

of the salt into a glass bulb into which a Teflon-coated magnetic stirring bar had been sealed prior to the bulb being fitted with a stopcock. When the salts from diisopropylethyl amine and triethylamine were studied the chloroform was removed at reduced pressure, then the bulb was stirred in a boron trifluoride atmosphere until absorption was completed at that temperature. Tetra-*n*-butylammonium tetrafluoroborate, which does not become liquid at room temperature when treated with boron trifluoride, was "freeze-dried" to give a solid of large surface area. The chloroform solution was diluted 3 to 1 with benzene, the contents frozen, and then the solvent removed at reduced pressure. In either instance the amount of boron trifluoride absorbed was calculated from the weight gain of the bulb (after correction for the boron trifluoride atmosphere in the bulb).

The infrared spectra were obtained in a NaCl cell. The cell plates were not affected by the salt.

Nmr measurements were made by Varian Associates, Palo Alto, Calif.

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Dimethylfluoramine

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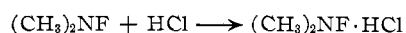
The fluorination of sulfamide in aqueous solution produced *N,N*-difluorosulfamide in moderate yield.¹ An attempt was made to extend this reaction to include the methyl-substituted sulfamides. It was found that the fluorination of unsymmetrical dimethylsulfamide in an unbuffered solution did not yield the desired dimethyldifluorosulfamide. Instead, dimethylfluoramine was isolated along with small amounts of methyldifluoramine. The yield of dimethylfluoramine could be increased by performing the fluorination under conditions which reduced the local fluorine concentration and promoted the rapid removal of the products from the reactor. For this reason, higher yields were obtained when the fluorination was carried out at 30° rather than at 0°. Potassium dimethylsulfamate could be used instead of the dimethylsulfamide. However, little or no dimethylfluoramine was obtained when tetramethylsulfamide was employed. This is, in part, believed to be due to the low solubility of the tetramethyl derivative in the aqueous media.

Dimethylfluoramine is a colorless volatile liquid which is not stable at ambient temperature (extrapolated bp 29.5°, mp -113 ± 0.5°). The F¹⁹ nmr spectrum of the compound consists of a septuplet ($J_{\text{HF}} = 35$ cps) centered at ϕ 24.5 while the H¹ nmr spectrum is a doublet ($J_{\text{HF}} = 35$ cps) centered at -2.95 ppm (*vs.* TMS). The coupling is consistent with that expected for one fluorine and six equivalent protons. The mass cracking pattern of dimethylfluoramine, in addition to containing a peak for the parent molecular ion, (CH₃)₂NF⁺, contains peaks for both molecular ions, HF⁺ and CF⁺. This suggests that some rear-

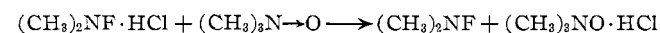
rangements occurred in the ionization process. The high boiling point relative to dimethylamine is probably due to an increase in the molecular weight of the molecule since the Trouton constant appears normal. The molecular weight of the vapor, determined by the mass spectral effusion method,² showed no association (found, 65; calcd, 63.0).

Dimethylfluoramine formed a nonvolatile, slightly yellow oil, on standing at room temperature for several hours. The oil was water soluble and did not oxidize hydrogen iodide. The decomposition could be followed in aqueous solution by F¹⁹ nmr, and after 30 min the septuplet began to decrease in intensity and a new signal appeared in the fluoride ion region. The half-life of the decomposition at 25° was approximately 3 hr. No decomposition was observed in samples stored at -5 to 0° over a 6-day period. Upon warming these stored samples to ambient temperature, decomposition occurred. The exact nature of the decomposition product is not known although its lack of volatility suggests that it may be polymeric. Dimethylfluoramine reacted with all conventional drying agents such as Drierite, magnesium sulfate, and molecular sieves.

Since difluoramine and methyldifluoramine still retain some basicity,³ it was of interest to test the basicity of dimethylfluoramine. When dimethylfluoramine was exposed to an atmosphere of dry hydrogen chloride, a white, crystalline solid formed and 1 mole of acid/mole of substrate was absorbed.



The solid was purified by sublimation under high vacuum at ambient temperature. It was soluble in water and alcohol producing a solution which readily oxidized hydrogen iodide. It was not soluble in acetonitrile, benzene, or methylene chloride. A concentrated aqueous solution decomposed violently when allowed to warm to room temperature. The pure compound melted at 64–65° (sealed tube) and was stable in a dry atmosphere if stored at temperatures below 10°. At higher temperatures slow decomposition occurred producing HCl, HF, and a colorless, nonvolatile oil similar to that formed from the decomposition of the free dimethylfluoramine. The F¹⁹ nmr spectrum of (CH₃)₂NF·HCl contained a broad, unresolved band at ϕ 8.5 which shows that the product does not contain fluoride ion. Further evidence for the retention of the N–F bond in (CH₃)₂NF·HCl is the fact that dimethylfluoramine could be regenerated from the adduct by treatment with bases such as trimethylamine N-oxide or pyridine.



This reaction provides an efficient method for the purification of dimethylfluoramine although the recovery of (CH₃)₂NF is not quantitative. The nature of the

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adduct formed between hydrogen chloride and dimethylfluoramine is not known, but it is likely that ionization, at least in solution, to $[(\text{CH}_3)_2\text{N}(\text{H})\text{F}]^+$ and Cl^- occurs.

Experimental Section

The Preparation of Dimethylfluoramine.—A solution of 1.24 g (10.0 mmoles) of dimethylsulfamide in 50 ml of water was placed into a cylindrical reactor tube (25-mm i.d.) equipped with a magnetic stirrer and a gas dispersion tube which was immersed as deeply as possible. The reactor was held at 30° by a water bath while fluorine diluted with 90 vol. % helium was introduced at a rate of 20 mmoles of fluorine/hr. The off-gas was passed through a series of traps which were maintained at -78° , -126° , and -196° . The contents of the -78° and -126° cold traps were removed after approximately 30 mmoles of fluorine had been passed through the reactor. The fluorination was then continued until an additional 30 mmoles of fluorine had been passed through the reactor. The contents of the -78° and -126° traps were combined with those from the first half of the fluorination, and the crude product was refractionated twice through traps held at -78° , -126° , and -196° . A product of 90–98% purity (0.21 g) was obtained in the -126° trap. Further purification could be achieved by reaction of the adduct formed with hydrogen chloride and trimethylamine N-oxide.

Anal. Calcd for $\text{C}_2\text{H}_5\text{NF}$: C, 38.1; H, 9.6; N, 22.2. Found: C, 37.9; H, 9.5; N, 21.9.

Preparation of $(\text{CH}_3)_2\text{NF}\cdot\text{HCl}$.—A 0.931-g (14.8 mmoles) sample of $(\text{CH}_3)_2\text{NF}$ was placed in a U tube on the vacuum line and cooled to -78° . Hydrogen chloride gas, 40.4 mmoles, contained in a 1-l. bulb was bled into the U tube at a rate such that the pressure did not exceed 50 mm, until no further takeup occurred. The mixture was warmed to -23° and the excess HCl was removed. A 24.9-mmmole sample of HCl was recovered. Sublimation of the crude product at 25° yielded 1.43 g of white crystals which melted at $64\text{--}65^\circ$ in a sealed tube.

Anal. Calcd for $\text{C}_2\text{H}_7\text{ClFN}$: C, 24.1; H, 7.1; N, 14.1. Found: C, 23.8; H, 7.1; N, 13.4.

Reaction of $(\text{CH}_3)_2\text{NF}\cdot\text{HCl}$ with Bases.—A 4.67-mmmole sample of $(\text{CH}_3)_2\text{NF}\cdot\text{HCl}$ was sublimed into a reactor containing 1.0 g of $(\text{CH}_3)_3\text{N}\rightarrow\text{O}$ in 10 ml of sulfolane. As the mixture was warmed, slow gas evolution occurred above the melting point. After standing at 30° for 2 hr, the mixture was fractionated through -78° and -126° cold baths. A 2.59-mmmole sample of pure $(\text{CH}_3)_2\text{NF}$ was obtained from the -126° cold trap.

Spectral Properties.—The F^{19} nmr spectra of $(\text{CH}_3)_2\text{NF}$ and $(\text{CH}_3)_2\text{NF}\cdot\text{HCl}$ were obtained in CCl_3F and $\text{C}_2\text{H}_5\text{OH}$ solutions, respectively, at approximately 0° using a Varian Model 4310 A spectrometer operating at 40 Mc. The mass spectrum of $(\text{CH}_3)_2\text{NF}$ was obtained with a Consolidated Engineering Corp. Model 21-260 spectrometer operating with an ionization voltage of 100 v. The data below summarize the mass number, molecular ion assignment, and the relative abundance for $(\text{CH}_3)_2\text{NF}$: 63, $(\text{CH}_3)_2\text{NF}^+$, 26.0%; 62, $\text{CH}_3\text{NFCH}_2^+$, 40.3%; 43, $\text{CH}_3\text{NCH}_2^+$, 52.6%; 42, $(\text{CH}_2)_2\text{N}^+$, 100%; 41, $\text{C}_2\text{H}_5\text{N}^+$, 18.9%; 40, $\text{C}_2\text{H}_5\text{N}^+$, 14.3%; 39, C_2HN^+ , 4.8%; 38, C_2N^+ , 3.8%; 31, CF^+ , 18.5%; 28, CH_2N^+ , 33.4%; 27, CHN^+ , 5.0%; 20, HF^+ , 31.6%; 15, CH_3^+ , NH^+ , 79.8%; 14, CH_2^+ , N^+ , 11.8%; 13, CH^+ , 4.6%.

Vapor Pressure of $(\text{CH}_3)_2\text{NF}$.—The vapor pressure of $(\text{CH}_3)_2\text{NF}$ was determined in an all-glass apparatus equipped with a Bourdon spoon gauge which was used as a null indicator. The values obtained (T (°K), P_{mm}) are: 249.1, 63.0; 253.0, 77; 255.9, 88.8; 257.3, 100.0; 260.2, 116.0; 262.3, 142.1; 268.0, 165.2; 273.2, 221.0. This gives a value of 22.8 for the Trouton constant and 6.9 kcal/mole for the heat of vaporization.

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Neutral and Anionic Complexes of Copper(I) Chloride with Diethylamine¹

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Reactions of copper(I) and copper(II) chlorides with triethylamine have been reported previously.² Reactions of copper(I) chloride with diethylamine and diethylammonium chloride have now been studied. The only examples of coordination of a copper(I) halide by a secondary aliphatic amine have been given by Peters,³ who reported a series of dimethylamine complexes.

Experimental Section

Materials.—Copper(I) chloride and diethylamine were purified as described previously.^{2,4} The amine hydrochloride, after recrystallization from 1-propanol and drying *in vacuo*, had mp 228° (lit. $228\text{--}229^\circ$).

Procedure.—All materials were handled in a dry nitrogen filled box or in a high vacuum line. Spectrovac stopcock grease was found to be preferable to other vacuum greases for work with diethylamine. Infrared spectra were obtained with a Beckman IR-8 spectrophotometer, and nmr spectra were obtained with a Varian A-60 spectrometer. X-Ray diffraction powder patterns were obtained using rotated thin-wall sealed glass capillary tubes and a Model A4969A General Electric Co. 14.32-cm diameter powder camera with copper $K\alpha$ radiation.

The System Diethylamine–Copper(I) Chloride.—An excess of diethylamine was distilled onto a weighed sample of copper(I) chloride in a tube attached to the vacuum line, and diethylamine was then removed at 0° in the course of pressure–composition measurements on the system. The isotherm is shown in Figure 1. When amine had been removed until constant weight was achieved, the reaction tube was transferred to the drybox and opened, and the product was taken for analysis. *Anal.* Calcd for $\text{CuCl}\cdot(\text{C}_2\text{H}_5)_2\text{NH}$: mole ratio, 1.00; Cu, 36.9; Cl, 20.6; $(\text{C}_2\text{H}_5)_2\text{NH}$, 42.5. Found: mole ratio, 1.00; Cu, 36.7; Cl, 20.6; $(\text{C}_2\text{H}_5)_2\text{NH}$, 42.2.

Solution of Copper(I) Chloride in Diethylamine.—Copper(I) chloride dissolved slowly but appreciably in diethylamine. The solution showed no measurable conductance. When a piece of sodium was added, the rate of hydrogen evolution resembled that of the pure solvent and was much slower than that of a suspension of diethylammonium chloride in diethylamine. The molecular weight of the solute species was determined at 28.0° by solvent vapor pressure lowering measurements, using Raoult's law. A value of 390 ± 20 was obtained; the formula weight of copper(I) chloride is 99.0. The infrared spectrum of a 4.5 wt % solution of copper(I) chloride in diethylamine was identical with that of the solvent. The solution showed a large thermal coefficient of solubility in the region of room temperature, giving a white crystalline product on cooling. This was separated by filtration under nitrogen in the drybox, washed with petroleum ether, dried briefly in a nitrogen stream, and analyzed. *Anal.* Calcd for $\text{CuCl}\cdot 2(\text{C}_2\text{H}_5)_2\text{NH}$: Cu, 26.0; Cl, 14.5; $(\text{C}_2\text{H}_5)_2\text{NH}$, 59.7. Found: Cu, 25.8; Cl, 14.9; $(\text{C}_2\text{H}_5)_2\text{NH}$, 60.3. The

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