suggests that steric considerations prevail over inductive factors[10] in the N,N,N′,N′-tetramethylen complexes since one would expect the increased electron density at the nitrogen atoms of N,N,N′,N′-tetramethylen to rank this ligand highest in coordinating ability, if the inductive property were the only consideration. Both steric and inductive factors operate in the same direction in determining the relative position of N,N′-diphenylen in the series.

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The Preparation of Tetrakis(triethylsilylamino)diborane(4)[1]

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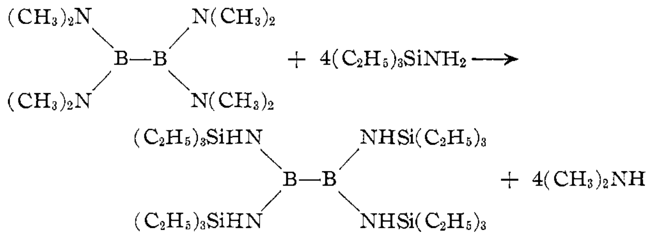
Tetra(amino)diborane(4) compounds have been synthesized and studied in some detail[3]; however, there has been no report made of a compound of this type containing silylamine groups. We wish to report the first preparation of such a compound, namely tetrakis(triethylsilylamino)diborane(4), by the direct transamination[3a,b] of tetrakis(dimethylamino)diborane(4) with triethylsilylamine.



Experimental

Reagents and Apparatus.—Research quantities of tetrakis(dimethylamino)diborane(4) were supplied by U. S. Borax Corp., Anaheim, Calif. Triethylsilyamine was prepared from triethylchlorosilane and liquid ammonia.[4] Volatile compounds were separated using a standard high vacuum line.[5] Elemental analyses were done by Schwarzkopf Laboratories, Woodside, N. Y. Infrared spectra were obtained using Perkin-Elmer 137 or 237 spectrophotometers. Proton nuclear magnetic resonance spectra were obtained using a Varian A-60 spectrometer. Mass spectra were obtained using a Bendix Model 14 time-of-flight mass spectrometer. An F and M Model 500 gas chromatograph equipped with a 2-ft. column containing 30% silicone gum rubber SE 30 substrate on 60/80 mesh Chromosorb-P was used for analytical purposes. Separation and isolation of products were accomplished using an Aerograph Autoprep Model A-70 gas chromatograph equipped with a 5-ft. column containing the same packing as noted above.

Preparation of $[(C_2H_5)_3SiNH]_4B_2$.—A 500-ml., one-neck, round-bottom flask was equipped with a Friedrich condenser and a side-arm gas inlet tube which was connected to a source of dry nitrogen. The condenser was connected to two traps, the first trap being cooled to −80° and the second trap being cooled to −195°. Finally, the outlet of the trap at −195° was connected to a mercury bubbler. A continuous flow of nitrogen was maintained in the system during the reaction.

For a typical reaction, 32.0 g. (0.240 mole) of triethylsilylamine, 8.50 g. (0.042 mole) of tetrakis(dimethylamino)diborane(4), and 300 ml. of toluene were added to the reaction flask. The reaction mixture was refluxed for 17 days, during which time the traps at low temperature were monitored with all volatile materials being collected. Dimethylamine (69.2 mmoles) and ammonia (38.6 mmoles) were isolated from the traps, these compounds being identified by their characteristic vapor pressures and/or infrared spectra. The solvent, some excess triethylsilylamine, and additional dimethylamine (5.0 mmoles) were removed from the reaction mixture at low pressures. Further separations of the solvent-free reaction mixture were made using gas chromatography techniques, and two major products with nearly identical infrared spectra were isolated. The product fraction having the longest retention time on the column was found to be tetrakis(triethylsilylamino)diborane(4) (yield 20%, estimated from gas chromatogram). The other major product has not been completely characterized.

Anal. Calcd. for $[(C_2H_5)_3SiNH]_4B_2$: C, 53.11; H, 11.89; B, 3.98; N, 10.32; Si, 20.70. Found: C, 53.40; H, 11.47; B, 3.97; N, 10.41; Si, 20.83.

The peak of highest mass in the mass spectrum appeared at 542.6 and 542.8 ± 0.5 as compared to two internal standards in two separate determinations. These data are in good agreement with the calculated molecular weight of 542.8. Also, the fragmentation pattern observed in the mass spectrum is consistent for the molecule $[(C_2H_5)_3SiNH]_4B_2$.

The infrared spectrum of the compound contained the following characteristic absorption bands: 3380 cm.$^{-1}$ (N–H), 838 cm.$^{-1}$ (Si–N), and 1313 cm.$^{-1}$ (B–N).

The proton n.m.r. spectrum was quite complex in the region 0.8–2.0 p.p.m. (*vs.* tetramethylsilane reference in a sealed capillary tube) and was not readily interpreted; however it was shown to be nearly the same as the spectrum of triethylsilylamine.

Discussion

Although the reaction time is quite long, and the yield is relatively low, it has been established that tetrakis(triethylsilylamino)diborane(4) is one of the major products formed in the reaction of triethylsilylamine with tetrakis(dimethylamino)diborane(4).

As expected, dimethylamine and ammonia were also generated during the course of the reaction. The dimethylamine is the primary volatile product in the transamination reaction; whereas the ammonia is a secondary product that is produced by the following reactions: (1) the condensation of triethylsilylamine to hexaethyldisilazane[6]; (2) the transamination reaction[7,8] of dimethylamine with triethylsilylamine to give N,N-dimethyltriethylsilylamine.[9] The infrared spectrum of one of the fractions separated from the reaction mixture gave evidence for the formation of

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[1] $[(C_2H_5)_3SiNH]_2B–B[HNSi(C_2H_5)_3]_2$; name approved by *Chemical Abstracts*. See: "The Naming and Indexing of Chemical Compounds," *Chem. Abstr.*, **56**, paragraph 288 (1962).

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[3] For example see the following and the references cited therein: (a) R. J. Brotherton, A. L. McCloskey, L. L. Petterson, and H. Steinberg, *J. Am. Chem. Soc.*, **82**, 6242 (1960); (b) M. P. Brown, A. E. Dann, D. W. Hunt, and H. B. Silver, *J. Chem. Soc.*, 4648 (1962); (c) L. L. Petterson and R. J. Brotherton, *Inorg. Chem.*, **2**, 423 (1963); (d) S. C. Malhotra, *ibid.*, **3**, 862 (1964).

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[5] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[6] R. M. Pike, *Rec. trav. chim.*, **81**, 28 (1962).

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[8] R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961).

[9] K. A. Andrianov, S. A. Golubstov, and E. A. Semenova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 47 (1958); *Chem. Abstr.*, **52**, 11734 (1958).

both hexaethyldisilazane and N,N-dimethyltriethylsilylamine.

Tetrakis(triethylsilylamino)diborane(4) is a colorless, viscous liquid, stable at room temperature, but sensitive to moisture. It is soluble in nonpolar solvents such as toluene, ether, and cyclohexane. Tetrakis(triethylsilylamino)diborane(4) decomposes at 280° and reacts with dry hydrogen chloride. Ammonium chloride, triethylchlorosilane, and a small amount of a solid that reduces a solution of silver nitrate were formed in the hydrogen chloride reaction. The exact composition of this latter solid is not known, and further investigations will be carried out in an effort to identify both this substance and the products of the pyrolysis of tetrakis(triethylsilylamino)diborane(4).

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CONTRIBUTION FROM AMERICAN CYANAMID COMPANY,[1]
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A Preparation of Chlorodifluoramine. Reaction of Chlorine and Difluoramine in the Presence of an Alkali Metal Fluoride

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Chlorodifluoramine has been prepared by the reactions of difluoramine with boron trichloride,[2a] phosgene,[2b] or hydrogen chloride.[2b] It can also be obtained by treating a mixture of sodium azide and sodium chloride with fluorine.[3] This paper reports the convenient synthesis of chlorodifluoramine by the reaction of chlorine and difluoramine in the presence of certain alkali metal fluorides.

The reaction appears to occur essentially as shown by the equation. Thus, chlorodifluoramine was formed in good yield when a gaseous mixture of equimolar amounts of chlorine and difluoramine was brought into contact with anhydrous potassium fluoride. The reaction was carried out in the dark to avoid possible photochemical reactions. The gaseous product amounted to 54% of the gaseous reagents charged and was mostly chlorodifluoramine according to infrared analysis. Purification of the gas by fractional codistillation[4] gave pure chlorodifluoramine in 66% yield. A control reaction showed that the potassium fluoride was necessary for significant reaction to occur.

$$HNF_2 + Cl_2 + MF \longrightarrow ClNF_2 + MF\cdot HCl$$

Similar results were obtained when an excess of chlorine was allowed to react with difluoramine in the presence of rubidium fluoride. No other metal fluorides were investigated as possible catalysts.

The catalytic activity of the fluoride salt is probably due to the basic nature of fluoride ions.[5] Interaction of the proton of difluoramine with a fluoride ion would increase the electron density on the nitrogen atom and hence promote electrophilic attack by chlorine.

$$\overset{\delta-}{F_2N}\cdots\overset{\delta+}{H}\cdots\cdots F^-M^+$$

Although the true intermediates involved are unknown, the postulation of an electrophilic attack by chlorine is supported by the known reaction of difluoramine with the Lewis acid, boron trichloride.[2a]

Experimental

Caution.—Chlorodifluoramine and difluoramine are highly explosive compounds.[6] Particular care must be used in condensing difluoramine.[7]

Vacuum line and drybox techniques were used, and the progress of the reactions was followed by infrared spectroscopy.[8] The infrared spectrum of chlorodifluoramine has strong absorptions at 10.75 (triplet), 11.7 (doublet), and 14.4 (triplet)[2a,8] μ and is easily distinguished from the spectrum of difluoramine, which has a strong triplet at 11.3 μ.[9] The reactions were carried out in Pyrex glass bulbs. Joints and stopcocks were lubricated with Kel-F No. 90 grease, and a layer of Kel-F oil was used to protect the mercury manometer.[2a]

The chlorine (Matheson Co.) was dried by repeated condensation onto phosphorus pentoxide. Finely ground anhydrous potassium fluoride (Baker and Adamson Co.) and anhydrous rubidium fluoride (American Potash and Chemical Co.) were used. They were handled in a drybox to avoid contact with atmospheric moisture. Difluoramine was prepared by the reaction of tetrafluorohydrazine with thiophenol.[10]

Reaction of Chlorine and Difluoramine in the Presence of Potassium Fluoride.—An equimolar mixture of chlorine and difluoramine was prepared by condensing[7] the gases into a Pyrex glass bulb from which light was excluded by several layers of aluminum foil. The gases were allowed to equilibrate at ambient temperature. Part (1.3 mmoles) of the gaseous mixture was admitted to an evacuated 164-ml. Pyrex glass reactor (covered with aluminum foil) which contained 5.0 g. of potassium fluoride. After 18 hr. at ambient temperature, the product amounted to 0.7 mmole and was mostly chlorodifluoramine based on an infrared spectrum.[2a,8] Analysis of the gas by fractional codistillation[4] showed that only small amounts of impurities were present.

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[1] This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract No. NOrd 18728.

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[5] L. Rand, J. V. Swisher, and C. J. Cronin, *J. Org. Chem.*, **27**, 3505 (1962), and references cited therein; E. A. Lawton and D. Pilipovich, U. S. Patent 3,109,711 (1963), describe the reaction of difluoramine with alkali metal fluorides.

[6] The various types of shielding to be used with such compounds are described by C. L. Knapp, *Ind. Eng. Chem.*, **55**, No. 2, 25 (1963).

[7] Difluoramine can probably be condensed more safely at −142° than at −196° (ref. 2b). Solid difluoramine is particularly explosive (ref. 8), and a referee has pointed out that a condensing bath higher than −116° should be used. It does appear possible to condense mixtures of difluoramine and certain reagents at −196°.

[8] Actual spectra of difluoramine and chlorodifluoramine have been published (C. B. Colburn in "Advances in Fluorine Chemistry," M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworths, Washington, 1963, p. 113).

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