of the University of Texas, Austin, Texas and of Mr. James L. Roark in obtaining nmr spectra is gratefully acknowledged. We wish to thank Mrs. M. K. Ready, Miss Carol J. Rawland, and Mr. Randall J. Rogers for experimental work in the preparation of some of the salts.

Notes

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Preparation and Properties of Pentafluorosulfanyliminosulfur Dichloride, $SF_5N{=}SCl_2$

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Pentafluorosulfanylamine, SF_5NH_2, reacts with active halides such as SF_4 splitting out hydrogen halide.[1] It was of interest to see whether the reaction with sulfur dichloride would yield the simple substitution product $SF_5N{=}S$ or some more complex compound.

Experimental Section

Materials and Equipment.—Sulfur dichloride, obtained from Hooker Chemical Co., was used without further purification. Technical grade silver difluoride and silver oxide were used as obtained from Harshaw Chemical Co. Pentafluorosulfanylamine, SF_5NH_2, was prepared as described by Clifford and Duncan.[2]

Reactions were carried out in Hoke stainless steel cylinders equipped with Model Y327A series needle valves. A copper high-vacuum system equipped with Whitey Model KS41 series control valves and Kel-F traps was used for preparing pentafluorosulfanylamine. A Pyrex glass high-vacuum system was used for handling the reactants and products. Stopcocks and joints were greased with Kel-F No. 90 grease. Swagelok unions afforded vacuum-tight glass-to-metal connections.

Preparation and Properties of Pentafluorosulfanyliminosulfur Dichloride.—Pentafluorosulfanylamine (0.935 g) and SCl_2 in a mole ratio of slightly less than 1:2 were allowed to react in a 30-ml stainless steel cylinder with no solvent at room temperature for 2 days. The principal volatile reaction products were HCl and a pale yellow liquid (1.45 g, 90%) subsequently identified as SF_5NSCl_2. Traces of SiF_4, NSF_3, SOF_2, and some unreacted SCl_2 were recovered, but no unreacted SF_5NH_2. The inside of the reaction cylinder was found to be coated with a yellow solid containing 4.26% sulfur with traces of fluorine.

When equimolar quantities (5.82 mmol) were allowed to react under the same conditions, much NSF_3 was recovered along with SiF_4. Some SF_5NH_2 was also recovered and smaller yields of SF_5NSCl_2 were obtained than with the 1:2 ratio of reactants. The SF_5NSCl_2 was collected in a −45° trap, which allowed the more volatile by-products to pass through. Repeated trap-to-trap distillation was necessary to free the product from SF_5NH_2.

Elemental analysis was difficult because of the great susceptibility of the compound to hydrolysis but yielded the following results. *Anal.* Calcd for SF_5NSCl_2: S, 26.2; N, 5.73; Cl, 29.1. Found: S, 28.1; N, 6.75; Cl, 28.95. Although the liquid reacted very rapidly with mercury making vapor-pressure measurements difficult in the equipment in use, it was determined that the vapor pressure was about 1 cm at room temperature. Vapor density studies indicated the molecular weight to be about 229 whereas SF_5NSCl_2 requires 244. However, mass spectral peaks at *m/e* 210 and 208, in an approximate ratio of 3:1, which are attributable to $S_2F_5NCl^+$ support the assignment of the formula as $S_2F_5NCl_2$. No freezing point was determined but the product remained liquid at −78°.

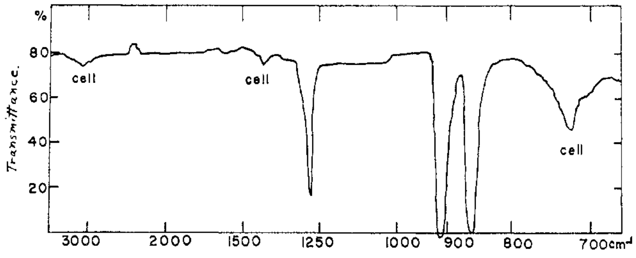

Figure 1.—Infrared absorption curve for SF_5NSCl_2.

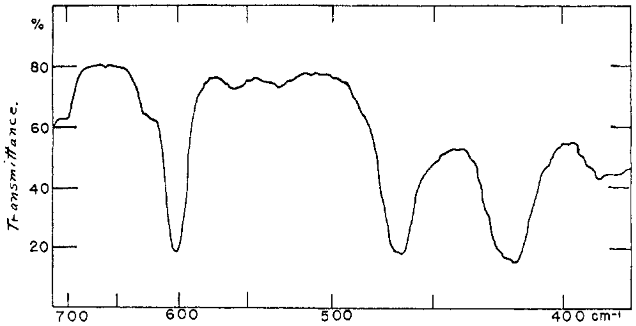

Figure 2.—Infrared absorption curve for SF_5NSCl_2.

The infrared spectrum of SF_5NSCl_2 in the 3000–700-cm^{-1} region was obtained on a Model 137 Perkin-Elmer Infracord spectrophotometer using a 10-cm gas cell with NaCl windows. The spectrum in the 700–375-cm^{-1} region was obtained with a Beckman IR5A spectrophotometer with CsBr optics using a 10-cm cell with KBr windows. Neither the NaCl nor the KBr windows were etched by the sample. The spectrum was found to bear a remarkable similarity to that of SF_5NSF_2 with the characteristic absorption bands at 760 and 714 cm^{-1} for $=SF_2$ being replaced by bands at 475 and 415 cm^{-1}, presumably for $=SCl_2$ group stretching frequencies.

When equimolar amounts of SF_5NH_2 and SCl_2 (6.28 mmol) were allowed to react at room temperature for 3 days in a 75-ml cylinder containing 10 ml of anhydrous diethyl ether, no SF_5NSCl_2 was found. About half of the SF_5NH_2 had separated into NSF_3 and HF. The remainder could not be separated from the ether by trap-to-trap distillation.

Reaction with AgF_2.—When 0.5 g of SF_5NSCl_2 was heated with AgF_2 in a steel cylinder at 100° for 1 hr and then kept at 50° for 24 hr, the principal volatile product was found to be SF_5NSF_2, identified by its infrared spectrum.[1] The yield was nearly quantitative and the reaction is presumed to be

$$SF_5NSCl_2 + AgF_2 \longrightarrow SF_5NSF_2 + AgCl + 0.5Cl_2$$

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

[2] A. F. Clifford and L. C. Duncan, *ibid.*, **5**, 692 (1966).

Although the Cl_2 was not identified, silver chloride was found in the solid.

Reaction with Ag_2O.—In an attempt to produce the compound SF_5NSO[1] about 0.2 g of SF_5NSCl_2 was condensed onto an excess of Ag_2O (about 5 g) and the cylinder was heated to 50° for 24 hr. No SF_5NSO was found, the principal products being equimolar amounts of NSF_3 and SOF_2. Silver chloride was found in the solid.

Discussion

Although no free sulfur or S_2Cl_2 was found among the products of the reaction leading to SF_5NSCl_2, the presence of sulfur in some form in the yellow deposit on the inside of the reaction cylinder suggests that the reaction was

$$SF_5NH_2 + 2SCl_2 \longrightarrow SF_5NSCl_2 + 2HCl + S$$

or perhaps

$$2SF_5NH_2 + 4SCl_2 + Fe \longrightarrow 2SF_5NSCl_2 + 4HCl + \text{“}FeS_2\text{”}$$

The identity of the compound is proved by the combined evidence of the elemental analysis, mass spectral evidence, and particularly the infrared spectrum. The sharp peak at 1240 cm^{-1} may confidently be assigned to the N=S stretch. (The N=S stretch in $SF_5N{=}SF_2$ occurs[1] at 1313 cm^{-1}.) Similarly, the peaks at 913, 862, and 600 cm^{-1} are highly characteristic of the SF_5 group, while the bands at 760 and 714 cm^{-1}, attributed to the SCl_2 group, are very close to those observed by Lustig[3] for the compound CF_3NSCl_2.

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Simple, High-Yield Preparations of Chlorodifluoramine and Difluorodiazine

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Chlorodifluoramine has been prepared by reaction of difluoramine with boron trichloride,[1] phosgene,[2] or hydrogen chloride;[2] by treatment of a mixture of sodium azide and sodium chloride with fluorine;[3] by reaction of chlorine trifluoride with ammonium fluoride;[4] by reaction of chlorine and difluoramine in the presence of potassium fluoride;[5] and by chlorination of $KOCF_2NF_2$.[6]

Difluorodiazine has been prepared by various techniques: the thermal decomposition of fluorine azide,[7] electrolysis of ammonium hydrogen fluoride,[8] reaction of nitrogen trifluoride with mercury vapor in an electric discharge,[9] dehydrofluorination of difluoramine,[10] treatment of a solution of N,N-difluorourea with a concentrated potassium hydroxide solution,[11] reaction of sodium azide and fluorine,[12] decomposition of $N_2F_3Sb_2F_{11}$,[13] and reaction of tetrafluorohydrazine and excess aluminum chloride at 78°.[14]

Although both chlorodifluoramine (NF_2Cl) and difluorodiazine (N_2F_2) have been prepared in a variety of ways, a convenient high-yield synthesis for each compound was not reported. A number of these preparations suffer the disadvantage of low[4,8,9,11,12,14] or erratic[2,3] yields or involve a somewhat circuitous route.[6,13] Explosions have occurred during their preparation.[8,4,7] Difluoramine is used frequently as a source of NF_2 in several of the above preparations;[1,2,5,10] however, this reagent is extremely shock sensitive as a solid and care must be exercised in handling.[5]

We describe herein a convenient method for the preparation of chlorodifluoramine and difluorodiazine in reproducibly good yields by the photolysis of tetrafluorohydrazine and thionyl chloride or bromine, respectively.

Experimental Section

In the following procedures a standard glass vacuum line equipped with a null-point pressure device such as a Booth–Cromer[15] pressure gauge or a spiral gauge was used.

Infrared spectra were recorded with a Beckman IR-5A or Perkin-Elmer 621 spectrophotometer by using a 5-cm gas cell equipped with NaCl or KBr windows. Fluorine-19 nmr spectra were obtained on a Varian HA-100 spectrometer. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. The ultraviolet light source was 450-W lamp equipped with a Vycor filter (Hanovia L-679A36, Engelhard Hanovia, Inc., Engelhard, N. J.).

For gas chromatographic separations a 25 ft × 0.25 in. copper column packed with 20% Kel-F-3 polymer oil or FC-43 (3M Co.) on acid-washed Chromosorb P was used at 25 or −63°. In some cases, fractional condensation was used to effect crude separations.

Tetrafluorohydrazine (Air Products Co.) and reagent grade bromine were used without further purification. Thionyl chloride was purified by a trap-to-trap distillation.

Caution! Care should be exercised in handling tetrafluorohydrazine, chlorodifluoramine, and difluorodiazine since nitrogen–halogen compounds are known to exhibit explosive properties. Any apparatus used should be clean and free of organic materials.

Preparation of NF_2Cl.—$SOCl_2$ (0.714 g, 0.006 mol) and N_2F_4 (0.104 g, 0.001 mol) were condensed into a 850-ml Pyrex vessel equipped with a water-cooled quartz probe. After the mixture had warmed to room temperature, it was photolyzed through a Vycor filter for about 1 hr and then passed through a series of

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