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PRELIMINARY NOTE

Chlorobis(dialkylamino)trifluoromethylsulfur(IV), $CF_3(NR_2)_2SCl$, and Chlorobis(dialkylamino)oxotrifluoromethylsulfur(VI), $CF_3(NR_2)_2S(O)Cl$ ($R = CH_3$, C_2H_5)

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We have shown recently that when difluorobis(perfluoroalkyl)sulfur(IV) compounds are reacted with primary or secondary amines, sulfur-carbon bond cleavage occurs with concomitant reduction of sulfur(IV) to sulfur(II) (1,2). We now report that chlorotetrafluoro(trifluoromethyl)sulfur(VI) is reduced to chlorobis(dialkylamino)trifluoromethylsulfur(IV) by reaction with bis(dialkylamino)trimethylsilane

$$CF_3SF_4Cl + R_2NSi(CH_3)_3 \dashrightarrow CF_3(NR_2)_2SCl + (CH_3)_3SiF$$
$$R = CH_3,\ C_2H_5$$

Although SF_3NR_2 and $CF_3SF_2NR_2$ are prepared via analogous reactions of SF_4 (3,4) and CF_3SF_3 (5) with $R_2NSi(CH_3)_3$, and SF_3OAr, $SF_2(OAr)_2$ and CF_3SF_2OAr from SF_4 and CF_3SF_3 with $ArOSi(CH_3)_3$ (6), we believe that $CF_3(NR_2)_2SCl$ is the first example of fluorine-containing sulfur(IV) compounds which contain a sulfur-chlorine bond and which do not contain oxygen, e.g., $R_fS(O)Cl$. The compounds are unexpectedly stable being unchanged after one week at 25° in a Pyrex glass vessel or after one hour at 100°. Spectral and elemental analyses data support the proposed structures. In the ^{19}F nmr spectra, single resonance peaks occur at 73.6 and 77.6 ϕ and infrared absorption bands at 488 and 470 cm^{-1} which are assigned to ν_{S-Cl} in $CF_3(N(CH_3)_2)_2SCl$ and $CF_3(N(C_2H_5)_2)_2SCl$, respectively (7). Molecule ions are observed in the mass spectra.

In a typical reaction, CF_3SF_4Cl (2 mmol) and $(CH_3)_2NSi(CH_3)_3$ (5 mmol) are condensed at -195° into a Pyrex glass vessel equipped with a Teflon stopcock. The reaction mixture is warmed slowly to 25° and allowed to remain for 5 hr. After trap-to-trap distillation, the colorless liquid, $CF_3(N(CH_3)_2)_2SCl$, was collected at -78° in 75% yield. The only other volatile compound formed is $(CH_3)_3SiF$. An unidentified solid residue remained in the reaction flask. In a similar manner, $CF_3(N(C_2H_5)_2)_2SCl$ was obtained in 80% yield. Hydrolysis of these compounds by water occurs slowly to form the respective trifluoromethyldialkylaminosulfoxides, $CF_3S(O)NR_2$ (2,8).

Oxidation of $CF_3(NR_2)_2SCl$ to $CF_3(NR_2)_2S(O)Cl$ occurs readily, but in low yield, with m-chloroperbenzoic acid (MCPBA) at 0° for 24 hr.

$$CF_3(NR_2)_2SCl \xrightarrow[0^o]{MCPBA} CF_3(NR_2)_2S(O)Cl$$

$$R = CH_3 \ (30\%),\ C_2H_5 \ (34\%)$$

These compounds are also stable, colorless liquids which are hydrolytically inert and which have been characterized by spectral and elemental analyses. The ^{19}F nmr spectra contain bands at 80.6 and 81.5 ϕ shifted upfield from the resonance bands assigned to CF_3 in the S(IV) compounds as is typically the case.

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