with nitrogen- or oxygen-containing nucleophiles. Thus, $CF_3S(NR_2)_2Cl$ results from a variety of nitrogen bases, such as R_2NH = piperidine, 2,6-dimethylpiperidine, 2,2,6,6-tetramethylpiperidine, morpholine, 3,5-dimethylmorpholine, and N,N'-dimethylethenediamine. With alcohols, $CF_3S(OR_f)_2Cl$ is formed where R_fOH = 2,2,2-trifluoroethanol and 1,1,1-trifluoro-2-propanol. Due to the low stability of all of these compounds, complete characterization was difficult.

INTRODUCTION

trans-Chlorotetrafluoro(trifluoromethyl)sulfur(VI) is a very useful precursor to a large number of CF_3SF_4-containing compounds [1-4]. In many of its reactions, CF_3SF_4Cl behaved identically with SF_5X (X = Cl, Br), e.g., with alkenes and alkynes where addition across the multiple bond occurred. However, with nucleophiles, the chemical behavior of CF_3SF_4Cl differed markedly from that of SF_5X [5,6], e.g.,

$$CF_3SF_4Cl + 3R_2NSiR'_3 \longrightarrow CF_3S(NR_2)_2Cl + 3R'_3SiF + [R_2NF]$$

$$SF_5X + R_2NSiR'_3 \longrightarrow R_2NSF_4X + R'_3SiF$$

X = Cl, Br

With R_3SiCN, partial defluorination occurred with CF_3SF_4Cl to form $CF_3SF_2(CN)_2Cl$ [7], while with SF_5Cl reduction to $S(CN)_2$ took place.

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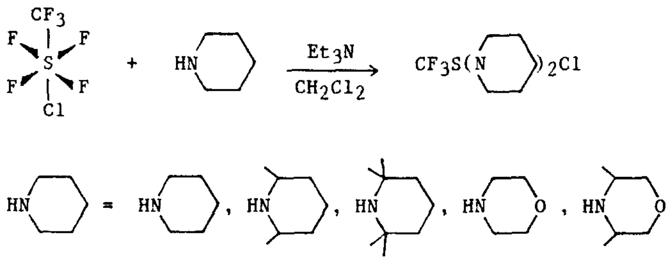
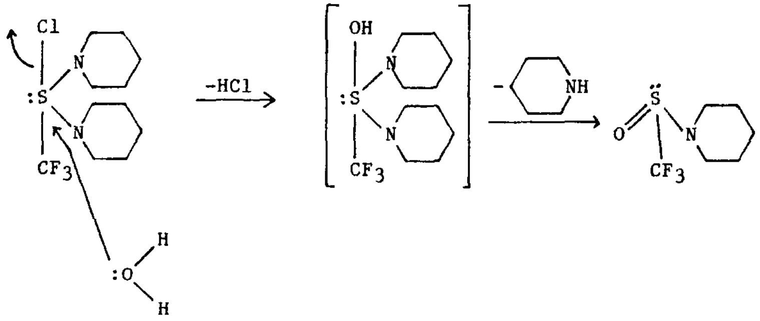
We now report further studies of CF_3SF_4Cl with nitrogen- and oxygen-containing nucleophiles, in this case with cyclic and difunctional amines and polyfluorinated alcohols where complete defluorination and reduction to S(IV) compounds occurred.

RESULTS AND DISCUSSION

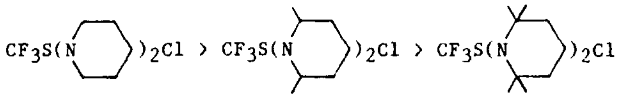
Cyclic amines readily react with CF_3SF_4Cl in the presence of triethylamine to form the corresponding trifluoromethyl sulfuranes. In the presence of even traces of moisture these interesting sulfuranes were converted to the sulfoxides, e.g.,



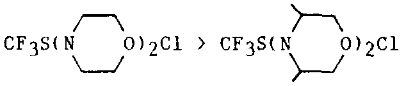
Yields 20-30%



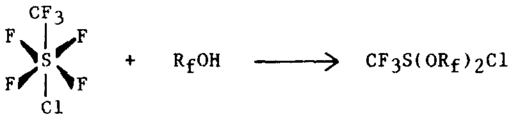
In contrast, $CF_3S(NR_2)_2Cl$ (R = CH_3, C_2H_5) only underwent very slow hydrolysis to the corresponding $CF_3S(O)NR_2$. Stability of the sulfuranes decreased as the degree of substitution on the ring increased, *i.e.*,



and



Although the cyclic amines react smoothly in the presence of triethylamine, the lithium salt of sym-dimethylethenediamine was more effective with CF_3SF_4Cl at -78 °C. As is typical of amine reactions with S(IV) or S(VI) compounds, reduction to a sulfur(IV)-containing heterocycle, $CF_3\overline{SN(CH_3)CH_2CH_2N}CH_3$, was accompanied by the formation of an acyclic sulfur(II) amine, $CF_3SN(CH_3)CH_2CH_2N(CH_3)SCF_3$. The polyfluorinated alcohols, $CF_3(CH_3)CHOH$ and CF_3CH_2OH, were sufficiently nucleophilic in the presence of $(C_2H_5)_3N$ to form the unstable sulfuranes, $CF_3S[(OCH(CH_3)CF_3]_2Cl$ and $CF_3S(OCH_2CF_3)_2Cl$.



R_f = CF_3CH_2, $CF_3C(CH_3)H$

These new compounds have been characterized by infrared, nuclear magnetic resonance and mass spectra and, in some cases, with elemental analyses.

EXPERIMENTAL

Materials

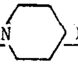
Literature methods were used to prepare trans-chlorotetrafluoro(trifluoromethyl)sulfur(VI) [8] and trifluoromethylsulfinyl chloride [9]. Piperidine, 2,6-dimethylpiperidine, 2,2,6,6-tetramethylpiperidine, morpholine, 3,5-dimethylmorpholine, and N,N'-dimethylethenediamine were obtained from Aldrich. These reagents were used as received.

General procedures

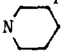
All gases and volatile liquids were handled in a Pyrex glass vacuum system equipped with a Heise-Bourdon tube gauge and measured by PVT techniques. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer using a 10 cm cell fitted with KBr plates for gaseous samples and capillary films between KBr plates for liquid samples. ^{19}F and ^{1}H NMR spectra were obtained on a Jeol FX90Q FT NMR spectrometer using CCl_3F and tetramethylsilane as external references, respectively. Mass spectra were recorded with a VG 7070 HS spectrometer. Fragments that contained chlorine had the appropriate isotope ratios. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany, and at the University of Idaho.

Preparation of $CF_3S(NR_2)_2Cl$

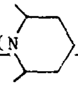
All of the $CF_3S(NR_2)_2Cl$ compounds were prepared in essentially the same manner. The cyclic amine (4 mmol), triethylamine (4 mmol), and methylene chloride (10 mL) were added to a 50 mL Pyrex reaction vessel. Then, CF_3SF_4Cl (2 mmol) was condensed into the reaction vessel at -196 °C. The reaction mixture was allowed to warm from -78 to 25 °C over a period of 12 h. When the volatile materials were removed under vacuum, a white residue remained. This product was extracted into hexane. Et_3NHF was left behind. After the hexane was evaporated, the liquid $CF_3S(NR_2)_2Cl$ was obtained in a trap at 0 °C. Since these compounds are very water sensitive, these reactions were carried out under anhydrous conditions. These compounds are very slightly volatile and do not lend themselves to trap-to-trap distillation because of their low stabilities.

Preparation of $CF_3S(N$  $)_2Cl$

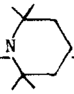
This colorless, involatile liquid was obtained in 25% yield. The infrared spectrum is as follows: 2980 vs, 2880 s, 1455 s, 1385 w, 1335 s, 1290 s, 1270 w, 1230 w, 1210 to 1150 vs, br, 1120 vs, 1055 vs, 1035 s, 950 vs, 865 s, 750 vs, 700 s, 600 s, 500 w, 480 w, (ν_{S-Cl}) cm^{-1}. The ^{19}F NMR spectrum consists of a singlet at Φ -76.04; the ^1H NMR spectrum has peaks centered at δ 3.24 (CH_2N) and 1.61 (CH_2). The CI positive mass spectrum contains peaks at m/e 287 ($C_{11}H_{22}N_2F_2SCl^+$, 0.1%), 281 ($C_{11}H_{16}N_2F_2ClS^+$, 0.1%), 207 ($C_8H_{13}N_2F_2S^+$, 0.2%), 202 ($C_6H_{11}F_2NClS^+$, 0.3%), 185 ($C_6H_{10}NF_3S^+$, 0.4%), 132 ($C_5H_{10}NOS^+$, 20%), 84 ($C_5H_{10}N^+$, 100%).

Anal. Calcd. for $C_{11}H_{20}F_3NSCl$: Cl, 11.62. Found: Cl, 12.42. The hydrolysis of $CF_3S(N$  $)_2Cl$ causes the ready formation of the sulfoxide $CF_3S(O)N$  even in the presence of traces of moisture.

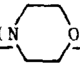
Anal. Calcd. for $C_6H_{10}F_3OSN$: S, 15.92. Found: S, 15.81.

Preparation of $CF_3S(N$  $)_2Cl$

A colorless, involatile liquid was obtained. The infrared spectrum is as follows: 2945 vs, 2870 s, 2760 s, 1915 w, 1450 vs, br, 1390 vs, 1230 vs, 1200 - 1110 vs, br, 1090 vs, 940 vs, 880 vs, 750 w, 610 s, 580 s, 500 s, cm^{-1}. The ^{19}F NMR spectrum consists of a singlet at ϕ -75.57; the ^{1}H NMR spectrum shows a complex collection of peaks centered at δ 1.29 and at 1.63 and a broad peak at δ 2.83. The CI positive ion mass spectrum contains peaks at m/e 345 (M^+-CH_3, 0.2%), 306 ($C_{15}H_{28}N_2F_2S^+$, 0.2%), 247 ($C_{11}H_{17}F_2N_2S^+$, 0.1%), 230 ($C_{10}H_{12}F_2N_2S^+$, 7.2%), 226 ($C_8H_{13}F_3N_2S^+$, 0.1%), 213 ($C_8H_{14}F_3NS^+$, 1.7%), 198 ($C_7H_{11}F_3NS^+$, 14.5%), 159 ($C_7H_{15}N_2S^+$, 82.4%), 145 ($C_7H_{15}NS^+$, 2.5%), 112 ($C_7H_{14}N^+$, 7.3%), 97 ($C_6H_{11}N^+$, 40.1%), 69 (CF_3^+, 20.1%), 55 ($C_3H_5N^+$, 100%).

Preparation of $CF_3S(N$  $)_2Cl$

A colorless, involatile liquid was obtained. The infrared spectrum is as follows: 2980 vs, 2885 vs, 1470 vs, 1375 vs, 1365 vs, 1240 vs, 1180 s, 1130 vs, 1110 vs, 1010 vs, 950 w, 910 w, 740 s, 670 s, 620 s, 495 w, 460 w, cm^{1}. The ^{19}F NMR spectrum consists of a peak at ϕ -69.79; the ^{1}H NMR spectrum shows peaks at δ 1.13 (12), and 1.30-1.60 (6). The CI positive ion mass spectrum has peaks at 241 ($C_{10}H_{18}NF_3S^+$, 0.7%), 240 ($C_{10}H_{17}NF_3S^+$, 1.2%), 225 ($C_9H_{13}NF_3S^+$, 7.7%), 221 ($C_{10}H_{17}NF_2S^+$, 1.8%), 208 ($C_9H_{16}NF_2S^+$, 1.7%), 174 ($C_4H_7NF_2SCl^+$, 8.3%), 159 ($C_3H_4NF_2SCl^+$, 45.3%), 126 ($C_8H_{16}N^+$, 100%), 108 ($C_4H_{10}N^+$, 24.6%).

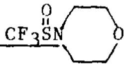
Preparation of $CF_3S(N$  $)_2Cl$

A colorless liquid of low volatility was obtained in 25% yield. The infrared spectrum is as follows: 2980 s, 2940 s, 2870 vs, 1455 vs, 1300 s, 1260 vs, 1225 - 1100 vs, br, 1065 s, 1000 w, 935 vs, 880 vw, 840 w, 680 s, 595 s, 570 vs, cm^{-1}. The ^{19}F NMR spectrum contains a singlet at ϕ -72.74; the ^{1}H NMR spectrum shows two sets of peaks centered at δ 3.77 and 3.37. The CI positive ion mass spectrum contains peaks at m/e 305 ($C_9H_{13}O_2N_2F_3ClS^+$, 0.1%), 289 ($C_9H_{16}O_2N_2F_2ClS^+$, 0.1%), 270 ($C_9H_{16}O_2N_2FClS^+$, 0.3%), 251 ($C_9H_{16}O_2N_2ClS^+$, 2.0%), 235 ($C_9H_{16}O_2N_2FS^+$, 1.3%), 203

($C_5H_{10}F_3ON_2S^+$, 4.0%), 187 ($C_5H_8F_3ONS^+$, 36.1%), 186 ($C_5H_7F_3ONS^+$, 2.8%), 168 ($C_5H_8F_2ONS^+$, 2.8%), 149 ($C_5H_8FONS^+$, 0.8%), 133 ($C_4H_9ON_2S^+$, 38.7%), 118 ($C_4H_8ONS^+$, 8.3%), 117 ($C_4H_7ONS^+$, 20.5%), 103 ($C_3H_7N_2S$, 3.6%), 86 ($C_4H_8NO^+$, 100%), 82 (CF_2S^+, 6.0%).

Anal. Calcd. for $C_9H_{16}N_2F_3O_2SCl$: Cl, 11.36. Found: Cl, 11.05.

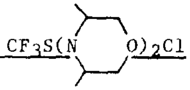
Preparation of



A colorless liquid of low volatility was obtained. The infrared spectrum is as follows: 2960 s, 2910 s, 2845 vs, 1445 vs, 1360 s, 1320 w, 1295 s, 1260 vs ($\nu_{S=O}$), 1200 - 1140 vs, br, 1105 vs, 1065 vs, 845 w, 740 s, 690 s, 625 w, 605 s, 570 s, 480 s, 440 s, cm^{-1}. The ^{19}F NMR spectrum consists of a singlet at ϕ -73.89; the ^{1}H NMR spectrum shows two sets of peaks centered at δ 3.77 and 3.37. The CI positive ion mass spectrum contains peaks at m/e 204 (M^++H, 0.2%), 187 ($C_5H_8F_3ONS^+$, 1.3%), 134 ($C_4H_8O_2NS^+$, 100%), 118 ($C_4H_8ONS^+$, 0.9%), 90 ($C_2H_4ONS^+$, 12.4%), 87 ($C_4H_9ON^+$, 19.6%), 69 (CF_3^+, 5.7%), 63 (CFS^+, 8.5%), 60 (CH_2NS^+, 8.3%), 56 ($C_3H_6N^+$, 19.1%).

Anal. Calcd. for $C_5H_8F_3O_2SN$: S, 15.76. Found: S, 15.60.

Preparation of



A colorless liquid was obtained in 15% yield. The infrared spectrum is as follows: 2980 vs, 2940 vs, 2880 vs, 1400 vs, 1380 vs, 1330 vs, 1275 s, 1240 s, 1225 s, 1200 - 1110 vs, br, 1080 vs, 1040 s, 1005 s, 970 s, 910 s, 880 w, 845 w, 720 w, 740 w, 605 w, 550 w, cm^{-1}. The ^{19}F NMR spectrum consists of a singlet at ϕ -73.08; the ^{1}H NMR spectrum shows a complex set of peaks between δ 2.49 and 3.84 and 0.92 and 1.60. The CI positive ion mass spectrum contains peaks at m/e 260 ($C_{12}H_{24}O_2N_2S^+$, 0.3%), 230 ($C_{10}H_{18}O_2N_2S^+$, 2.8%), 215 ($C_9H_{15}O_2N_2S^+$, 10.0%), 200 ($C_8H_{12}O_2N_2S^+$, 1.00%), 196 ($C_6H_{10}ON_2SF_2^+$, 5.8%), 162 ($C_6H_9NOSF^+$, 40.9%), 146 ($C_6H_{12}NOS^+$, 1.3%), 116 ($C_4H_6NOS^+$, 26.3%), 114 ($C_6H_{12}NO^+$, 100%), 84 ($C_4H_6NO^+$, 7.3%), 70 ($C_4H_8N^+$, 81.5%), 69 (CF_3, 12.5%), 57 ($C_3H_7N^+$, 13.7%), 56 ($C_3H_6N^+$, 16.1%).

Preparation of $CF_3\overline{S(Cl)N(CH_3)CH_2CH_2N}CH_3$

To a solution of $HN(CH_3)CH_2CH_2N(CH_3)H$ (2 mmol) in dry ether and cooled to -78 °C, a hexane solution of n-butyllithium (4 mmol) was added in a dry nitrogen gas atmosphere. The mixture was held at -40 °C for 0.25 h, and then CF_3SF_4Cl (2 mmol) was condensed into the mixture at -196 °C. The reaction mixture was held at -78 °C for 12 h. A liquid, $CF_3\overline{S(Cl)N(CH_3)CH_2CH_2N}CH_3$ (25%), was obtained in the trap at 0 °C. The infrared spectrum is as follows: 2940 m, 2870 m, 2780 w, 1470 vs, 1240 vs, 1160 m, 1125 vs, 1040 w, 925 w, 875 w, 750 s, 590 w, 490 w, cm^{-1}. The ^{19}F NMR spectrum consists of a singlet at ϕ -77.66; the ^1H NMR spectrum has bands at δ 5.5 (CH_3,6H) and δ 7.1 (CH_2,4H). The CI positive ion spectrum contains peaks at m/e 221 (M^+-H, $C_5H_9F_3N_2SCl^+$, 0.2%), 207 ($C_4H_7F_3N_2SCl^+$, 0.2%), 187 ($C_5H_{10}F_3N_2S^+$, 4.3%), 168 ($C_5H_{10}F_2N_2S^+$, 0.4%), 156 ($C_3H_3F_3N_2S^+$, 2.7%), 144 ($C_3H_5F_3NS^+$, 83.2%), 130 ($C_5H_{10}N_2S^+$, 2.5%), 124 ($C_3H_7NClS^+$, 0.9%), 111 ($C_2H_6NSCl^+$, 6.0%), 89 ($C_3H_7NS^+$, 14.4%), 86 ($C_4H_{10}N_2^+$, 0.1%), 69 (CF_3^+, 44.7%), 63 (SCF^+, 5.9%), 57 ($C_3H_7N^+$, 100%).

Preparation of $CF_3S(OCH_2CF_3)_2Cl$

2,2,2-Trifluoroethanol (4 mmol), CF_3SF_4Cl (2 mmol), triethylamine (4 mmol), and hexane (10 mL) were added to a 50 mL Pyrex reaction vessel at -196 °C. The reaction mixture was warmed slowly from -78 to 25 °C. The mixture of products was passed through a series of traps held at -10, -60, and -78 °C. $CF_3S(OCH_2CF_3)_2Cl$ (25%) was retained in the last trap. Its infrared spectrum is as follows: 2965 s, 2925 s, 1450 s, 1275 vs, 1230 vs, 1160 s, 1100 s, br, 960 vs, 825 vs, 680 s, 550 vs, cm^{-1}. The ^{19}F NMR spectrum contains peaks at ϕ -74.47 (s) (CF_3S, 1) and ϕ -78.64 (tr) (CF_3C, 2); the ^1H NMR spectrum contains a peak at δ 4.54 (q), J_{H-F} = 7.83 Hz. The CI positive ion mass spectrum contains peaks at m/e 334 (M^+, 0.3%), 332 (M^+-2H, 1.0%), 316 ($C_5H_5F_8O_2ClS^+$, 0.4%), 299 ($C_5H_4F_9O_2S^+$, 0.5%), 282 ($C_5H_6F_8O_2S^+$, 2.9%), 266 ($C_4H_5F_6O_2SCl^+$, 6.7%), 233 ($C_3F_5H_3O_2ClS^+$, 11.7%), 216 ($C_3F_6H_2O_2S^+$, 5.7%), 202 ($C_3F_6H_4OS^+$, 11.8%), 181 ($C_3F_5H_2OS^+$, 6.4%), 164 ($C_3F_4H_4OS^+$, 29.7%), 152 (CF_3OSCl^+, 8.7%), 147 ($C_2F_3H_2O_2S^+$, 17.8%), 124 ($C_3FH_5O_2S^+$, 8.0%).

Preparation of $CF_3S[OCH(CF_3)CH_3]_2Cl$

The reaction was carried out as above. A colorless liquid was obtained in low yield in a trap held at -40 °C after having passed through a trap at -10 °C. The infrared spectrum is as follows: 2980 s, 1435 w, 1415 m, 1295 vs, 1225 vs, 1185 vs, 1020 vs, 970 s, 805 m, 715 w, 735 vs, 665 m, cm^{-1}. The ^{19}F NMR spectrum contains peaks at Φ -79.69 (d) and -79.69 (d) (CF_3C), and at Φ -66.66 (s); the ^1H NMR spectrum has peaks at δ 1.332 (d) and 1.324 (d) (CH_3, $J_{CH_3-H} = 6.6$ Hz) and at 4.069 (sept) (CH, $J_{CF_3-H} = 6.6$ Hz). The CI positive ion mass spectrum contains peaks at 349 ($C_6F_9H_7ClSO_2^+$, 0.3%), 316 ($C_5F_8H_5ClSO_2^+$, 0.4%), 314 ($C_6F_9H_7SO_2^+$, 0.6%), 298 ($C_5F_9H_3SO_2^+$, 0.4%), 282 ($C_7F_7HSO_2^+$, 3.4%), 280 ($C_5F_8H_4SO_2$, 5.5%), 242 ($C_5F_6H_4SO_2^+$, 0.3%), 204 ($C_5F_2H_7ClSO_2^+$, 8.4%), 169 ($C_4F_3SO_2^+$, 6.8%), 133 (CF_2SOCl, 8.4%), 117 (CF_3SO^+, 3.2%), 101 (CF_3S, 15.7%), 69 (CF_3, 31.5%).

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