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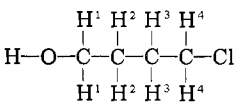

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Hydrolysis of $CF_3SF_2Cl{=}NCF(CF_3)_2$. Preparation of $CF_3(S{=})(O)[N{=}C(CF_3)_2]$-Containing Compounds

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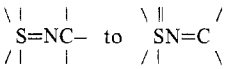
Hydrolysis of $CF_3SF_2Cl[{=}NCF(CF_3)_2]$ results in the formation of (trifluoromethyl)(hexafluoroisopropylidenimino)sulfuroxydifluoride, $CF_3S(O)F_2[N{=}C(CF_3)_2]$, which is a ready precursor to $CF_3S(O)(=NCH_3)[N{=}C(CF_3)_2]$, $CF_3S(O)[=NCF(CF_3)_2][N{=}C(CF_3)_2]$, and $CF_3S(O)(=NH)[N{=}C(CF_3)_2]$. The latter compound can be reacted with $CF_3C(O)F$, $(CH_3)_3SiCl$, and Ag_2O to form $CF_3S(O)[=N\text{-}C(O)CF_3][N{=}C(CF_3)_2]$, $CF_3S(O)[=NSi(CH_3)_3][N{=}C(CF_3)_2]$, and $CF_3S(O)(=NAg)[N{=}C(CF_3)_2]$.

Substituted sulfur(VI)oxydifluorides, $RN{=}S(O)F_2$ (R = alkyl, FSO_2), are stable compounds which result either from the reaction of primary amines, RNH_2, with sulfinyl tetrafluoride or from the photolysis of RNSO with fluorine.[1] Earlier we reported the synthesis of bis(perfluoroalkyl)sulfuroxydifluorides via the oxidative fluorination of bis(perfluoroalkyl) sulfoxides with chlorine monofluoride at −78 °C.[2] We now find that it is possible to form a new, reactive member of this family, (trifluoromethyl)(hexafluoroisopropylidenimino)sulfuroxydifluoride, $[CF_3S(O)F_2[N{=}C(CF_3)_2]$, by the hydrolysis of $CF_3SF_2Cl[{=}NCF(CF_3)_2]$[3] which is accompanied by a concomitant double-bond shift



The sulfur is susceptible to attack by nucleophiles, e.g., CH_3NH_2, NH_3, and $LiN{=}C(CF_3)_2$, to form $CF_3S(O)(=NR)[N{=}C(CF_3)_2]$. Further reactions of the latter, where R = H, lead to additional new sulfoximides.

Results and Discussion

The hydrolysis of $CF_3SF_2Cl[{=}NCF(CF_3)_2]$ provides a direct route to the preparation of $CF_3S(O)F_2[N{=}C(CF_3)_2]$

$$CF_3SF_2Cl[{=}NCF(CF_3)_2] \xrightarrow[-HCl]{H_2O} CF_3\underset{\underset{H}{|}}{\overset{O}{S}}F_2[{=}NCF(CF_3)_2] \xrightarrow{-HF} CF_3S(O)F_2[N{=}C(CF_3)_2]$$

Elucidation of the structure of this compound is facilitated by the presence of bands in the infrared spectrum which are assigned to $\nu_{S=O}$ (1335 cm^{-1}) and asymmetric and symmetric ν_{S-F} (800, 538 cm^{-1}). These regions are typical for analogous stretching frequencies for axial S—F bonds in similar compounds, e.g., OSF_4.[4] The ^{19}F nuclear magnetic resonance spectrum contains resonances typical of fluorine atoms in environments consistent with the proposed structure,[2] e.g.: CF_3S, ϕ^* 66.2; S–F, ϕ^* −70.8; $C(CF_3)$, ϕ^* 67.1, 68.6. The magnetic nonequivalence of the two trifluoromethyl groups in the hexafluoroisopropylidenimino group is well established.[5-8]

Subsequent nucleophilic displacement reactions of $CF_3S(O)F_2[N{=}C(CF_3)_2]$ with CH_3NH_2 and $(CF_3)_2C{=}NLi$ result in the formation of sulf- and carbodiimides. In the latter case, fluorine migration occurs to give the diimide.[3,9-11]

$$CF_3S(O)F_2[N{=}C(CF_3)_2] \xrightarrow{CH_3NH_2} CF_3S(O)(=NCH_3)[N{=}C(CF_3)_2]$$

$$CF_3S(O)F_2[N{=}C(CF_3)_2] \xrightarrow{(CF_3)_2C{=}NLi} CF_3S(O)[=NCF(CF_3)_2][N{=}C(CF_3)_2]$$

Previous work in this laboratory resulted in the preparation of bis(perfluoroalkyl)sulfoximides.[12] In a similar manner, $CF_3S(O)F_2[N{=}C(CF_3)_2]$ undergoes reaction with ammonia to produce the (trifluoromethyl)(hexafluoroisopropylidenimino)sulfoximide.

$$CF_3S(O)F_2[N{=}C(CF_3)_2] + 3NH_3 \rightarrow CF_3\overset{\overset{O}{\|}}{\underset{\underset{N}{\|}}{\underset{\underset{H}{|}}{S}}}N{=}C(CF_3)_2 + 2NH_4F$$

In the infrared spectrum, the absorption band at 3445 cm^{-1} is assigned to ν_{N-H}. This sulfoximide is a useful precursor to new substituted oximides. In the cases examined, bases were used to enhance the loss of HX.

$$CF_3S(O)(=NH)[N{=}C(CF_3)_2] \xrightarrow[NaF]{CF_3C(O)F} CF_3S(O)[=NC(O)CF_3][N{=}C(CF_3)_2]$$

$$CF_3S(O)(=NH)[N{=}C(CF_3)_2] \xrightarrow[(CH_3)_3N]{(CH_3)_3SiCl} CF_3S(O)[=NSi(CH_3)_3][N{=}C(CF_3)_2]$$

The silver salt of bis(trifluoromethyl)sulfoximide is formed by the reaction of $(CF_3)_2S(O)(=NH)$ and Ag_2O in benzene.[12-14] In an analogous manner, $CF_3S(O)(=NAg)[N{=}C(CF_3)_2]$ is formed quantitatively. The existence of this salt was demonstrated by reacting it with methyl iodide to yield $CF_3S(O)(=NCH_3)[N{=}C(CF_3)_2]$ which was formed in the reaction between CH_3NH_2 and the sulfoximide above.

$$CF_3S(O)(=NH)[N{=}C(CF_3)_2] + Ag_2O \xrightarrow{PhH} CF_3S(O)(=NAg)[N{=}C(CF_3)_2] \xrightarrow{CH_3I} CF_3S(O)(=NCH_3)[N{=}C(CF_3)_2]$$

Experimental Section

Materials. Methods in the literature were used to prepare $CF_3SF_2Cl[{=}NCF(CF_3)_2]$[3] and $LiN{=}C(CF_3)_2$.[5] Commercially available materials, $CF_3C(O)F$, CH_3NH_2, NH_3, and $(CH_3)_3SiCl$, were used without further purification.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus and measured using standard *PVT* techniques. Infrared spectra were recorded by a Perkin-Elmer Model 457 spectrometer. The ^{19}F and ^1H nuclear

magnetic resonance spectra were obtained from a Varian HA-100 (CCl_3F) and a Varian EM-360 [$(CH_3)_4Si$] spectrometer, respectively. A Hitachi Perkin-Elmer RMU-6E mass spectrometer was used to record mass spectral data.

Hydrolysis of $CF_3SF_2Cl[=NCF(CF_3)_2]$. Into a Pyrex-glass vessel (50 mL) equipped with a Kontes stopcock which contained 1 g of water, $CF_3SF_2Cl[=NCF(CF_3)_2]$ (1.5 mmol) was condensed at −196 °C. The reaction mixture was warmed to 25 °C and allowed to remain for 30 min. A nearly quantitative yield of $CF_3S(O)F_2[N=C(CF_3)_2]$ was obtained in a trap at −98 °C (passed −78 °C) after trap-to-trap distillation. This compound is a colorless liquid with a boiling point of 123 °C from the equation $\log P_{Torr} = 7.51 - 1833/T$. The molar heat of vaporization is 8.4 kcal and the Trouton constant is 21.2 eu.

The ^{19}F NMR spectrum shows resonances at ϕ^* −70.8 (S–F), 66.2 (CF_3S), and 67.1, 68.6 [$C(CF_3)_2$] in the ratio of 2:3:3:3. Coupling between CF_3S and SF is J = 22 Hz. The infrared spectrum is as follows: 1440 (s), 1375 (m), 1335 (ms), 1240 (s), 1208 (s), 1173 (s), 995 (s), 870 (s), 843 (s), 800 (ms), 750 (m), 745 (m), 538 (w), cm^{-1}.

Anal. Calcd for C_4NSOF_{11}: C, 15.06; N, 4.39. Found: C, 15.23; N, 4.17.

Preparation of $CF_3S(O)(=NCH_3)[N=C(CF_3)_2]$. Monomethylamine (4.3 mmol) and $CF_3S(O)F_2[N=C(CF_3)_2]$ (1.5 mmol) were condensed together as above. The mixture was allowed to remain at 25 °C for 10 h. By using trap-to-trap separation, the $CF_3S(O)(=NCH_3)[N=C(CF_3)_2]$ passed a trap at −78 °C and stopped at −98 °C in 65% yield. This compound boils at 144 °C from the equation $\log P_{Torr} = 7.38 - 1922/T$. The molar heat of vaporization is 8.8 kcal and the Trouton constant is 20.6 eu.

The ^{19}F NMR spectrum shows resonances at ϕ^* 52.7 (CF_3S) and 64.8, 74.5 [$C(CF_3)_2$] and the ^1H spectrum shows τ 7.68. All resonances are singlets. The infrared spectrum is as follows: 2961 (m), 1385 (ms), 1265 (ms), 1213 (s), 1150 (s), 964 (m), 928 (m), 778 (m), 736 (m) cm^{-1}.

Anal. Calcd for $C_5H_3N_2SOF_9$: C, 19.36; H, 0.98; N, 9.03. Found: C, 19.25; H, 1.08; N, 9.10.

Preparation of $CF_3S(O)[=NCF(CF_3)_2][N=C(CF_3)_2]$. Into vigorously flame-dried 50-mL Pyrex reaction vessel in which 1.5 mmol of $LiN=C(CF_3)_2$[5] had been prepared, was condensed 1.5 mmol of $CF_3S(O)F_2[N=C(CF_3)_2]$ at −196 °C. The mixture was allowed to remain at 25 °C for 10 h. By use of trap-to-trap distillation, the product was stopped in a trap at −50 °C in 68% yield. It boils at 178 °C from the equation $\log P_{Torr} = 6.96 - 1851/T$. The molar heat of vaporization is 8.0 kcal and the Trouton constant is 18.5 eu.

The ^{19}F NMR spectrum shows resonances at ϕ^* 52.8 (CF_3S), 65.1, 74.9, 79.6 [$C(CF_3)_2$], and 144.7 (CF); J_{CF_3S-CF} = 0.6 Hz and J_{CF-CF_3C} = 3.4. The infrared spectrum is as follows: 1341 (ms), 1252 (s), 1216 (s), 1170 (s), 1128 (s), 1031 (m), 989 (s), 775 (m), 708 (w), cm^{-1}.

Anal. Calcd for $C_7N_2SOF_{16}$: C, 18.12; N, 6.04. Found: C, 18.03; N, 6.33.

Preparation of $CF_3S(O)(=NH)[N=C(CF_3)_2]$. Ammonia (5.6 mmol) and $CF_3S(O)F_2[N=C(CF_3)_2]$ (2 mmol) were condensed as above. The mixture was warmed to and allowed to remain at −78 °C for 1 h and then warmed slowly to 25 °C. After 3 h, the new imine was collected at −116 °C during trap-to-trap distillation. The yield was 60%. The compound boils at 115 °C based on the equation $\log P_{Torr} = 7.9 - 1948/T$. The molar heat of vaporization is 8.9 kcal and the Trouton constant is 22.9 eu.

The ^{19}F NMR spectrum shows resonances at ϕ^* 54.9 (CF_3S) and 62.9, 67.5 [$C(CF_3)_2$] and the ^1H spectrum shows τ 7.60. All resonances are singlets. The infrared spectrum is as follows: 3445 (w), 1623 (w), 1398 (m), 1245 (ms), 1212 (s), 1140 (s), 965 (m), 938 (m), 761 (m), 732 (m) cm^{-1}.

Anal. Calcd for $C_4HN_2SOF_9$: C, 16.23; N, 9.46; H, 0.34. Found: C, 15.97; N, 9.46; H, 0.47.

Preparation of $CF_3S(O)[=NC(O)CF_3][N=C(CF_3)_2]$. Trifluoroacetyl fluoride (6 mmol) was allowed to react with $CF_3S(O)(=NH)[N=C(CF_3)_2]$ (3 mmol) in a Pyrex-glass vessel (as above) which contained an excess of dry NaF. By use of trap-to-trap distillation, $CF_3S(O)[=NC(O)CF_3][N=C(CF_3)_2]$ was retained in a trap at −78 °C in 69% yield. It boils at 131 °C from the equation $\log P_{Torr} = 7.62 - 1915/T$. ($\Delta H_v$ = 8.8 kcal/mol; ΔS_v = 21.7 eu.)

The ^{19}F NMR spectrum shows resonances at ϕ^* 56.8 (CF_3S), 63.5, 68.1 [$C(CF_3)_2$], and 74.5 [$C(O)CF_3$]. All resonances are singlets. The infrared spectrum is as follows: 1758 (ms), 1410 (m), 1370 (m), 1290 (m), 1261 (s), 1210 (s), 1146 (s), 971 (m), 929 (m), 763 (m), 728 (m) cm^{-1}.

Anal. Calcd for $C_6N_2SO_2F_{12}$: C, 18.38; N, 7.14. Found: C, 18.00; N, 7.45.

Preparation of $CF_3S(O)[=NSi(CH_3)_3][N=C(CF_3)_2]$. Trimethylsilyl chloride (4.0 mmol) and $CF_3S(O)(=NH)[N=C(CF_3)_2]$ (2.5 mmol) were condensed at −196 °C into a Pyrex glass vessel which contained $(CH_3)_3N$ (3 mmol). The mixture was warmed to and allowed to remain at 25 °C for 1 h. The new silylimide $CF_3S(O)[=NSi(CH_3)_3][N=C(CF_3)_2]$ was trapped at −78 °C while unreacted $(CH_3)_3SiCl$ and $(CH_3)_3N$ passed into a trap at −196 °C. The yield was 79%. The compound boils at 156 °C based on the equation $\log P_{Torr} = 7.70 - 2058/T$ (ΔH_v = 9.4 kcal/mol; ΔS_v = 22.1 eu).

The ^{19}F NMR spectrum shows resonances at ϕ^* 55.1 (CF_3S) and 63.1, 66.8 [$C(CF_3)_2$], and the ^1H spectrum shows τ 9.74. No coupling is observed. The infrared spectrum is as follows: 2971 (w), 2910 (w), 1501 (m), 1425 (s), 1275 (ms), 1245 (s), 1211 (s), 1151 (s), 979 (m), 931 (m), 768 (m), 721 (m) cm^{-1}.

Anal. Calcd for $C_7H_9N_2SiSOF_9$: C, 24.71; H, 2.67; N, 8.23. Found: C, 24.51; H, 2.42; N, 8.55.

Preparation of $AgN=S(O)CF_3[N=C(CF_3)_2]$. Silver(I) oxide (0.6 mmol) was placed in a Pyrex vessel and $CF_3S(O)(=NH)[N=C(CF_3)_2]$ (1.0 mmol) and benzene (10 mL) were added. The mixture was allowed to react for 5 h at 25 °C and the benzene subsequently removed under dynamic vacuum. The salt was dried by continued exposure to dynamic vacuum.

Reaction of $AgN=S(O)CF_3[N=C(CF_3)_2]$ and CH_3I. Equimolar amounts (1.0 mmol) of the silver salt and methyl iodide were mixed and allowed to remain at 25 °C for 5 h. The product, $CF_3S(O)(=NCH_3)[N=C(CF_3)_2]$, was obtained in >98% yield and identified by comparison with the data reported above.

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Registry No. $CF_3S(O)F_2[N=C(CF_3)_2]$, 62609-62-5; $CF_3S(O)(=NCH_3)[N=C(CF_3)_2]$, 62609-63-6; $CF_3S(O)[=NCF(CF_3)_2][N=C(CF_3)_2]$, 62609-64-7; $CF_3S(O)(=NH)[N=C(CF_3)_2]$, 62609-65-8; $CF_3S(O)[=NC(O)CF_3][N=C(CF_3)_2]$, 62609-66-9; $CF_3S(O)[=NSi(CH_3)_3][N=C(CF_3)_2]$, 62609-67-0; $AgN=S(O)CF_3[N=C(CF_3)_2]$, 62609-68-1; $CF_3SF_2Cl[=NCF(CF_3)_2]$, 62609-69-2; CH_3NH_2, 74-89-5; $LiN=C(CF_3)_2$, 31340-36-0; NH_3, 7664-41-7; $CF_3C(O)F$, 354-34-7; $(CH_3)_3SiCl$, 75-77-4; Ag_2O, 20667-12-3; CH_3I, 74-88-4.

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