dimethyloctylamine, N,N-dimethyldodecylamine, N,N-dimethylcyclohexylamine, N,N-dimethylbenzylamine (40%), N,N,-N′,N′-tetramethylethylenediamine (93%), and triethylenediamine (used in benzene solution). Analytical data for several of these complexes are given in Table I.

Attempts to prepare the analogous triethylamine and N,N-dimethylaniline complexes were unsuccessful. With pyridine a dark green resinous solid was formed, which contained no active hydride groups.

Method B.—To a 1-l. stainless steel jar mill containing 350 cm^3 of 0.5-in. steel balls were added about 2 g of beryllium hydride and 70–100 ml of amine. The jar was sealed and rotated at room temperature for periods of 1–3 days. The reaction mixture was decanted and the mill contents rinsed with fresh amine. After filtration the filtrate was allowed to stand overnight at −10°. The crystalline product was recovered, washed with petroleum ether, and vacuum dried. Complexes containing the following amines were prepared by this method (at the yields given): triethylamine (16%), N-methylpyrrolidine (93%), methyldiethylamine (93%), and N-methylmorpholine (60%).

Acknowledgment.—The authors are indebted to Dr. F. J. Impastato for infrared and nmr analyses, to Mr. J. B. Chidester for X-ray measurements, to Mr. R. E. Boucher for chemical analyses, and to Drs. F. Conrad and F. W. Frey for helpful suggestions.

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Preparation and Properties of Pentafluorosulfanyldichloramine, SF_5NCl_2[1]

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Received October 21, 1968

The reaction of NSF_3 and ClF yields pentafluorosulfanyldichloramine, SF_5NCl_2. The compound is a light yellow liquid with a boiling point of 64° and a melting point of −120°. It is sensitive to mechanical shock and is thermally unstable at 80°. Hydrolysis and the reaction of SF_5NCl_2 with mercury were slow.

Introduction

The addition of HF to the triple bond in NSF_3 to form SF_5NH_2 has been reported.[2] The preparation of perfluoroalkyldichloramines by the addition of ClF to perfluoronitriles was also reported recently.[3] In an analogous manner, ClF reacted with NSF_3 yielding the new compound pentafluorosulfanyldichloramine, SF_5NCl_2.

Experimental Section

Apparatus.—Reactions were carried out in Hoke stainless steel cylinders. An all-glass high-vacuum system was used for handling the materials. Stopcocks and joints were lubricated with Kel-F No. 90 grease. The mercury in the manometers was covered with Halocarbon oil to reduce attack by ClF on the mercury.

Materials.—Chlorine (Matheson), chlorine trifluoride (Matheson), sulfur tetrafluoride (Matheson), silver(I) fluoride (Harshaw), and silver(II) fluoride (Harshaw) were used without purification.

Chlorine monofluoride was prepared by the reaction of ClF_3 with a slight excess of Cl_2. The reaction mixture was heated to 400° and then quenched in water. The products were passed through a −119° trap (ethyl bromide slush). The ClF passed through and was stored in stainless steel cylinders until used.

Fluoroformyliminosulfur difluoride, prepared by the reaction of silicon tetraisocyanate and sulfur tetrafluoride at 120°,[4] was fluorinated with AgF_2 to give thiazyl trifluoride, NSF_3.[5]

Reaction of Thiazyl Trifluoride with Chlorine Monofluoride.—In a typical reaction 7 mmol of NSF_3 and 28 mmol of ClF were condensed into a 75-ml stainless steel cylinder and held at −78° (Dry Ice–trichloroethylene). The reaction was complete after 2 hr. The products were passed through −95° (toluene slush), −131° (*n*-pentane slush), and −196° (liquid nitrogen) traps. The SF_5NCl_2 collected at −95°, the −131° trap collected Cl_2, and SF_6 and unreacted ClF collected at −196°. Some noncondensable material passed through to the pump.

With a ratio of ClF to NSF_3 of greater than 4:1, pure liquid SF_5NCl_2 was collected at −95°. A typical yield was 1.48 g of SF_5NCl_2 (2.2 mmol) based on NSF_3.

With a 2:1 ratio of ClF to NSF_3, impurities were present in the SF_5NCl_2 fraction, and SF_5Cl was obtained instead of SF_6. Some unreacted NSF_3 was also recovered under these conditions.

Properties of Pentafluorosulfanyldichloramine, SF_5NCl_2.—The product is a light yellow liquid with a melting point of −119 to −121° and an extrapolated boiling point of 64°. The material could be handled in a vacuum line without decomposition but was unstable at 80° giving SF_5Cl, N_2, and Cl_2. On one occasion a sample exploded when subjected to mechanical shock. The compound reacted slowly with mercury producing NSF_3.

The molecular weight was determined by vapor density measurements to be 211.2. The theoretical value for SF_5NCl_2 is 212.

Anal. Calcd for SF_5NCl_2: Cl, 33.2; S, 13.8. Found: Cl, 33.5; S, 15.1.

Vapor pressures were determined using a mercury manometer in a vacuum system. The data are presented in Table I.

Results and Discussion

The reaction of NSF_3 and ClF at −78° gave 25–32% yields of the new compound SF_5NCl_2. With an excess of ClF, the products Cl_2 and N_2 were also obtained. It is postulated that there were two reactions occurring.

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[1] Taken in part from the thesis submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy by G. R. Zeilenga.

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[3] J. B. Hynes and T. F. Austin, *ibid.*, **5**, 488 (1966).

[4] A. F. Clifford and C. S. Kobayashi, *ibid.*, **4**, 511 (1965).

[5] A. F. Clifford and J. W. Thompson, *ibid.*, **5**, 1424 (1966).

TABLE I
VAPOR PRESSURE OF SF_5NCl_2[a]

Temp, °C	Vapor pressure, mm
−45.0	1.0
−30.6	6.5
−15.0	16.5
0.0	48.0
13.0	86.2
20.0	122.1
23.0	138.9

[a] The heat of vaporization was calculated to be 8.18 kcal/mol and the Trouton constant, 24.3.

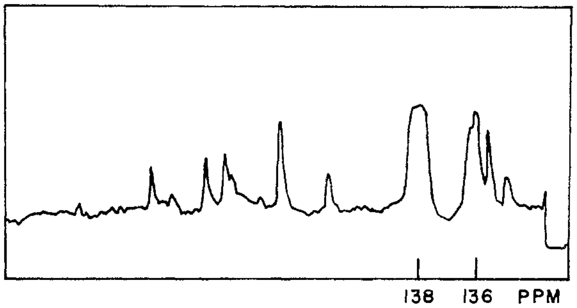

Figure 1.—Nuclear magnetic resonance spectrum of SF_5NCl_2

$$NSF_3 + 2ClF \longrightarrow SF_5NCl_2$$

$$NSF_3 + 3ClF \longrightarrow SF_6 + {}^3/_2Cl_2 + {}^1/_2N_2$$

When stoichiometric amounts of ClF were used, some unreacted NSF_3 was recovered and SF_5Cl and SF_4 were obtained instead of SF_6. SF_5Cl and SF_4 must have further reacted with ClF when an excess was present. The necessity of excess ClF probably indicated only that the starting material was impure. When the lower ratio of ClF to NSF_3 was used, SF_5NCl_2 was contaminated by at least two impurities. One of these, with a sharp infrared peak at 1300 cm^{-1}, the region of S=N stretch, may have been $SF_4{=}NCl$.

The infrared spectrum of SF_5NCl_2 vapor was obtained in the 5000–700-cm^{-1} region using a Perkin-Elmer Model 137 Infracord spectrometer. A Beckman IR5A spectrometer equipped with CsBr optics was employed for the 700–400-cm^{-1} region. Strong peaks were observed at 913, 862, and 600 cm^{-1} which are characteristic of the $-SF_5$ group.[2,5–7] A medium-strength peak at 692 cm^{-1} is in the region of N–Cl stretch.[8]

The ^{19}F nuclear magnetic resonance spectrum of SF_5NCl_2 is shown in Figure 1. It is complex and similar to other $-SF_5$ compounds.[9,10] The major resonance peaks are at −136 and −138 ppm relative to CF_3COOH.

The mass spectrum of SF_5NCl_2 was taken on a Hitachi Perkin-Elmer RMU-6A mass spectrometer using an ionization voltage of 75 V. An initial spectrum with the inlet tube at 185° showed no chlorine-containing fragments, as the compound apparently decomposed and reacted within the inlet. Even with the inlet at room temperature, reactions occurred. Three consecutive spectra were run on the same sample. Some peaks increased steadily while others decreased.

No parent peak was observed for SF_5NCl_2. The largest peaks from the product were at m/e 159 and 157 with intensities 5.5 and 17.5, respectively, relative to SF_5^+ set at m/e 100. These were attributed to $SF_4N^{37}Cl^+$ and $SF_4N^{35}Cl^+$ and are in the expected ratio to each other. Another ion due to SF_5NCl_2 was SF_3NCl^+ at m/e 140 and 138 with relative intensities of 1.5 and 5, respectively. Peaks attributable to SF_5NCl_2 decreased with time while various oxygen-containing species such as SOF_4^+ and hydrogen-containing species increased. The S–F fragments were relatively unchanged. The highest peaks occurring at m/e 179 and 177 with relative intensities of 3 and 7 were attributed to SF_5NHCl^+. These with the peaks at m/e 160 (0.8) and 158 (3) for SF_4NHCl^+ support the belief that the SF_5NCl_2 underwent hydrolysis with small amounts of water in the spectrometer inlet according to the equations

$$SF_5NCl_2 + H_2O \longrightarrow SF_5NHCl + HOCl$$

$$2SF_5NCl_2 + H_2O \longrightarrow 2SF_5NHCl + Cl_2O$$

The peaks at m/e 88, 86, 53, 52, and 51 unfortunately cannot be assigned unambiguously to hypochlorite fragments. However, the weak peaks at m/e 90 (3) and 63 (0.3) may be attributable to $^{37}Cl_2O^+$ and $HO^{37}Cl^+$, respectively.

Further hydrolysis should produce SF_5NH_2. The mass peaks at m/e 143 (23), 124 (4.5), 86 (7), and 67(10) may be attributed to $SF_5NH_2^+$ and its fragments, but not unambiguously so.

In addition to the peaks already discussed, important m/e peaks occurred at: 108 (14.5), SF_4^+; 104 (14.5), $HNSF_3^+$; 103 (37), NSF_3^+; 91 (14), $^{34}SF_3^+$; 89 (100), $^{32}SF_3^+$; 84 (13), NSF_2^+; 70 (65.5), SF_2^+; and 49 (14), $N^{35}Cl^+$.

Acknowledgment.—This work was supported by the National Science Foundation under Grant No. GP-4974

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