hydroxybiphenyl are formed but no biphenyl or *p*-terphenyl could be isolated. Neither the manner in which these products are formed nor the nature of the deamination reaction is evident.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Silyl-Amino Boron Compounds[1]

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The existence of aminodiborane[2] and its N-methyl derivatives[3] leads to the question whether it is possible to find many similar derivatives involving a wide variety of types of substituting groups. As a step toward a full exploration of this subject, two new aminodiboranes, containing respectively the $(SiH_3)_2N$ and CH_3NSiH_3 units, have been prepared. As a study contributory to the planning of these preparations, the existence of the corresponding aminoborines and aminoboron dichlorides was investigated.

The preparation of such compounds requires a method somewhat different from the aminolytic processes used for the methyl derivatives, for there are no primary nor secondary amines in which the SiH_3 group is bonded to N. It is known, however, that the SiH_3 groups in tris-silylamine are quite labile, as in the fast reaction $(SiH_3)_3N + 4\ HCl \rightarrow 3\ SiH_3Cl + NH_4Cl$.[4] It thus becomes a reasonable prediction that electron receptors such as boron trichloride will react with $(SiH_3)_3N$ in much the same manner as HCl does. Accordingly, it was found that the reaction $(SiH_3)_3N + BCl_3 \rightarrow SiH_3Cl + (SiH_3)_2NBCl_2$ occurs cleanly at −78°, with indications of an intermediate addition compound such as $(SiH_3)_3NBCl_3$. The new compound N,N-bis-silyl-aminoboron dichloride is like the known $(CH_3)_2NBCl_2$[5] in several respects, including volatility and polymerization.

A somewhat similar experiment showed that the compound $(SiH_3)_3NBF_3$ forms reversibly in the temperature range −78 to −40°, but decomposes irreversibly at higher temperatures. This preliminary work was not so cleanly quantitative as that with boron trichloride, but it served to show the weakness of $(SiH_3)_3N$ as an electron donor.

A parallel reaction between tris-silylamine and diborane does not occur, evidently because the former is such a weak electron donor that it is not possible to form the intermediate complex $(SiH_3)_3NBH_3$, analogous to the very stable $(CH_3)_3NBH_3$.[6] Hence in order to produce the new compound $(SiH_3)_2NBH_2$ it was necessary to render the borine group more electron-receptive, by substitution of a more electronegative atom for one hydrogen. This was accomplished by the use of bromodiborane, the BH_2Br part of which was consumed by the reaction $2(SiH_3)_3N + 2B_2H_5Br \rightarrow 2SiH_3Br + B_2H_6 + 2(SiH_3)_2NBH_2$.

The resulting new volatile compound, bis-silyl-aminoborine, appears partly as a monomer and partly as a dimer from which the monomer cannot be regenerated. The monomeric form reacts with diborane below room temperature, to produce the new compound $(SiH_3)_2NB_2H_5$. This substance, N,N-bis-silyl-aminodiborane, is almost as volatile as the corresponding dimethyl compound but differs in its spontaneous inflammability and in the ease of its decomposition to form diborane and polymers of $(SiH_3)_2NBH_2$.

Methyl-bis-silylamine, $CH_3N(SiH_3)_2$,[7] behaves like $(SiH_3)_3N$ in a parallel series of reactions, but the products differ considerably from expectations based purely on analogy. The reaction with boron trichloride at −78° stops at the stage shown by the equation $CH_3N(SiH_3)_2 + BCl_3 \rightarrow SiH_3Cl + (CH_3NSiH_3)BCl_2$, but at higher temperatures a second stage is rapidly completed according to the equation $3(CH_3NSiH_3)BCl_2 \rightarrow 3SiH_3Cl + (CH_3NBCl)_3$. The resulting trimer appears to be N,N′,N″-trimethyl-B,B′,B″-trichloroborazole, a new compound which is formed quantitatively by this process.

The first step of the reaction of methyl-bis-silylamine with bromodiborane at −78° probably is $2CH_3N(SiH_3)_2 + 2B_2H_5Br \rightarrow 2SiH_3Br + B_2H_6 + 2(CH_3NSiH_3)BH_2$, but if so the hypothetical N-methyl-N-silylaminoborine is rapidly removed by at least three reactions at −78°: a polymerization–decomposition yielding major proportions of silane, a split yielding a trace of N,N′,N″-trimethylborazole, and the addition of diborane to form the relatively stable new compound $(CH_3NSiH_3)B_2H_5$, N-methyl-N-silylaminodiborane. This spontaneously inflammable liquid is a little more volatile than $(SiH_3)_2NB_2H_5$ but less so than $(CH_3)_2NB_2H_5$. Its decomposition (slow at room temperature but rapid at 50°) yields diborane and the products ascribed to the hypothetical $(CH_3NSiH_3)BH_2$.

Like bromodiborane, dimethylboron bromide reacts with tris-silylamine to liberate bromosilane.

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[1] Presented in part in the Symposium on Structural Problems in Inorganic Chemistry at the 115th (San Francisco) National Meeting of the American Chemical Society, March, 1949.

[2] Schlesinger, Ritter and Burg, THIS JOURNAL, **60**, 2297 (1938).

[3] Burg and Randolph, *ibid.*, **71**, 3451 (1949).

[4] Stock and Somieski, *Ber.*, **54B**, 743 (1921).

[5] Wiberg and Schuster, *Z. anorg. allgem. Chem.*, **213**, 77 (1933).

[6] Burg and Schlesinger, THIS JOURNAL, **59**, 785 (1937).

[7] Emeléus and Miller, *J. Chem. Soc.*, 819 (1939).

This reaction has been studied only in a preliminary way, at room temperature, but the following products were identified: SiH_3Br, SiH_4, $B(CH_3)_3$, and the new compound $(CH_3)_2BN(SiH_2Br)_2$. This is a barely volatile, viscous liquid, spontaneously inflammable in air, and tending to form non-volatile material. Other products are yet to be identified, and more appropriate conditions for the reaction are still to be tried.

Experimental

Preparation of Source Materials

Silane was prepared by adding silicon tetrachloride to an ether solution of lithium aluminum hydride,[8] and purified by distillation in the high-vacuum apparatus. Chlorosilane was produced by the Al_2Cl_6-catalyzed action of hydrogen chloride upon silane[9]: equal volumes, heated 8 hours at 120° (2 atm.) gave a 48% yield of SiH_3Cl, with 18% SiH_2Cl_2 and 34% recovery of SiH_4.

Tris-silyl-amine was prepared by the reaction between chlorosilane and ammonia.[10] For a good yield, the chlorosilane must be pure, and the gaseous ammonia must be introduced slowly into the gaseous SiH_3Cl *from below;* otherwise one obtains large proportions of silane and solid material which HCl will convert to SiH_2Cl_2—probably polymeric SiH_2NH, formed by disproportionation of the hypothetical SiH_3NH_2. The best yield of $(SiH_3)_3N$ represented 80% of the ammonia employed.

Methyl-bis-silyl-amine was prepared from chlorosilane and methylamine,[7] using the same method of mixing; yield 85%.

Diborane was prepared by adding boron fluoride etherate to ethereal lithium aluminum hydride,[11] with final purification through formation of the ether-complex $(CH_3)_2OBH_3$. Boron chloride and bromide were prepared from the corresponding aluminum halides by reaction with boron trifluoride,[12] and bromodiborane by the reaction of diborane with boron tribromide.[13] Dimethylboron bromide was prepared by the reaction between $B(CH_3)_3$ (from methylmagnesium bromide with BF_3 etherate) and HBr at 300°.[14]

Preliminary Studies

The electron-donor bonding power of $(SiH_3)_3N$ was tested in experiments showing its inability to bond $B(CH_3)_3$ or B_2H_6 at temperatures down to $-78°$ and in a further experiment in which the compound $(SiH_3)_3NBF_3$ was formed during a half-hour at $-78°$. This decomposed reversibly, showing equilibrium pressures of 3.7 mm. at $-55°$ and 10.0 mm. at $-41°$. On standing at $-40°$, it began to decompose irreversibly, forming products of higher and lower volatility. During seventy minutes at 100°, nearly half of the silyl groups were converted to SiH_4, SiH_2F_2 and $SiHF_3$ in proportions suggesting SiH_3F as an intermediate, while the rest of the silicon remained in a non-volatile nitrogenous residue. It was concluded that $(SiH_3)_3N$ is a far weaker electron-donor than $(CH_3)_3N$, and that the SiH_3 group is fairly labile. It also appeared that the clearest results would not be obtained from the reaction with boron trifluoride.

In another experiment, 4.43 mmoles of $(SiH_3)_3N$ and 12.6 mmoles of $(CH_3)_2BBr$ were allowed to react at room temperature during four days. Among the products were 0.8 mmole of SiH_4, 4 mmoles of $B(CH_3)_3$, 4 mmoles of SiH_3Br, an unidentified unstable material of intermediate volatility, and a viscous liquid of low volatility. From the last it was possible to isolate a spontaneously inflammable, rather unstable substance conforming to the vapor tension equation $\log_{10} p_{\text{mm.}} = 8.168 - (2406/T)$. This indicated a pure substance boiling at 180° (or a little higher) and having a Trouton constant of 24.2. Its molecular weight was determined as 270 ± 4. Analysis for carbon by nitric acid (conversion to carbon dioxide), bromine by the Mohr method (after reducing the acid solution by magnesium), Si–H bonds by alkaline hydrolysis, nitrogen by titration of ammonia from the hydrolysis, boron by titration of the mannitol spirane, and silicon (roughly) by conversion to $SiCl_4$, gave the literal formula as $(CH_3)_{2.07}B_{1.05}N_{0.90}(Si_{1.2}H_{2.05}Br_{1.05})_2$, or essentially $(CH_3)_2BN(SiH_2Br)_2$ (calcd. mol. wt. 274.85). The experiment showed the importance of maintaining low temperatures during such experiments with $(SiH_3)_3N$, if secondary and side reactions are to be avoided. A further study of this particular reaction should yield interesting results.

N,N-Bis-silyl-aminoboron Dichloride

Preparation.—A mixture of equal gas-volumes of $(SiH_3)_3N$ and BCl_3 was observed to change from a liquid to white crystals during a half-hour, in a closed tube at $-78°$; then during the next eighteen hours at $-78°$ it reliquefied. Now one volume of SiH_3Cl was distilled off and identified by its vapor tensions.[9] The residue at $-78°$ was volatilized at room temperature and measured as the same volume of gas at standard conditions. These facts correspond to the formation of the complex compound $(SiH_3)_3NBCl_3$ and its subsequent quantitative decomposition into SiH_3Cl and $(SiH_3)_2NBCl_2$—a process which is far faster and cleaner than the corresponding reaction of $(SiH_3)_3N$ with BF_3. The numerical results of three such experiments are given in Table I.

TABLE I

REACTION OF $(SiH_3)_3N$ WITH BCl_3

Volumes of reactants (cc. gas at S. C.)		Volumes of products (cc. gas at S. C.)	
$(SiH_3)_3N$	BCl_3	SiH_3Cl	$(SiH_3)_2NBCl_2$
28.1	28.1	27.2	..
20.8	20.9	20.7	20.0
28.7	28.7	29.0	28.6

Properties and Formula.—The product indicated as $(SiH_3)_2NBCl_2$ was purified by fractional condensation *in vacuo* and its vapor tension was measured as 22 mm. at 25°. It thus is about as volatile as monomeric $(CH_3)_2NBCl_2$. Its molecular weight was determined as 157.8 (calcd. 157.9) by the vapor density method. However, as the evaporated sample stood at room temperature, a gradual decrease of pressure indicated polymerization.

A 10.77-cc. sample (gas at S. C.) of the new compound was analyzed by hydrolysis in aqueous ammonia, yielding 65.6 cc. (6.08 volumes) of hydrogen, 1.01 me. of chloride (2.1 volumes of Cl gas), and 0.447 me. of boric acid (0.93 B per molecule). These results confirm the formula $(SiH_3)_2NBCl_2$.

This new compound, like other mono-substitution derivatives of silane, is spontaneously inflammable upon exposure to air. At 60–65° it slowly decomposed, yielding hydrogen, SiH_4, SiH_2Cl_2, and a yellowish glassy residue. A wide-range series of vapor tensions was not determined, on account of its tendency to polymerize. Attempts to hydrogenate it by an exchange of Cl for H with diborane, or with $LiAlH_4$ in ether, were unsuccessful.

N,N-Bis-silyl-aminoborine

Preparation.—Equal gas-volumes of $(SiH_3)_3N$ and B_2H_5Br were placed together in a closed system at $-78°$, and a reaction soon was indicated by the precipitation of needle-like crystals. After eighteen hours at $-78°$, diborane and bromosilane (identified by its vapor tensions,[15]

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[8] Finholt, Bond, Wilzbach and Schlesinger, THIS JOURNAL, **69**, 2694 (1947).

[9] Stock and Somieski, *Ber.*, **52**, 695 (1919).

[10] Stock and Somieski, *ibid.*, **54B**, 740 (1921).

[11] Finholt, Bond and Schlesinger, THIS JOURNAL, **69**, 1199 (1947).

[12] Gamble, Gilmont and Stiff, *ibid.*, **62**, 1257 (1940).

[13] Schlesinger and Burg, *ibid.*, **53**, 4328 (1931).

[14] F. L. McKennon, Ph.D. Dissertation, The University of Chicago Libraries, 1936.

[15] Stock and Somieski, *Ber.*, **50**, 1751 (1917).

molecular weight, and hydrolytic analysis) were isolated in proportions indicating the equation $2(SiH_3)_3N + 2B_2H_5Br \rightarrow 2(SiH_3)_2NBH_2 + 2SiH_3Br + B_2H_6$. The numerical results of four such experiments are given in Table II. In one of these experiments, the residue at −78° was hydrolyzed in aqueous hydrochloric acid (24 hours at 100°) to show 8.12 active hydrogen atoms per NH_3, as demanded by the empirical formula $(SiH_3)_2NBH_2$.

TABLE II

REACTION OF $(SiH_3)_3N$ WITH B_2H_5Br

Volumes of reactants (cc. gas at S. C.)		Volumes of products (cc. gas at S. C.)	
$(SiH_3)_3N$	B_2H_5Br	SiH_3Br	B_2H_6
17.7	18.0	18.0	9.0
17.6	17.6	17.8	8.8
41.7	41.7	42.6	20.8
22.9	22.9	22.9	11.8

Properties.—The presumed $(SiH_3)_2NBH_2$, appearing as a non-volatile crystalline residue at −78°, evidently was in a state of metastable polymerization, for it melted to a viscous liquid in the range −40 to −35°, and thereafter remained liquid even at temperatures well below −78°; it then was possible to isolate a monomer form (10–15% of the whole) having a vapor tension of 7 mm. at −78°. All components of the product were volatile at room temperature, and the average molecular weight values varied from 142 to 161 (monomer, 89). The main fraction remaining after removal of the monomer evidently was the dimer form; vapor tension 10 mm. at 25°. The dimer yielded no monomer on heating; instead, both the monomer and the dimer polymerized irreversibly (completely in 72 hours at room temperature), forming a non-volatile glassy material which, on heating *in vacuo*, yielded only hydrogen, silane, and a red residue.

The molecular weight values for the monomer ran 13 to 20% high, on account of its rapid polymerization. However, the belief in the formula $(SiH_3)_2NBH_2$ for the monomer is supported by the reaction whereby it was converted to $(SiH_3)_2NB_2H_5$ in 80% yield, as described below.

N,N-Bis-silyl-aminodiborane

Preparation.—By analogy with $(CH_3)_2NBH_2$, it was supposed that $(SiH_3)_2NBH_2$ might absorb diborane to form $(SiH_3)_2NB_2H_5$, and in fact, this reaction does occur far more readily than the formation of $(CH_3)_2NB_2H_5$, although the per cent. yield is far lower. In the first experiment, a sample of the original monomer–dimer mixture was allowed to stand four days at room temperature with diborane in considerable excess. It then was possible to isolate a fraction condensing *in vacuo* at −90 to −100°; the gas volume of this was twice that of the diborane consumed, as required by the equation $2(SiH_3)_2NBH_2 + B_2H_6 \rightarrow 2(SiH_3)_2NB_2H_5$. The yield was roughly equivalent to the monomeric component of the original mixture—about 15%, based upon the original tris-silyl-amine.

Next, the monomeric and dimeric components of $(SiH_3)_2NBH_2$ were separately treated with diborane, each for thirty hours at room temperature. The yield of $(SiH_3)_2NB_2H_5$ from the monomer was 80%; that from the dimer, only 10%, and even that may have been due chiefly to incomplete removal of the monomer.

Since the addition reaction seemed to be a property only of the monomer, the next experiment was planned to utilize it as fully as possible before polymerization could occur. A quantity of diborane sufficient to develop six atmospheres pressure at room temperature was placed with the original crystalline product at −78°, and the mixture was slowly warmed to −40° and held at that point for three hours; then it was warmed very slowly to room temperature and left for eighteen hours. The new compound now was isolated in 30% yield—nearly twice as efficient a conversion of the original tris-silylamine as in the best of the earlier experiments. Still better yields might be attained under conditions yet to be determined.

Determination of the Formula.—The vapor density of the new compound indicated the molecular weight to be 101.5 (calcd., 102.85). Hydrolysis in aqueous HCl (20 hours at 120°) gave 11.05 volumes of hydrogen and 0.98 volume of ammonia. Another sample yielded 2.03 equivalents of boric acid per mole of the compound. These results, taken together, are sufficient to establish the molecular formula as $(SiH_3)_2NB_2H_5$.

Physical Properties.—The melting range of pure $(SiH_3)_2NB_2H_5$ was visually observed as −69.4 to −68.8°. The vapor tension values shown in Table III were obtained with the aid of a micrometer-slide cathetometer reading directly to 0.01 mm. At the higher temperatures, the decomposition was fast enough to require repurification between readings, and at 0° even this did not suffice for the desired precision. The results determine the equation $\log_{10} p_{\text{mm.}} = 7.974 - (1669/T)$, from which the heat of vaporization is estimated as 7640 cal./mole and the Trouton constant 23.3 cal./deg. mole. These values are a little too high, and the extrapolated boiling point (54°) too low, for the graph of log p *vs.* $1/T$ is not quite linear.

TABLE III

VAPOR TENSIONS OF LIQUID $(SiH_3)_2NB_2H_5$

t (°C.)	−53.8	−49.3	−39.8	−33.4	−22.7	−15.3	−6.6	0.0
$p_{\text{mm.}}$ (obsd.)	2.28	3.27	6.69	10.71	20.92	31.87	51.7	74.5
$p_{\text{mm.}}$ (calcd.)	2.39	3.32	6.68	10.35	20.61	31.92	51.9	73.5

Chemical Properties.—Like most compounds containing the SiH_3 group, this new substance spontaneously inflames upon exposure to air. During storage at room temperature, it decomposes into diborane and monomeric $(SiH_3)_2NBH_2$, a process which is rendered irreversible by the polymerization of the latter. The rate of loss is slow enough, however, to permit measurement of gas-volumes and other reasonably quantitative work.

Products from Methyl-bis-silylamine

The Reaction with Boron Trichloride.—Equal gas volumes of $CH_3N(SiH_3)_2$ (16.70 cc.) and BCl_3 (16.62 cc.) reacted (without appearance of solid) at −78°, in a closed system during 24 hours to yield 18.70 cc. of SiH_3Cl. The excess over the ideal equation $CH_3N(SiH_3)_2 + BCl_3 \rightarrow (CH_3NSiH_3)BCl_2 + SiH_3Cl$ is attributed to slight warming during visual inspection, for the supposed $(CH_3NSiH_3)BCl_2$ proved to be quite stable at −78°, but lost a further 14.60 cc. of SiH_3Cl on warming to room temperature. This would correspond to the equation $(CH_3NSiH_3)BCl_2 \rightarrow CH_3NBCl + SiH_3Cl$. In a second experiment, 13.15 cc. each of BCl_3 and $CH_3N(SiH_3)_2$ yielded 14.80 cc. of SiH_3Cl at −78°, and a further 11.31 cc. of SiH_3Cl on warming.

The material which the reaction balance indicated to have the empirical formula CH_3NBCl appeared as a non-volatile white solid residue after all possible chlorosilane had been removed *in vacuo* at room temperature. A new sample was formed in an immersible tensimeter[6]: 15.95 cc. each of the original reactants yielded 32.0 cc. of SiH_3Cl. The vapor-volume of the residue now was measured at 150°, as 5.19 cc. gas at 0° and 760 mm. (theoretical for trimer, 5.32). Hence the molecular formula was $(CH_3NBCl)_3$.

TABLE IV

VAPOR TENSIONS OF SOLID $(CH_3NBCl)_3$

t (°C.)	90.7	103.3	110.8	113.0	117.6	122.9	130.3
$p_{\text{mm.}}$ (obsd.)	3.5	6.1	9.0	9.7	12.1	15.9	22.7
$p_{\text{mm.}}$ (calcd.)	3.1	6.1	8.9	9.9	12.4	15.9	22.4

The uniformity of this sample was indicated by measuring a series of vapor tensions. The results, presented in Table IV, determine the equation $\log_{10} p_{\text{mm.}} = 9.238 - (3183/T)$, indicating the heat of sublimation as 14.56 kcal./mole.

This new substance would appear to be the ring compound N,N′,N″-trimethyl-B,B′,B″-trichloroborazole. It is completely stable in dry air.

The Reaction between $CH_3N(SiH_3)_2$ and B_2H_5Br.—The reaction $2CH_3N(SiH_3)_2 + 2B_2H_5Br \rightarrow 2(CH_3NSiH_3)BH_2 + B_2H_6$ was expected to occur cleanly at −78°, and accordingly 27.55 cc. of the methyl-bis-silylamine and 27.62 cc. of B_2H_5Br (gases at S.C.) were brought together and allowed to react at that temperature. A white solid was formed at once. After 36 hours the products, volatile at −78°, were separated and identified as 28.10 cc. of SiH_3Br, 7.0 cc. of SiH_4, and 6.7 cc. of B_2H_6. After warming, the less volatile material was resolved into three components: 5.78 cc. of a substance later proved to be the new compound $(CH_3NSiH_3)B_2H_5$, 0.7 cc. of a less volatile material which proved to be the known compound N,N′,N″-trimethylborazole, $(CH_3NBH)_3$, and a non-volatile residue. It would appear that the initial step was the usual formation of SiH_3Br, but that the accompanying $(CH_3NSiH_3)BH_2$ was destroyed in at least three ways: (1) by disproportionation to form SiH_4 and some kind of amino-silico-boron polymer; (2) by a split to form a trace of the borazole derivative; (3) by absorbing borine groups from the initial reaction, to form the desired $(CH_3NSiH_3)B_2H_5$.

Identification of $(CH_3NBH)_3$.—The 0.7-cc. component was volatile at −8° but completely condensed *in vacuo* at −25°. Its melting range was observed as −8.2 to 7.5° and its hydrolysis yielded 3.2 volumes of hydrogen. These properties conform to those of N,N′,N″-trimethylborazole, $(CH_3NBH)_3$.[16] It would appear to have been formed in a manner parallel to the previously mentioned $(CH_3NBCl)_3$, namely, by the reaction $3(CH_3NSiH_3)BH_2 \rightarrow (CH_3NBH)_3 + 3SiH_4$, which evidently plays a very small role in the decomposition of methyl-silyl-aminoborine.

Improved Preparation of $(CH_3NSiH_3)B_2H_5$.—Although it was considered probable that compound $(CH_3NSiH_3)BH_2$ existed as an intermediate in the foregoing experiment, a considerable fraction of it evidently disproportionated before effective addition of diborane could occur. In order to divert more of the intermediate material toward formation of the desired $(CH_3NSiH_3)B_2H_5$, two experiments involving extra diborane were tried, as follows.

First, 16.6 cc. each of $CH_3N(SiH_3)_2$ and B_2H_5Br were left together for 36 hours at −78°, to yield 16.8 cc. of SiH_3Br, 3.9 cc. of SiH_4 and 3.9 cc. of B_2H_6. Now a 30.2-cc. portion of diborane was added, and the mixture slowly warmed to room temperature. The mixture then was resolved into 31.1 cc. of B_2H_6, 1.25 cc. of SiH_4, and 6.25 cc. of $(CH_3NSiH_3)B_2H_5$ (38% yield).

Second, 33.3 cc. of $CH_3N(SiH_3)_2$, 33.4 cc. of B_2H_5Br, and 26.0 cc. of B_2H_6 were brought together and, after standing at −78°, slowly warmed to room temperature. This time the yield of $(CH_3NSiH_3)B_2H_5$ was 14.7 cc., or 44%.

It thus appears that an improved yield results if extra diborane is added to the $(CH_3NSiH_3)BH_2$ before the disproportionation has gone too far at −78°, but that the yield is still better if diborane is present at the start. The addition reaction apparently is too slow at −78° for utilization of all of the $(CH_3NSiH_3)BH_2$ as fast as it forms, but the effect probably could be improved by the use of a far higher pressure of diborane.

Determination of Formula.—Two determinations of the molecular weight of the new compound by the vapor density method gave the values 84.5 and 85.8; calculated for $(CH_3NSiH_3)B_2H_5$, 86.7. The analysis by hydrolysis gave 7.78 volumes of H_2, 0.975 of CH_3NH_2, and 2.05 volume-equivalents of boron, clearly indicating the molecular formula $(CH_3NSiH_3)B_2H_5$.

Physical Properties of $(CH_3NSiH_3)B_2H_5$.—The melting point of the new compound was visually observed as −39.0°. The vapor tensions of the solid were measured by the aid of a micrometer cathetometer. The results, presented in Table V, conform to the equation $\log_{10} p_{\text{mm.}} = 9.01 - (1910/T)$.

TABLE V

VAPOR TENSIONS OF SOLID $(CH_3NSiH_3)B_2H_5$

t (°C.)	−59.0	−54.3	−49.2	−43.4
$p_{\text{mm.}}$ (obsd.)	1.39	2.09	3.26	5.38
$p_{\text{mm.}}$ (calcd.)	1.35	2.09	3.31	5.37

The vapor tensions of liquid methyl-silyl-aminodiborane are given in Table VI. These results determine the equation $\log_{10} p_{\text{mm.}} = 8.081 - (1686/T)$, from which a long extrapolation gives the boiling point as 51°, the heat of vaporization as 7716 cal./mole, and the Trouton constant as 23.8 cal./deg. mole. The heat of fusion is roughly estimated as 1020 cal./mole. It is evident by comparison of the trend of deviations in the range 0 to 8° with that in the range 10–15°, that the true curve of log *p* *vs.* $1/T$ would be concave downward, implying that the true boiling point might be as high as 60° and the Trouton constant considerably lower than 23.8.

TABLE VI

VAPOR TENSIONS OF LIQUID $(CH_3NSiH_3)B_2H_5$

t (°C.)	−36.3	−31.4	−23.7	−19.1	−13.0	−8.7	−5.4
$p_{\text{mm.}}$ (obsd.)	9.3	12.8	21.7	28.7	39.7	50.4	59.3
$p_{\text{mm.}}$ (calcd.)	9.2	12.8	20.3	27.9	39.8	50.7	60.8
t (°C.)	0.0	2.1	4.9	7.8	10.7	13.4	15.0
$p_{\text{mm.}}$ (obsd.)	81.5	92.6	106.4	121.9	138.6	156.7	169.6
$p_{\text{mm.}}$ (calcd.)	81.4	90.5	104.2	120.1	138.7	157.4	169.8

Chemical Properties of $(CH_3NSiH_3)B_2H_5$.—The new methyl-silyl-aminodiborane proved to be spontaneously inflammable in air, but far more stable than its analog $(SiH_3)_2NB_2H_5$. For example, a 4.2-cc. sample was only 12% decomposed during three days at 25–30°, to yield 0.4 cc. of a mixture of B_2H_6 and SiH_4, and 0.2 cc. of hydrogen. At 55°, however, it was 29% decomposed in fifteen minutes.

The Reaction of $(CH_3NSiH_3)B_2H_5$ with $N(CH_3)_3$.—As a part of the process of characterizing the new compound methyl-silyl-aminodiborane, it was considered useful to learn whether it forms 1:1 addition compounds with nitrogen bases, as $H_2NB_2H_5$, $CH_3NHB_2H_5$, and $(CH_3)_2NB_2H_5$ are known to do. Trimethylamine was chosen as the base for this purpose, on account of the relative simplicity of the possible products.

The experiment involved 5.73 cc. of the methyl-silyl compound with 17.7 cc. of $N(CH_3)_3$. The mixture was left at −78° for 24 hours, after which 8.85 cc. of amine could be recovered at that temperature; the mole ratio of amine added thus was 1.545. Of this, 0.550 (3.15 cc.) came off easily *in vacuo* as the temperature rose to −35°, leaving 0.995 mole of amine per mole of the silyl compound. The formula of the residue thus was the expected $(CH_3NSiH_3)B_2H_5 \cdot N(CH_3)_3$. This product was non-volatile and stable *in vacuo* up to 0°, but at higher temperatures it began to decompose, finally yielding 4.78 cc. of SiH_4 (hydrolyzed to give 18.8 cc. H_2), an unmeasured sample of $(CH_3)_3NBH_3$ (m. p. 94.5–94.7°; vapor tensions checking the literature), 0.8 cc. of material melting at −8° (presumably N,N′,N″-trimethylborazole), and polymeric solids.

Discussion

It now is possible to compare five compounds of the aminodiborane type, and to evaluate trends in terms of structural principles. For such considerations, a reasonable assumption is made—that all five compounds have the same structural pattern: a B–N–B linkage paralleling a B–H–B bond of the type assumed to exist in the

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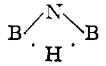
[16] Schaeffer and Anderson, THIS JOURNAL, **71**, 2145 (1949).

bridge model of diborane, a pattern which electron diffraction studies strongly support for $(CH_3)_2NB_2H_5$ and $H_2NB_2H_5$.[3]

Volatility.—As one compares the vapor tensions of these compounds at 0°—$H_2NB_2H_5$ 32 mm., $CH_3NHB_2H_5$ 48 mm., $(CH_3)_2NB_2H_5$ 101 mm., $(SiH_3)_2NB_2H_5$ 74 mm., and $(CH_3NSiH_3)B_2H_5$ 81 mm.—it is clear that the increase of volatility with methylation can be attributed to an increasing separation of  $\mathrm{B}\overset{\mathrm{N}}{\underset{\mathrm{H}}{\diagup\ \diagdown}}\mathrm{B}$ bridge units, in which a dipole exists. A similar effect could be a factor in the relatively high volatility of the silyl compounds, but these are yet more volatile than might be expected on such grounds, and one seeks a further reason. Such a reason emerges from a consideration of the base-weakness of $(SiH_3)_3N$—an effect which might be largely attributable to the wandering of the unshared electron pair from nitrogen into any of fifteen 3d orbitals (possibly hybridized with 3p) of silicon. Such an electron-wandering toward silicon in bis-silyl-aminodiborane would tend to cancel the dipole between N and the BHB system, permitting this compound to be actually more volatile than the most compact isomers of hydrocarbons of similar molecular weight. The dipole-cancelling effect would naturally be less in the methyl silyl compound, so that its volatility is very little higher than that of $(SiH_3)_2NB_2H_5$ in spite of the lower molecular weight.

Stability.—The same principle of electron drift toward silicon would account for the weakness of the N-B bonding in both $(SiH_3)_2NB_2H_5$ and $(CH_3NSiH_3)B_2H_5$—a weakness indicated by the incomplete character and evident reversibility of the reactions by which they are formed from $(SiH_3)_2NBH_2$ and the hypothetical $(CH_3NSiH_3)BH_2$. The same bond weakness appears in the relative ease with which trimethylamine removes a BH_3 group from $(CH_3NSiH_3)B_2H_5$—a reaction which, in the parallel cases of the methylaminodiboranes, requires higher temperatures.

The behavior of the CH_3NSiH_3 compounds fails to be intermediate between the $(CH_3)_2N$ and $(SiH_3)N$ compounds in one respect: the extreme instability of the borine derivatives $(CH_3NSiH_3)BCl_2$ and $(CH_3NSiH_3)BH_2$. It is possible that compounds having two SiH_3 groups attached to the same atom generally tend to be more stable than those having only one SiH_3 group so bonded. The relatively stable existence of $(CH_3NSiH_3)B_2H_5$ can be attributed to the stabilizing effect of the four-bonded nitrogen atom and the bond energy of the BHB bridge link.

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Summary

The compound $(SiH_3)_3N$ at −78° bonds either BF_3 or BCl_3 in 1:1 ratio, with subsequent evolution of halogenated silane. The new volatile compound, $(SiH_3)_2NBCl_2$, was produced quantitatively by this method. Similarly, B_2H_5Br attacks $(SiH_3)_3N$ at −78°, with quantitative formation of B_2H_6, SiH_3Br, and the monomer and dimer of $(SiH_3)_2NBH_2$. The monomer readily adds diborane to form the highly volatile but unstable $(SiH_3)_2NB_2H_5$.

The room temperature reaction of $(SiH_3)_3N$ and $(CH_3)_2BBr$ yields many products, including the new, barely volatile compound $(CH_3)_2BN(SiH_2Br)_2$.

The compound $CH_3N(SiH_3)_2$ reacts with BCl_3 at −78° to form SiH_3Cl and the new compound $(CH_3NSiH_3)BCl_2$, which decomposes with quantitative formation of SiH_3Cl and the new compound $(CH_3NBCl)_3$. With B_2H_5Br at −78°, $CH_3N(SiH_3)_2$ reacts to form SiH_3Br, SiH_4, B_2H_6, a trace of $(CH_3NBH)_3$, a non-volatile solid, and the new highly volatile compound $(CH_3NSiH_3)B_2H_5$.

The compounds $(SiH_3)_2NB_2H_5$ and $(CH_3NSiH_3)B_2H_5$ are regarded as H-bridged structures—an assumption permitting a reasonable comparison of properties with other aminodiboranes.

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