$$(C_3H_7)_2B_2H_4 + 12O_2 \longrightarrow 6CO_2 + 2B(OH)_3 + 6H_2O$$

Sample[7]	CO_2 calcd.	CO_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.251	1.506	1.523	0.502	0.521

Relative Stability of the Alkyl Diboranes.—Numerous experiments were performed to determine the relative rates of decomposition of the methyl, ethyl and *n*-propyl diboranes at room temperature. The experiments were of qualitative character as only the changes of vapor tension at some definite temperature were noted and these changes are not proportional to the amount of substance decomposed. The results, however, did not indicate any marked difference in the stability of analogous alkyl derivatives of diborane.

The authors take pleasure in acknowledging the aid furnished by a grant from the National Research Council for liquid nitrogen, extensively used in this work.

Summary

The four ethyl derivatives of diborane and mono-*n*-propyldiborane and di-*n*-propyldiborane have been prepared by reactions of boron triethyl and of boron tri-*n*-propyl with diborane.

The compounds are shown to be entirely analogous to the corresponding methyl derivatives of diborane.

CHICAGO, ILLINOIS RECEIVED DECEMBER 30, 1935

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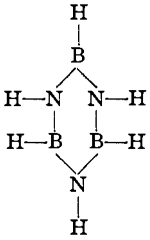
[7] The sample consisted of the residue left by the hydrolysis of the 0.251 millimole of di-*n*-propyldiborane as reported above.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. VI. The Action of Ammonia on the Methyl Diboranes

BY H. I. SCHLESINGER, LEO HORVITZ[1] AND A. B. BURG

Stock and Pohland[2] have found that when the diammoniate of diborane, a salt-like substance first prepared by Stock and Kusz,[3] is rapidly heated to 200° in a closed tube the relatively stable, volatile compound $B_3N_3H_6$ is obtained. To this they assigned the ring structure



on the basis of fairly convincing but not perfectly conclusive evidence. In order to learn more about the mode of formation and the structure of this compound, we first prepared the diammoniates of the four known methyl derivatives of diborane[4] at low temperatures, and then converted them (or the corresponding mixtures of ammonia and methyl diboranes) by rapid heating into methyl derivatives of the ring compound.[5]

Before these studies are described in detail, the results of the high temperature reaction may be surveyed briefly. When the diammoniate of monomethyldiborane (or the corresponding mixture of ammonia and monomethyldiborane) is rapidly heated to 200° at a total pressure of from two to six atmospheres, and kept at this temperature for twenty to thirty minutes, a vigorous reaction occurs. The major products are hydrogen and the mono, di and trimethyl derivatives of $B_3N_3H_6$.[5] Unmethylated $B_3N_3H_6$ and the new compound, dimethylaminoborine $(CH_3)_2BNH_2$[6] are formed in smaller amounts.

These reactions are so complex that it becomes useful to formulate a mechanism for the reaction of ammonia with diborane itself. The following suggestion has proved valuable in correlating logically the results obtained for diborane with those obtained with the methyl derivatives. It is assumed that the first step, in the case of dibo-

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[1] This article represents a part of a dissertation submitted by Leo Horvitz to the Faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Stock and Pohland, *Ber.*, **59B**, 2216 (1926).

[3] Stock and Kusz, *ibid.*, **56B**, 807 (1923). An investigation of the behavior of this substance toward sodium in liquid ammonia solutions promises to throw some light on its as yet not definitely established structure, as will be described in a forthcoming publication from this Laboratory.

[4] The methyl derivatives of diborane are described by Schlesinger and Walker, THIS JOURNAL, **57**, 621 (1935).

[5] In all of these derivatives, the methyl groups are attached to boron atoms. Corresponding isomers in which the methyl groups are attached to nitrogen will be described in a later publication. The existence of these and other derivatives of $B_3N_3H_6$ strongly supports the ring structure proposed by Stock and his co-workers.

[6] The substance might also be called dimethyl ammonoboric acid, a name which seems less in agreement with its properties than the other one suggested. Since no suitable name has been suggested for $B_3N_3H_6$ and its structure is not definitely established, we are following the example of Stock, and his co-workers in using its formula in place of a name. It might be called triborine triamine.

rane, is an ammonolysis to form hydrogen and the hypothetical $B_2H_4(NH_2)_2$.[7] This step may then be followed by a severance of the boron to boron bond, with the production of two similar fragments, H_2BNH_2. Condensation of three such groups with the loss of hydrogen would result in the formation of the ring.

According to this hypothesis, monomethyldiborane should give two dissimilar fragments, $(CH_3)HBNH_2$ and H_2BNH_2. Condensation of three molecules of the former, accompanied by loss of hydrogen, would produce the trimethyl derivative of $B_3N_3H_6$; condensation of H_2BNH_2 would account for the formation of the unmethylated product, while condensation of the two fragments with each other in appropriate proportions could account for the monomethyl and dimethyl derivatives of $B_3N_3H_6$.[8]

The intermediate fragments in the case of the tetramethyldiborane should be molecules of dimethylaminoborine $(CH_3)_2BNH_2$, which, because they do not contain hydrogen atoms bound to boron, might be expected to be far more stable than the fragments $(CH_3)HBNH_2$ or H_2BNH_2. Actually the reaction of ammonia with tetramethyldiborane yields only the compound predicted.

In the case of trimethyldiborane, the intermediate fragments should be $(CH_3)_2BNH_2$ and $(CH_3)HBNH_2$. Condensation of the latter should then give $(CH_3)_3B_3N_3H_3$. In agreement with this prediction, only traces of $B_3N_3H_6$ and its mono or dimethyl derivatives were obtained. But the quantity of $(CH_3)_2BNH_2$ was considerably in excess of that to be expected according to the postulated mechanism, while the quantities of hydrogen and $(CH_3)_3B_3N_3H_3$ were considerably below the theoretical. Trimethyldiborane is, however, very unstable, disproportionating readily into di- and tetramethyldiborane, from the latter of which it is with difficulty separated. This reaction might occur even in the presence of ammonia at the higher temperatures, and could account for the discrepancy noted.

The reaction of dimethyldiborane (unsymmetrical)[9] and ammonia, however, did not yield the products expected. According to the proposed mechanism, the intermediate fragments should be $(CH_3)_2BNH_2$ and H_2BNH_2, and the only products to be expected are the unchanged $(CH_3)_2BNH_2$ and unmethylated $B_3N_3H_6$. Actually very little of the latter was obtained; instead, its three methyl derivatives and only about two-thirds of the expected quantities of $(CH_3)_2BNH_2$ were found. It was suspected at once that this substance might act as a methylating agent as does boron trimethyl in its reaction with diborane.[4] If this were true $(CH_3)_2BNH_2$ and $B_3N_3H_6$, initially formed, might interact to give methyl derivatives of the latter. When appropriate mixtures of the two substances were heated together, the expected derivatives were obtained. But the reaction is slow and incomplete. It seems more likely, therefore, that $(CH_3)_2BNH_2$ methylates the fragment H_2BNH_2 before condensation occurs, and that subsequent polymerization then leads to the products observed.[10]

In spite of the fairly good agreement of the experimental results with the hypothesis, the latter is nevertheless not to be considered as an established mechanism. Only in the case of the reaction between ammonia and tetramethyldiborane are the results quantitatively in agreement with the demands of the hypothesis. As Stock and Pohland have reported, in the reaction of ammonia with diborane[11] the formation of the supposed ring compounds is accompanied by the production of a non-volatile solid of unknown composition. In the cases of diborane, of monomethyldiborane and of dimethyldiborane, the side reaction is fairly extensive; trimethyldiborane gives only a trace of these solids. There apparently are other side reactions. One of the products obtained in the case of dimethyldiborane is methane, which is also formed in the reaction between $(CH_3)_2BNH_2$ and $B_3N_3H_6$. The whole investigation is complicated by the difficulty of obtaining pure methyl diboranes since these com-

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(7) The formation of hydrogen by the interaction of diborane and ammonia is analogous to the reaction between diborane and water. The compound, $B_2H_5NH_2$, has recently been isolated in this Laboratory. Stock and Pohland (ref. 2) have already suggested that its formation might be an intermediate step in the reaction producing $B_3N_3H_6$.

(8) The small amount of $(CH_3)_2BNH_2$ in the reaction product may be due to the presence of more highly methylated derivatives of diborane in the starting product. This contamination in small amounts cannot be avoided because mere heating of monomethyldiborane causes rapid disproportionation into B_2H_6 and $B_2H_4(CH_3)_2$.

(9) Symmetrical dimethyldiborane has not yet been prepared (see ref. 5).

(10) The reaction between $(CH_3)_2BNH_2$ and the fragment H_2BNH_2 would give CH_3HBNH_2. Another interpretation which might account for the discrepancies observed, but which is too unlikely to warrant further discussion, is that, at the temperatures of these experiments, the unsymmetrical dimethyldiborane is partially converted to the unknown symmetrical isomer.

(11) The yields of the "ring" compounds have been found to be greatly improved by rapid heating and by the use of higher pressures than Stock and Pohland describe.

pounds are spontaneously interconverted[4] (p. 624) at temperatures above their melting points. Furthermore, quantitative separation of the reaction products is very difficult with the small amounts of material involved because the various substances formed have very similar vapor tensions.

Experimental

A. Apparatus and Technique.—The apparatus and technical methods used in this investigation have been adequately described in previous publications by Stock,[12] and by Schlesinger and his co-workers.[13]

B. Analytical Methods.—Treatment of the methyl derivatives of $B_3N_3H_6$ for six hours at 200–250° with a 20% aqueous solution of hydrochloric acid produces hydrogen, ammonium chloride, boric and monomethylboric acids. Of these, only hydrogen and ammonium chloride were determined at this point.[14] For this purpose the reaction tube[15] was connected to the vacuum system through the tube opener and cooled to liquid nitrogen temperature. The hydrogen was transferred into a eudiometer tube by means of a Toepler pump. The reaction tube was then warmed to room temperature, and the methylboric acid and excess of hydrochloric acid were distilled away, leaving behind a mixture containing boric acid and ammonium chloride. Treatment of this residue with a 50% sodium hydroxide solution liberated the ammonia which was titrated in the usual way.

Boron and carbon were determined by oxidation of a separate sample of the original material to boric acid and carbon dioxide as previously described,[4] (p. 623) except that longer heating (eight to ten hours) was necessary.

The procedure for the analysis of $(CH_3)_2BNH_2$ differed from the preceding only in that hydrogen is not evolved as a result of treatment with hydrochloric acid. The same is true of the analysis of $(CH_3)_3B_3N_3H_3$.

Molecular weights were calculated from vapor densities. Inasmuch as the quantities of the substances available for these measurements were in most cases very small, the agreement between the calculated and observed values reported below must be considered quite satisfactory.

C. Preparation and Properties of the Ammoniates of the Methyl Diboranes.—Since the methods for the preparation of the diammoniates of the various methyl diboranes differ only in minor points, description of the details may be limited to the case of monomethyldiborane. An excess of ammonia, 70.3 cc.,[16] was condensed on 13.14 cc. of monomethyldiborane at −196°. The mixture was warmed to −115° and maintained at that temperature for fifteen minutes. During this interval the total pressure fell rapidly to an apparently constant value of about 1 mm. At this point, the temperature of the mixture was raised during an interval of ten hours to −78.5°, and there kept constant for twenty-four hours longer. During this period the ammonia which distilled off was recondensed and its volume determined. When the ratio of moles of ammonia in the residue to moles of monomethyldiborane had fallen to 2.09, loss of ammonia ceased.

In the preparation of the corresponding diammoniate of dimethyldiborane the reaction was carried out in essentially the same way, except that removal of ammonia had to be completed at −50°. The composition of the final product corresponded to the formula $(CH_3)_2B_2H_4 \cdot 2.03NH_3$. In the cases of trimethyl and tetramethyl diboranes, the reactions were carried out at −78.5° instead of −115°, and the last portions of ammonia were removed at −25°. The diammoniate of trimethyldiborane is the most difficult to obtain in the pure condition. This is due largely to the fact that trimethyldiborane fairly rapidly goes over into the dimethyl and tetramethyldiboranes. Furthermore, the diammoniate itself undergoes very slight decomposition during the removal of the excess of ammonia, yielding traces of volatile, condensable products. The diammoniate of tetramethyldiborane is somewhat less stable, but more easily obtained because of the greater stability of the mother substance. The compositions of these ammoniates corresponded to the formulas $(CH_3)_3B_2H_3 \cdot 1.96NH_3$ and $(CH_3)_4B_2H_2 \cdot 2.08NH_3$.

The ammoniates, with the exception of that of tetramethyldiborane, which undergoes rapid decomposition at 10°, are all white, powdery solids at room temperature. Occasionally well-formed crystals are seen. The substances are more stable than the methyl diboranes themselves; in particular, there seems to be no interconversion of any one into the others. The diammoniate of monomethyldiborane may be heated to 50° without noticeable change; above that temperature evolution of hydrogen begins and complete decomposition takes place rapidly at 85°. The corresponding compound of dimethyldiborane loses hydrogen slowly at room temperature, while the others begin to decompose at −35°.[17]

The effect of rapid heating of these ammoniates to higher temperatures (180–200°) and the resulting formation of compounds analogous to $B_3N_3H_6$ was the primary purpose of this investigation, and requires more detailed description.[18]

D. Isolation of the Products of the Reactions of the Methyldiboranes with Ammonia at Elevated Temperatures.—The reactions of ammonia with methyldiboranes produce $B_3N_3H_6$, its three[5] possible methyl derivatives, hydrogen, $(CH_3)_2BNH_2$, methane and some solid, as well as traces of liquid, non-volatile products. For each of the methyldiboranes these products appear in different proportions, but these differences necessitate only minor changes in the procedure for their separation. Conse-

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[12] A. Stock, *Ber.*, **50**, 998 (1917); **54A**, 142 (1921).

[13] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **53**, 4321 (1931); A. B. Burg, *ibid.*, **56**, 499 (1934); ref. 4, p. 623.

[14] In two experiments, monomethylboric acid together with the excess of hydrochloric acid and water were separated from the other reaction products. After removal of the hydrochloric acid by granulated zinc, the aqueous solution was oxidized by nitric acid in the usual way. The amount of carbon dioxide obtained corresponded with that calculated on the assumption that the methyl derivative had been decomposed to monomethylboric acid.

[15] The tube was of Pyrex glass (approximately 15 cm. long and 15–20 mm. in diameter) to which was attached a side tube to enable the transfer of the products to the vacuum apparatus.

[16] All volumes recorded in this paper refer to the gaseous state at 0° and 760 mm.

[17] There was some evidence of the existence of ammoniates containing more than two moles of ammonia per mole of methyldiborane. The determination of their composition was not attempted.

[18] It was found unnecessary always to prepare the ammoniates themselves; the results were the same when mixtures of the substituted diborane and two moles of ammonia were heated without previous interaction at lower temperatures. In the following description no distinction is made between the two procedures.

TABLE I

Compound	Sample	H_2		NH_3		CO_2		$B(OH)_3$	
		obsd.	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.
$CH_3B_3N_3H_5$	0.152[14]	0.309	0.304	0.440	0.456	0.148	0.152	..	..
	.135	..	..	..	..	.139	.135	0.414	0.405
$(CH_3)_2B_3N_3H_4$	.107[14]	.104	.107	.305	.321	.212	.214	..	..
$(CH_3)_3B_3N_3H_3$	.092	.0	.0	.280	.276	..	..	..	..
	.061	.0	.0	..	..	.182	.183	.183	.183
$(CH_3)_2BNH_2$	.338	.0	.0	.346	.338	..	..	..	..
	.240	.0	.0	..	..	.480	.480	.235	.240

quently, it will be sufficient to describe the method employed for the mixture resulting from one experiment in which 29.02 cc. of monomethyldiborane and 59 cc. of ammonia were heated at 190°. The pressure developed was calculated to be approximately six atmospheres. The hydrogen produced (117.4 cc.) was removed, and the volatile material condensed in the vacuum apparatus. The condensate was allowed to evaporate and pass through a U-tube at −78.5° in which $CH_3B_3N_3H_5$ and more highly methylated derivatives again condensed; $(CH_3)_2BNH_2$, $B_3N_3H_6$ and unchanged ammonia were trapped out at −196°. The condensate obtained at −78.5° was next distilled through a similar series in which the first tube was kept at −65°. At this temperature most of the more highly substituted derivatives were condensed while $CH_3B_3N_3H_5$ passed into the tube at −196°. Complete purification of this compound was a long and tedious process. In the next distillation of the impure $CH_3B_3N_3H_5$ all the components of the mixture except traces of $B_3N_3H_6$ (not removed in the initial distillation) were condensed at −90°. This condensate was subjected to a very slow distillation (six hours) under which conditions $CH_3B_3N_3H_5$ passed through a −78.5° tube and was condensed at −196°. A homogeneous sample was obtained only after several repetitions of this procedure. The amount of pure $CH_3B_3N_3H_5$ thus isolated was 3.07 cc.[17]

The material retained at −65° was reëvaporated, and fractionally condensed in U-tubes at −40 and −196°. The trimethyl derivative condensed at −40°, while the dimethyl derivative passed on to the tube at −196°. The latter material was freed of impurities by repeated distillation through a series of U-tubes at −40, −65 and −196°, respectively. After each distillation the condensates in the tubes at −40 and −196° were rejected. The quantity of pure $(CH_3)_2B_3N_3H_4$ finally obtained in the U-tube maintained at −65° was 2.87 cc.

The trimethyl derivative was purified by pumping the material in the tube at −40° for about one hour. The yield of this compound was 2.13 cc.[19]

The mixture consisting of $(CH_3)_2BNH_2$, $B_3N_3H_6$ and unchanged ammonia was passed into a series of U-tube at −90 and −196°. The $B_3N_3H_6$ was trapped out at −90° while the ammonia and $(CH_3)_2BNH_2$ condensed at −196°. The ammonia was removed from the latter by slow evaporation at −120°. Since $(CH_3)_2BNH_2$ also exerts a slight vapor tension at this temperature, a small amount of this material was lost in the procedure. The amount of ammonia thus obtained was 0.61 cc. and that of $(CH_3)_2BNH_2$, 1.81 cc.; the quantity of $B_3N_3H_6$ was not determined in this experiment.

A brief description of the compound, **dimethylaminoborine**[6] $(CH_3)_2BNH_2$, which is one of the principal products of the pyrolytic action of ammonia on di, tri and tetramethyl diboranes is desirable. The substance exists in several forms. At temperatures below −60° it assumes a glassy appearance (very similar to cellophane). When warmed to room temperature the glass volatilizes very slowly. When the vapor is recooled to −78.5°, the pressure drops rapidly to about 10 mm. and then very gradually falls to an apparently constant value of 2 mm. If the cooling of the vapor is stopped at −50°, the material is obtained in liquid form. When warmed, the liquid vaporizes very rapidly. If the liquid is allowed to stand at temperatures between −50 and −60° for some time, long, transparent needles are observed on the walls of the containing vessel; if, however, the liquid is cooled rapidly to liquid nitrogen temperature it solidifies to the glassy variety. Molecular weight determinations of the vapor at room temperature gave values corresponding to a monomer.

The analytical data on which characterization of the various methyl derivatives is based are assembled in Table I. All data are expressed in millimoles. These values were either calculated from the weights in grams of the substance recorded or from the measured volumes at known temperatures and pressures, except in the cases of boric acid[20] and ammonia which were determined by titration. The theoretical values for hydrogen and ammonia for the methyl derivatives of $B_3N_3H_6$ were calculated according to appropriate equations of the type

$$(CH_3)_xB_3N_3H_{(6-x)} + (9 - x)H_2O \longrightarrow (3 - x)H_2 + 3NH_3 + (3 - x)B(OH)_3 + xCH_3B(OH)_2$$

The theoretical values for carbon dioxide and boric acid were calculated according to equations of the type[21]

$$(CH_3)_xB_3N_3H_{(6-x)} + \left(\frac{10.5 + 3x}{2}\right) O_2 \longrightarrow xCO_2 + 3B(OH)_3 + 3NO \left(\frac{2x - 3}{2}\right) H_2O$$

The calculated values for $(CH_3)_2BNH_2$ were obtained from the following equations

$$(CH_3)_2BNH_2 + H_2O \longrightarrow (CH_3)_2BOH + NH_3$$

and

$$(CH_3)_2BNH_2 + 5.25O_2 \longrightarrow 2CO_2 + B(OH)_3 + NO + 2.5H_2O$$

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[19] Fractionations of the condensates rejected at various points in the distillations yielded small additional quantities of the methyl derivatives of $B_3N_3H_6$. A quantitative separation was impossible in view of the small amount of reaction product.

[20] A. Stock and E. Kusz, *Ber.*, **56**, 790 (1923).

[21] The oxidizing agent actually was nitric acid, instead of oxygen, and several oxides of nitrogen were obtained. The equation merely represents the ratios of carbon dioxide and boric acid to the substance analyzed.

The melting points together with the observed and calculated molecular weights of the new substances are given in Table II.

TABLE II

Compound	Mol. wt. obsd.	Mol. wt. calcd.	M. p., °C.
$CH_3B_3N_3H_5$	94.9	94.6	−59
$(CH_3)_2B_3N_3H_4$	109.3	108.6	−48
$(CH_3)_3B_3N_3H_3$	124.1	122.6	31.5
$(CH_3)_2BNH_2$	56.5	56.9	..

Vapor tensions of each of the three methyl derivatives of $B_3N_3H_6$ were determined at several temperatures. The data fit equations of the type $\log P = (-A/T) + B$. In Table III are recorded the constants for these equations and derived physical constants for the compounds.

TABLE III

Compound	*A* of equation	*B* of equation	B. p.,[a] °C.	Ht. of vap., cal.	Trouton[a] const.
$CH_3B_3N_3H_5$	1800	7.880	87	8230	22.8
$(CH_3)_2B_3N_3H_4$	2019	8.200	107	9230	24.3
$(CH_3)_3B_3N_3H_3$	2054	7.992	129	9390	23.3

[a] Due to the large extrapolation involved, these values must be considered approximate only.

The agreement between the observed temperatures and those calculated by use of the constants reported in Table III is quite satisfactory, as can be seen from the following data.

$CH_3B_3N_3H_5$

V. t., mm.	19.5	25	35.3	43	53	70
T, °A., obsd.	273.1	278.1	284.1	288.2	292.1	298.3
T, °A., calcd.	273.1	277.7	284.3	288.1	292.4	298.3

$(CH_3)_2B_3N_3H_4$

V. t., mm.	6.5	8.5	11.8	15.5	20.7	26.5
T, °A., obsd.	273.1	278.1	283.1	288.1	293.1	298.1
T, °A., calcd.	273.3	277.7	283.2	288.0	293.3	297.9

$(CH_3)_3B_3N_3H_3$

V. t., mm.	20.9	22.1	24	33.1	38	42.7
T, °A., obsd.	307.6	309.3	310.3	317.6	320.1	323.1
T, °A., calcd.	307.9	309.0	310.6	317.4	320.3	322.9

Inasmuch as only one experiment was described in detail, the results of several typical reactions of the various methyldiboranes with ammonia are tabulated (Table IV) to show the varying proportions in which the different products are formed. The volume of ammonia used was in some experiments slightly more (2–3%) than twice that of the methyldiborane. Unless otherwise specified the reaction was allowed to proceed at 180–200° for twenty to thirty minutes. Slight deviations from these conditions caused no noticeable differences in the results. The noncondensable gas produced in all the reactions was found to consist almost entirely of hydrogen and is recorded as such in the table. The experiments in which methane was found and determined are considered in the following discussion.

Discussion of Results

It is seen that in the reaction of *tetramethyldiborane* the results are quantitatively in agreement with the postulated mechanism, inasmuch as the volumes of hydrogen and of $(CH_3)_2BNH_2$ are each double the amount of diborane within the limits of experimental error. Whatever the mechanism, the reaction is evidently simple.

The reaction of *monomethyldiborane* with ammonia gives the expected amount of hydrogen with only slight deviations, apparently due to experimental error. The total quantity of reaction products determined is much too small to account for the amount of starting material employed. This is due in part to difficulties in the separation of these substances, but must be accounted for chiefly by the relatively large amount of the unknown, non-volatile solid mentioned in the introductory paragraphs. The *dimethyldiborane* yields even larger quantities of this solid material as well as traces of a non-volatile liquid. The amount of hydrogen is greater than corresponds to the simple hypothesis advanced for these reactions; it is, however, easy to account for the excess of hydrogen by the reaction between $(CH_3)_2BNH_2$ and

TABLE IV

Methyl-diborane	Sample, cc.	*P*,[a] atm.	H_2 obsd. cc.	H_2[b] calcd. cc.	Methyl deriv. of $B_3N_3H_6$ obsd., cc. Mono	Di	Tri	$(CH_3)_2BNH_2$ obsd., cc.
Mono	29.02	6	117.4	116.1	3.07	2.87	2.13	1.81
	19.00[c]	2	73.3	76.0	2.66	1.90	1.06	0.96
	13.14	3	53.7	52.6	[d]	[d]	[d]	[d]
Di	28.60	4.5	95.5	85.8	3.00	[d]	[d]	18.00
	22.30	4	74.5	66.9	1.00	0.40	0.20	13.00
	11.25	2	36.8	33.8	[d]	[d]	[d]	[d]
Tri	21.80	3	54.5	65.4	None	None	2.65	26.80
Tetra	12.33	1.2[e]	24.8	24.7	None	None	None	23.90

[a] The pressures are only approximate. They were calculated on the basis of the quantity of hydrogen produced, the volume of the reaction vessel and the temperature attained during the reaction. [b] The calculated values for hydrogen were obtained on the assumption that the reactions occur in accordance with the proposed mechanism. [c] This reaction was allowed to proceed at 170° for only five minutes. Although there was evidence of the formation of unmethylated $B_3N_3H_6$ in all the reactions involving monomethyl and dimethyl diboranes, the quantity present was determined in only this experiment and found to be 0.95 cc. [d] Present but quantities not measured. [e] The yields in the reaction of tetramethyldiborane with ammonia are independent of pressure.

$B_3N_3H_6$. The hydrogen was contaminated with methane; in one reaction 36.8 cc. of non-condensable gas contained 1.26 cc. of methane. The details of the reaction of *trimethyldiborane* with ammonia were discussed in the introduction.

Reaction of $(CH_3)_2BNH_2$ with $B_3N_3H_6$.[22]—The only purpose of undertaking this study was to determine whether methyl derivatives of $B_3N_3H_6$ could be obtained by its interaction with $(CH_3)_2BNH_2$. For this reason the data are of preliminary character only. In one experiment 13.47 cc. of $(CH_3)_2BNH_2$ was heated for thirty minutes at 190–200° with 13.2 cc. of $B_3N_3H_6$. The pressure developed was less than one atmosphere. The reaction product contained 3.7 cc. of hydrogen, 1.83 of methane, 0.8, 0.3 and 0.2 cc., respectively, of mono-, di- and trimethylated $B_3N_3H_6$, together with a relatively large amount of non-volatile solid and liquid. Of the starting material, 14.1 cc. remained unchanged.

E. Structure of the Methyl Derivatives of $B_3N_3H_6$.—That, in the compounds described in this paper, the methyl radicals are bound to boron atoms follows (1) from their mode of formation and (2) from the amount of hydrogen obtained by hydrolysis, as shown in Table I and by the equations preceding the table. These equations are based on the assumption that free hydrogen results only from hydrolysis of B–H bonds. The ring structure for $B_3N_3H_6$ is also assumed, and is corroborated by the agreement between the calculated and observed quantities of hydrogen.

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Summary

The diammoniates of the four methyldiboranes have been prepared and some of their properties described. The results indicate that the stability of these compounds is greater than that of the methyldiboranes themselves; there appears to be no conversion of any one into the others. The stability decreases with increase in number of methyl groups; the diammoniate of monomethyldiborane is the most stable, while the corresponding compound of tetramethyldiborane is the least stable of the series.

The reactions of the methyldiboranes with ammonia at high temperatures (180–200°), and pressures ranging from two to six atmospheres have been investigated. From these reactions, dimethylaminoborine $(CH_3)_2BNH_2$ and the compounds $CH_3B_3N_3H_5$, $(CH_3)_2B_3N_3H_4$ and $(CH_3)_3B_3N_3H_3$ have been isolated and characterized. Vapor densities, vapor tensions and freezing points, together with other derived physical constants for these compounds, have been determined.

A mechanism for the formation of the products of the reactions of diborane and of its methyl derivatives with ammonia has been proposed.

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[22] The reaction between $(CH_3)_2BNH_2$ and diborane at room temperature was also studied in a preliminary fashion. The reaction product consisted of all the methyldiboranes together with a solid, non-volatile addition product, suggesting that $(CH_3)_2BNH_2$ gives rise to two types of reaction, the one analogous to that of boron trimethyl and the other analogous to that of ammonia with diborane.