

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

**Hydrides of Boron. XII. Symmetrical Dimethyldiborane and the Methyl Derivatives of Borine Trimethylamine**BY H. I. SCHLESINGER, NESTOR W. FLODIN<sup>1</sup> AND ANTON B. BURG

The reaction between diborane and boron trimethyl leads to the formation of mono-, di-, tri-, and tetramethyl derivatives of diborane.<sup>2</sup> But only one dimethyldiborane, namely, the unsymmetrical compound, is obtained by this reaction. It therefore seemed desirable to seek for a method by which the symmetrical isomer,  $\text{CH}_3\text{BH}_2\text{BH}_2\text{CH}_3$ , could be prepared. The success of this search was a direct consequence of the hypothesis that the molecular group  $\text{BH}_3$  (borine) plays an important role in many of the reactions of diborane; the usefulness of this hypothesis is thus further demonstrated.

Earlier work had shown that diborane reacts with substances such as trimethylamine, to form complex compounds of borine.<sup>3</sup> As described below, the methyl derivatives of diborane react with trimethylamine in analogous fashion, producing methyl derivatives of borine trimethylamine—derivatives in which the complex bond is less stable than in borine trimethylamine itself. It therefore seemed feasible to search for a reagent which would form a complex compound of borine at a temperature at which this reagent could not form an analogous complex compound of methylborine. Such a reagent would be expected to react with methyldiborane ( $\text{CH}_3\text{BH}_2\text{BH}_3$ ) to remove the borine group, leaving the methylborine free to form the desired symmetrical dimethyldiborane by direct association. The whole process thus would be represented by the equations  $2\text{CH}_3\text{BH}_2\text{BH}_3 + 2\text{X} \rightarrow 2\text{BH}_3\cdot\text{X} + (2\text{BH}_2\text{CH}_3)$  and  $(2\text{BH}_2\text{CH}_3) \rightarrow \text{CH}_3\text{BH}_2\text{BH}_2\text{CH}_3$ .

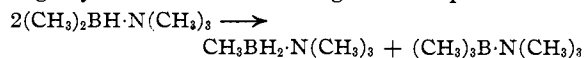
Trimethylamine is not a suitable reagent for this purpose, because its complex compounds with the borines are too stable. But dimethyl ether reacts with diborane to form the compound  $\text{BH}_3\cdot(\text{CH}_3)_2\text{O}$ , whose decomposition pressure at  $-80^\circ$  is more than half as great as the vapor tension of the ether at this temperature.<sup>4</sup> Since complex

compounds of methyl borines are, in general, less stable than those of borine, it seemed likely that the methyl ether compound of methylborine could not exist at this temperature. In agreement with this reasoning, monomethyldiborane was found to react with dimethyl ether according to the equation

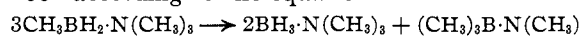
$$2\text{CH}_3\text{BH}_2\text{BH}_3 + 2(\text{CH}_3)_2\text{O} \rightleftharpoons 2\text{BH}_3\cdot(\text{CH}_3)_2\text{O} + \text{CH}_3\text{BH}_2\text{BH}_2\text{CH}_3$$

The conclusion that the stabilities of complex compounds of borine and its methyl derivatives decrease with increase in the number of methyl groups, is based upon evidence of the following type. Molecular weight determinations in the gas phase show that trimethylborine trimethylamine,  $(\text{CH}_3)_3\text{B}\cdot\text{N}(\text{CH}_3)_3$ , is about 70% dissociated at  $80^\circ$  into its constituents, trimethylborine and trimethylamine. The compound  $(\text{CH}_3)_2\text{BH}\cdot\text{N}(\text{CH}_3)_3$ , on the other hand, has a molecular weight of 102 (at  $68^\circ$ ), a value which shows that no appreciable dissociation has occurred. Monomethylborine trimethylamine is undissociated at  $100^\circ$ , as is borine trimethylamine itself.

Additional evidence of the order of stability of these compounds is found in their disproportionation reactions. The complex compound of dimethylborine decomposes at a temperature only slightly above  $68^\circ$ , according to the equation



The complex compound of monomethylborine, which is stable at  $100^\circ$ , disproportionates at  $200^\circ$  according to the equation



Since trimethylborine trimethylamine is the least stable of the complex compounds, the driving force of the latter reaction must be the fact that borine trimethylamine is more stable than monomethylborine trimethylamine. By similar reasoning it follows from the former reaction that monomethylborine trimethylamine is more stable than dimethylborine trimethylamine.

The symmetrical dimethyldiborane has been identified by a determination of its molecular weight and by its quantitative reactions (1) with trimethylamine to give monomethylborine tri-

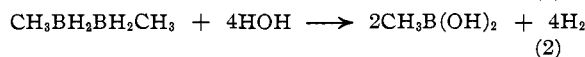
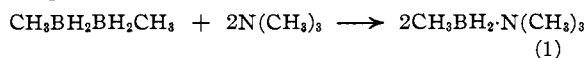
(1) This paper is taken from a dissertation presented by Nestor W. Flodin to the Faculty of the Division of the Physical Sciences of the University of Chicago, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Its contents were presented at the Ninety-sixth meeting of the American Chemical Society, Milwaukee, September 7, 1938.

(2) Schlesinger and Walker, *THIS JOURNAL*, **57**, 621 (1935).

(3) Burg and Schlesinger, *ibid.*, **59**, 780 (1937).

(4) Schlesinger and Burg, *ibid.*, **60**, 296 (1938).

methylamine, and (2) with water to give hydrogen and methylboric acid



Symmetrical dimethyldiborane may be kept in the gas phase at room temperature for several minutes without detectable decomposition. On longer standing, it undergoes transformation into unsymmetrical dimethyldiborane. Thus a sample held at room temperature and 250 mm. pressure for half an hour was 2.4% converted into the unsymmetrical derivative. A sample kept for three days at 25 mm. pressure, was 33% transformed. No other compound appears until more than three days have elapsed; small quantities of monomethyl- and trimethyldiborane then begin to be noticed. As time progresses, less and less of the symmetrical derivative remains, and it appears that no more than a trace of it will be present when equilibrium finally is attained. The presence of nearly equal volumes of mono- and trimethyldiboranes in the mixtures resulting from long standing, indicates that the final state will be the same as that observed by Schlesinger and Walker<sup>2</sup> in mixtures derived from equal volumes of boron trimethyl and diborane. The absence of symmetrical dimethyldiborane in equilibrium mixtures of the methyldiboranes is thus consistent with its essential instability.

The preparation of symmetrical dimethyldiborane makes available for the first time a pure source of the monomethylborine radical. Thus its reaction with trimethylamine produces a quantitative yield of monomethylborine trimethylamine. Furthermore, its reaction with ammonia at 200° has given a 40% yield of tri-B-methyl triborine triamine, a substance otherwise difficult to prepare in good yield. There are many other possible reactions in which the new compound may be advantageously employed.

### Experimental Part<sup>5</sup>

#### The Stabilities of the Methyl Derivatives of Borine Trimethylamine

Trimethylborine trimethylamine,  $(\text{CH}_3)_3\text{B}\cdot\text{N}(\text{CH}_3)_3$ , was prepared by condensing boron trimethyl with a slight

(5) The apparatus and technical methods used in this investigation were similar to those described in previous publications by Stock, *Ber.*, **50**, 998 (1917); **54A**, 142 (1921), by Schlesinger and Burg, *This Journal*, **53**, 4321 (1931), and by Burg, *ibid.*, **56**, 499 (1934). Cf. also footnote 3. As in those publications, all volumes of gases and vapors are reduced to standard conditions.

excess of trimethylamine, at  $-196^\circ$ , and then warming the mixture to room temperature. After half an hour, the mixture was fractionally condensed in traps at  $-80$  and  $-196^\circ$ , in order to remove the excess amine. The compound trapped at  $-80^\circ$  is a white, sublimable solid which crystallizes from the vapor phase as long, colorless needles or small quartz-like lumps. Its melting point is  $120^\circ$ . Its vapor tensions were measured by means of a device similar to that used by Burg and Schlesinger<sup>3</sup> for work with borine trimethylamine. The observed values, given in Table I, do not agree with the Clapeyron-Clausius equation, because the dissociation of the vapor increases with temperature.

TABLE I

VAPOR TENSIONS OF TRIMETHYLBORINE TRIMETHYLAMINE

Temp., °C.	14	20.1	23.4	29.2	34.6	41.8	48.4
<i>p</i> , mm.	0.8	1.3	2.1	3.0	4.8	8.7	14.7
Temp., °C.	56.3	63.9	72.1	82.2	91.6	99.3	
<i>p</i> , mm.	26.9	35.4	79.5	145.2	245	358	

The extent of dissociation of trimethylborine trimethylamine at various temperatures and pressures was determined by measurements of the pressure of unsaturated vapor. These measurements and the derived results are given in Table II.

TABLE II

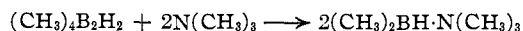
DISSOCIATION OF TRIMETHYLBORINE TRIMETHYLAMINE IN THE VAPOR PHASE

Size of sample, cc. of $\text{B}(\text{CH}_3)_3$	Temp., °C.	Volume of apparatus, cc.	Pressure, mm. at $0^\circ$	% dissociation
3.75	73.0	115.4	52.5	67.8
	79.0	115.4	55.0	72.7
	93.1	115.5	60.4	82.5
	99.2	115.7	62.0	84.8
10.01	80.7	238.1	70.4	70.0
	99.8	238.4	79.7	83.0
10.03	80.6	238.0	70.6	70.9
	99.8	238.4	79.9	83.0
6.96	85.4	115.3	102.6	70.5
	93.0	115.4	108.8	77.1
	99.7	115.5	113.6	81.9
6.99	83.4	115.2	102.5	70.5
	91.0	115.3	108.3	76.4
	99.2	115.4	114.0	81.8
9.91	89.5	115.4	148.0	70.9
	99.1	115.4	159.5	79.4

Dimethylborine trimethylamine,  $(\text{CH}_3)_2\text{BH}\cdot\text{N}(\text{CH}_3)_3$ , was prepared by the action of trimethylamine upon tetramethyldiborane. A sample of the latter, prepared by the method of Schlesinger and Walker,<sup>2</sup> was measured as 22.1 cc. After the measurement, during which slight decomposition may have occurred, the sample was held at  $-80^\circ$  while a 2.2-cc. fraction was removed by direct distillation. The residual 19.9 cc. of pure<sup>6</sup> tetramethyldiborane was treated with 52.7 cc. of trimethylamine; the mixture was allowed to remain at  $-80^\circ$  for eight hours,

(6) Previous experience had shown that this procedure is a very effective method of final purification of tetramethyldiborane.

after which the excess amine was distilled off (last traces removed by fractional condensation at  $-80^{\circ}$  and  $-196^{\circ}$ ). According to the volume of recovered amine (12.6 cc.), 40.1 cc. of amine had reacted with the tetramethyldiborane, in satisfactory agreement with the equation



The vapor tensions of dimethylborine trimethylamine, at temperatures below its region of inconveniently rapid decomposition, are given in Table III. The data are

TABLE III

VAPOR TENSIONS OF DIMETHYLBORINE TRIMETHYLAMINE

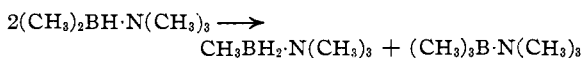
Temp., $^{\circ}\text{C}$ .	0.0	10.3	15.7	20.7	25.7	35.0
$p_{\text{mm.}}$ , obsd.	1.0	1.5	2.0	2.9	3.6	6.3
$p_{\text{mm.}}$ , calcd.	0.8	1.6	2.1	2.9	3.7	6.1
Temp., $^{\circ}\text{C}$ .	39.4	45.6	51.0	55.3	60.5	65.4
$p_{\text{mm.}}$ , obsd.	7.7	10.3	13.1	16.6	20.6	25.1
$p_{\text{mm.}}$ , calcd.	7.7	10.3	13.3	16.2	20.4	25.1

expressed by the equation  $\log_{10} p_{\text{mm.}} = 7.610 - (2102/T)$ , from which the heat of vaporization is calculated to be 9614 cal. per mole and the normal boiling point,  $171.4^{\circ}$ . The Trouton constant is 21.6.

The melting point of dimethylborine trimethylamine is  $-18.0^{\circ}$ .

Two determinations of the molecular weight of this compound gave the values 102.5 and 102.0 (theoretical, 101.0). The sample volumes were measured rapidly at  $68^{\circ}$ .

The compound decomposes at an appreciable rate when it is heated to temperatures above  $70^{\circ}$ , for the fully vaporized substance then shows a steady increase of pressure at a fixed temperature. Thus a sample whose molecular weight was normal at  $68^{\circ}$ , showed a 4% increase of pressure during fifteen minutes at  $75^{\circ}$ , and a further 5% increase during a second quarter-hour period at the same temperature. During one hour at  $100^{\circ}$ , the process reached completion with a 30% total increase in the corrected volume. This result is intelligible in terms of the equation



if one recalls that the latter of the products is highly dissociated at the temperature and pressure (less than 30 mm.) of the experiment.

The equation here given was justified by the actual separation and identification of the products. This task was very difficult, because these amines are almost equally volatile, but it was rendered possible by the fact that one is solid, the other, liquid. The solid trimethylborine trimethylamine, having poor thermal contact with the walls of the container, as well as a high heat of vaporization, volatilized far more slowly than the liquid monomethylborine trimethylamine. On the other hand, the vapors of the solid passed more easily through a trap at  $-10^{\circ}$  than did those of the liquid.

The nearly purified trimethylborine trimethylamine was identified tentatively by its average molecular weight (65, instead of the value 60 observed on known samples under the same conditions), and then with greater certainty by its reaction with hydrogen chloride: 4.0 cc.

of the largely dissociated vapor reacted to give 0.4 cc. of hydrogen and 2.0 cc. of boron trimethyl (vapor tension 32 mm. at  $-78.5^{\circ}$ ). These results indicate that the sample was approximately 90% pure trimethylborine trimethylamine.

The liquid product of the decomposition of dimethylborine trimethylamine, after exhaustive fractionation, had a molecular weight of 85 (theoretical for monomethylborine trimethylamine, 86.9). Its identity was confirmed by its reaction with hydrogen chloride (present in excess) at room temperature; during twenty-four hours a 2.44-cc. sample of the compound produced 4.61 cc. of hydrogen (theoretical, 4.88).

**Monomethylborine trimethylamine**,  $\text{CH}_3\text{BH}_2\cdot\text{N}(\text{CH}_3)_3$ , is best prepared by the action of trimethylamine upon symmetrical dimethyldiborane; the preparation of the latter is described in a later section of this paper. A 12.36-cc. sample of the amine and a 5.81-cc. sample of symmetrical dimethyldiborane were condensed together and permitted to remain at  $-80^{\circ}$  for two hours. The excess amine was then removed by fractional condensation at  $-80^{\circ}$  and  $-196^{\circ}$ : it amounted to 0.76 cc., only 0.02 cc. more than the expected excess. The volume of monomethylborine trimethylamine (measured at  $100^{\circ}$ ) was 11.61 cc., only 0.01 cc. less than the theoretical value. The results therefore are in excellent agreement with the equation  $\text{CH}_3\text{BH}_2\text{BH}_2\text{CH}_3 + 2\text{N}(\text{CH}_3)_3 \longrightarrow 2\text{CH}_3\text{BH}_2\cdot\text{N}(\text{CH}_3)_3$ .

The vapor tensions of monomethylborine trimethylamine at various temperatures are given in Table IV.

TABLE IV

VAPOR TENSIONS OF MONOMETHYLBORINE TRIMETHYLAMINE

Temp., $^{\circ}\text{C}$ .	13.0	17.2	21.6	26.0	31.5	34.3	39.6	45.1
$p_{\text{mm.}}$ , obsd.	1.3	1.8	2.3	3.1	3.9	4.6	6.1	7.8
$p_{\text{mm.}}$ , calcd.	1.4	1.8	2.3	3.0	4.0	4.6	6.1	8.0
Temp., $^{\circ}\text{C}$ .	51.8	56.0	62.1	65.4	70.9	76.1	80.0	84.7
$p_{\text{mm.}}$ , obsd.	10.9	13.5	17.6	20.6	26.0	32.3	37.4	44.8
$p_{\text{mm.}}$ , calcd.	11.0	13.5	17.7	20.5	25.8	32.0	37.4	45.0

These data are represented by the equation  $\log_{10} p_{\text{mm.}} = 7.676 - (2155/T)$ , from which the heat of vaporization is calculated to be 9860 cal. per mole and the normal boiling point,  $176.4^{\circ}$ . The Trouton constant is 21.9.

The melting point of monomethylborine trimethylamine is  $0.8^{\circ}$ .

The molecular weight of this compound was determined as 88.5; theoretical, 86.9. The deviation may be attributed to the fact that the sample was not far from its condensation point when the volume was determined.

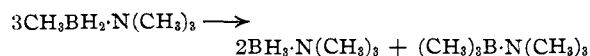
The compound was analyzed by heating measured samples with excess nitric acid at  $300^{\circ}$  for two hours. The resulting nitrogen oxides were destroyed by passage through a hot tube containing copper turnings; water was trapped at  $-80^{\circ}$  and carbon dioxide at  $-196^{\circ}$ . The volume of carbon dioxide was measured, and the boric acid was determined by titration. The data are given in Table V. in which the quantities are expressed in millimoles.

Monomethylborine trimethylamine is unchanged during several hours at  $100^{\circ}$ , but at  $200^{\circ}$  it disproportionates into borine trimethylamine and trimethylborine trimethylamine. No separation of these two solids could be made by sublimation methods, but the presence

TABLE V

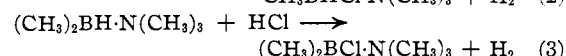
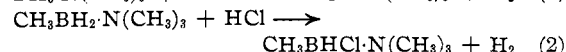
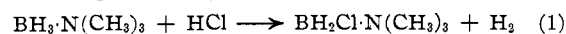
ANALYSIS OF MONOMETHYLBORINE TRIMETHYLAMMINE				
Millimoles of the compound	Carbon dioxide		Boric acid	
	Obsd.	Calcd.	Obsd.	Calcd.
0.240	...	...	0.236	0.240
.201	0.799	0.805	.199	.201

of the trimethylborine compound in the mixture was proved by treatment with hydrogen chloride for twelve hours at room temperature. The decomposition products from a 3.0-cc. sample of monomethylborine trimethylamine thus produced 1.4 cc. of hydrogen and 1.0 cc. of pure boron trimethyl (vapor tension 32 mm. at  $-78.5^\circ$ ). The quantity of the latter is in strict agreement with that predicted from the equation



#### The Reactions of Borine Trimethylamine and its Methyl Derivatives with Hydrogen Chloride

In addition to the direct gradation of stabilities of the methylborine trimethylamines, there is a step-wise progression in their rates of reaction with hydrogen chloride, according to the equations



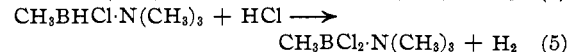
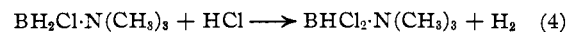
The rates increase in the order (1), (2), (3), as indicated by the data of Table VI. A large excess of hydrogen chloride was used in each experiment.

TABLE VI

#### THE ACTION OF HYDROGEN CHLORIDE UPON BORINE AMMINES

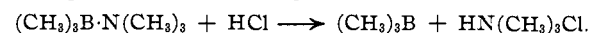
Compound treated	Temp., °C.	% of reaction completed during					
		2 min.	3 min.	7 min.	13 min.	20 min.	30 min.
$\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$	-80	..	..	...	...	93	100
$\text{CH}_3\text{BH}_2\cdot\text{N}(\text{CH}_3)_3$	-80	..	96	...	100	...	...
$(\text{CH}_3)_2\text{BH}\cdot\text{N}(\text{CH}_3)_3$	-100	90	..	100	...	..	...

Similar relations are found for the second stage of the reaction of the borine and the monomethylborine compounds with hydrogen chloride



Namely, reaction (4) can be completed only by long heating at  $100^\circ$ , whereas reaction (5) is complete after twenty hours at room temperature.

Trimethylborine trimethylamine is the only compound of the series whose B-N link can be broken by reaction with hydrogen chloride. As might be expected from its high degree of dissociation, this compound undergoes the following reaction at room temperature

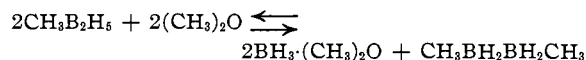


#### Symmetrical Dimethyldiborane

**Preparation of Monomethyldiborane.**—Monomethyldiborane was prepared by treatment of boron trimethyl with diborane, present in great excess, at a temperature

of  $80^\circ$  and pressure near atmospheric. Equilibrium was established within ten minutes. The excess of diborane was recovered by distillation from a tube at  $-150^\circ$ ; then the temperature was raised to  $-130^\circ$ , and the monomethyldiborane distilled into another receiver. The practical completion of the latter distillation was recognized by the lowering of the vapor tension of the residue to 15 mm. at  $-80^\circ$ . This final residue, consisting mainly of polymethyldiboranes, was remixed with the recovered diborane, along with a small additional quantity of boron trimethyl, and the whole exposed again to a temperature of  $80^\circ$ . After several repetitions of this process, the total product was purified by very slow distillation from a tube at  $-140^\circ$ , into a trap at  $-160^\circ$ , which allowed the remaining diborane to pass into the final trap at  $-196^\circ$ . By the method here described, it was found convenient to prepare 200 cc. of monomethyldiborane from 100 cc. of boron trimethyl, treated in small portions with 450 cc. of diborane.

**Preparation of Symmetrical Dimethyldiborane.**—Monomethyldiborane was allowed to react with four times its volume of methyl ether at  $-80^\circ$ . After ten minutes, all material volatile at that temperature was distilled away from the white solid formed in the reaction, and again allowed to stand at  $-80^\circ$  for ten minutes (longer periods were of no advantage because the reaction is rapid, but reversible). After ten repetitions of the process, further production of the white residue became negligible. The residues proved to be pure borine dimethyl etherate; this substance, although having a decomposition pressure of 18 mm. at  $-80^\circ$ , decomposes so slowly at that temperature that its clean separation as a residue offers no difficulty. The total quantity of the etherate, as determined by measuring the volumes of its decomposition products, indicated the equation



Thus 32.3 cc. of monomethyldiborane<sup>7</sup> gave residues which produced 32.1 cc. of methyl ether and 16.2 cc. of diborane, both of which were recovered in pure condition by repeated fractional condensation at  $-140$  and  $-196^\circ$ . Again, 61.3 cc. of monomethyldiborane gave residues leading to 61.4 cc. of methyl ether and 30.7 cc. of diborane.

The separation of symmetrical dimethyldiborane from the excess methyl ether is difficult to accomplish by distillation alone, but this impurity may be removed by treatment of the mixture with boron fluoride, of which only a slight excess is used. The non-volatile complex compound  $\text{BF}_3\cdot(\text{CH}_3)_2\text{O}$  is formed at  $-80^\circ$ ; the symmetrical dimethyldiborane is then easily separated from the remaining boron fluoride. A large excess of the latter is to be avoided, since it reacts with the desired compound to form an impurity very difficult to separate. The presence of silicon fluoride seems to cause no difficulty.

The final purification of the product was achieved by repeated fractional condensation: first by a rapid distillation with traps at  $-120$  and  $-196^\circ$ ; then the material

(7) On account of its extreme instability, this substance could be measured only by very rapid work. Its decomposition was only slight when it was allowed no more than fifteen seconds at room temperature. Fortunately, its first products of disproportionation seem to be diborane and symmetrical dimethyldiborane.

trapped at the former temperature was distilled from a tube at  $-110^{\circ}$ , leaving less volatile impurities behind.

The purity of the symmetrical dimethyldiborane was established by hydrolytic analysis, by determination of its molecular weight, by the constancy of its vapor tension at  $-78.5^{\circ}$  and the agreement of the other vapor tensions with the Clapeyron-Clausius equation, and by its conversion to pure monomethylborine trimethylamine when treated with trimethylamine (as described in an earlier section).

**Hydrolysis.**—A sample of symmetrical dimethyldiborane was allowed to react with excess water in a small sealed tube at room temperature. After a few minutes, the products other than hydrogen were condensed in the lower end of the tube at  $-196^{\circ}$ ; an hour was allowed for completion of this condensation. The tube was then opened into the vacuum apparatus by means of the tube-opener, and the hydrogen was pumped off through a trap and measured in the Töpler pump system. The residue was entirely volatile at room temperature; hence it was free of boric acid. Dimethylboric acid was shown to be absent by taking off a 2-cc. top fraction, and measuring its vapor tension at  $0^{\circ}$ . The value, 4.5 mm., showed that this most volatile part of the mixture was pure water; since dimethylboric acid is far more volatile, it could not have been present. The only products of the hydrolysis thus were hydrogen and methylboric acid;<sup>8</sup> the latter could be determined by titration in a solution saturated with mannitol, using phenolphthalein as the indicator. As shown in Table VII, the results agree with the equation  $\text{CH}_3\text{BH}_2\text{BH}_2\text{CH}_3 + 4\text{HOH} \longrightarrow 2\text{CH}_3\text{B}(\text{OH})_2 + 4\text{H}_2$ .

TABLE VII

## HYDROLYSIS OF SYMMETRICAL DIMETHYLDIBORANE

Millimoles of the compound	Millimoles of hydrogen		Millimoles of Methylboric acid	
	Obsd.	Calcd.	Obsd.	Calcd.
0.120	0.476	0.480	0.237	0.240
.215	.856	.860	.428	.430

The vapor tensions of symmetrical dimethyldiborane at various temperatures are given in Table VIII. These

TABLE VIII

## VAPOR TENSIONS OF SYMMETRICAL DIMETHYLDIBORANE

Temp., $^{\circ}\text{C}$ .	-73.8	-71.2	-65.4	-62.4	-59.2
$p_{\text{mm.}}$ , obsd.	10.9	13.4	20.7	25.0	31.1
$p_{\text{mm.}}$ , calcd.	11.2	13.6	20.5	25.1	31.1
Temp., $^{\circ}\text{C}$ .	-56.2	-52.7	-48.2	-43.2	
$p_{\text{mm.}}$ , obsd.	37.8	46.8	61.1	81.6	
$p_{\text{mm.}}$ , calcd.	37.6	46.8	61.2	81.6	

data are expressed by the equation  $\log_{10} p_{\text{mm.}} = 7.523 - (1290/T)$ , from which the heat of vaporization is calculated as 5902 cal. per mole and the normal boiling point,  $4.9^{\circ}$ . The Trouton constant is 21.2. Below  $-70^{\circ}$  the vapor tensions fall below the line represented by the equation; thus at  $-78.5^{\circ}$  the observed value is 7.0 mm., and the calculated, 7.9 mm. Such behavior is often shown by pure substances.

(8) This compound has been prepared by another method, and studied in some detail. It will be described more fully in another paper.

The melting point of symmetrical dimethyldiborane was determined from measurements on four samples. The values were  $-125.0$ ,  $-124.7$ ,  $-125.0$ , and  $-124.8^{\circ}$ ; average,  $-124.9^{\circ}$ . (Unsymmetrical dimethyldiborane has m. p.  $-150.2^{\circ}$  and b. p.  $2.6^{\circ}$ .)

The molecular weight was determined from two samples by the vapor density method. The values obtained were 54.8 and 56.5; theoretical, 55.7.

**The Reaction of Symmetrical Dimethyldiborane with Ammonia.**—An 11.75-cc. sample of symmetrical dimethyldiborane was condensed with 35.30 cc. of ammonia at  $-196^{\circ}$ . The mixture was allowed to stand at  $-100^{\circ}$  for half an hour, and then at  $-80^{\circ}$  for an hour. The excess ammonia was distilled off at  $-50^{\circ}$ , and was measured as 11.40 cc., leaving an ammoniate of the composition  $(\text{CH}_3)_2\text{B}_2\text{H}_4 \cdot 2.03\text{NH}_3$ . At room temperature, this white amorphous solid slowly evolved 0.3 cc. of non-condensable gas; no further decomposition was observed. The compound now was heated for half an hour at  $200^{\circ}$  and a pressure near five atmospheres. The reaction products were separated and identified by methods described previously.<sup>9</sup> Forty per cent. of the boron content of the diammoniate was recovered as tri-B-methyl triborine triamine, 20% as a mixture of mono- and di-B-methyl triborine triamine, 4% as triborine triamine, and 2% as the compound  $(\text{CH}_3)_2\text{BNH}_2$ . The rest of the boron evidently was contained in the white non-volatile solid which remained in the tube.

**The Stability of Symmetrical Dimethyldiborane.**—Samples of symmetrical dimethyldiborane, left at room temperature for periods of three days or less, underwent no change in volume. Furthermore, at the end of the period of standing, each sample had a vapor tension lower than 1 mm. at  $-110^{\circ}$ , and yet could be completely distilled away from a tube at that temperature in a short time. It was thus evident that no appreciable quantity of lighter or heavier decomposition products had been formed; that the only change which could have occurred was the rearrangement to form the unsymmetrical dimethyl diborane. This indication was confirmed by the results of hydrolysis, which produced essentially equal quantities of boric acid and dimethylboric acid.<sup>10</sup> The data of three such experiments are given in Table IX.

TABLE IX

## DECOMPOSITION OF SYMMETRICAL DIMETHYLDIBORANE

Vol. <sup>a</sup> of sym. $(\text{CH}_3)_2\text{B}_2\text{H}_4$ , cc.	4.16	3.37	2.4
Pressure at room temp., mm.	250	37	25
Time at room temp., hours	0.5	20	72
Vol. <sup>a</sup> $(\text{CH}_3)_2\text{BOH}$ , cc.	.10	0.20	0.8
Vol. <sup>a</sup> $\text{B}(\text{OH})_3$ , cc.	.10	.20	1.0
% change to unsymm. compound	2.4	7	33

<sup>a</sup> For direct comparison, all quantities of material are here expressed as volumes of gas at standard conditions.

On still longer standing at room temperature, the mixture begins to produce monomethyldiborane and trimethyl-

(9) Schlesinger, Horvitz and Burg, *THIS JOURNAL*, **58**, 409 (1936).

(10) The dimethylboric acid was separated from water by passage through a U-tube at  $-50^{\circ}$ , and identified by its vapor tension of 36 mm. at  $0^{\circ}$ . The separation of boric and methylboric acids was more difficult, but it was accomplished by distillation in the presence of enough water to prevent the formation of a compound between the two acids (perhaps a mixed anhydride or meta-acid).

diborane, with a probable trace of diborane itself. The course of the whole process can be recognized by occasional measurement of the vapor tension of the mixture at  $-78.5^{\circ}$ ; Table X presents such data for 8.1 cc. of symmetrical dimethyldiborane, decomposing during eight days at room temperature, in a space of 33 cc. The gradual rise of the vapor tension to a value above that of the unsymmetrical dimethyldiborane (10 mm.) demonstrates the formation of more volatile material. At the end of eight days, the process still had not reached equilibrium. The mixture now was fractionated, yielding 0.5 cc. of monomethyldiborane, 0.5 cc. of trimethyldiborane, and 7.1 cc. of a mixture of symmetrical and unsymmetrical dimethyldiborane. This mixture was hydrolyzed, producing 28.3 cc. of hydrogen (3.98 volumes) and 4.9 cc. of dimethylboric acid (boric and methylboric acids not determined). Hence the 7.1-cc. portion consisted of 4.9 cc. of the unsymmetrical derivative and 2.2 cc. of the original symmetrical compound; 72% of the latter had decomposed, yielding 60 parts of its unsymmetrical isomer and 6 parts each of mono- and trimethyldiboranes.

TABLE X

CHANGES OF VAPOR TENSION DURING THE DECOMPOSITION OF SYMMETRICAL DIMETHYLDIBORANE

Hours at room temp.	0	1	24	48
$p$ , mm. at $-78.5^{\circ}$	7.0	7.3	7.9	8.1
Hours at room temp.	72	144	168	192
$p$ , mm. at $-78.5^{\circ}$	8.3	10.0	10.8	11.7

### Summary

The methyl derivatives of borine trimethylamine have been prepared and characterized. In these compounds the stability decreases as the number of methyl groups increases; all are less

stable than borine trimethylamine itself. Methylation of borine trimethylamine increases the rate at which hydrogen chloride attacks the remaining B-H links to produce hydrogen. Only in the trimethyl derivative is the B-N link broken by hydrogen chloride.

By treatment of monomethyldiborane with dimethyl ether at  $-80^{\circ}$ , borine dimethyl etherate and the new compound, symmetrical dimethyldiborane, were obtained. The dimethyl etherate of monomethylborine apparently does not exist at  $-80^{\circ}$ .

The structure of symmetrical dimethyldiborane (m. p.  $-124.9^{\circ}$ ; extrapolated b. p.  $4.9^{\circ}$ ) has been established by its reaction with water to produce methylboric acid and hydrogen, and with trimethylamine to produce monomethylborine trimethylamine.

The diammoniate of symmetrical dimethyldiborane has been prepared. On heating at  $200^{\circ}$ , it gives a 60% yield of B-methyl derivatives of triborine triamine (mostly the tri-B-methyl compound).

A study of the stability of symmetrical dimethyldiborane has shown that it changes slowly, but probably almost completely, into the symmetrical isomer; this next disproportionates partially, yielding other methyl derivatives of diborane. The failure of earlier attempts to prepare the compound is thus explained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT CORNELL UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY AT SMITH COLLEGE]

## Formation of Aminomonopersulfuric Acid by the Interaction of Fuming Sulfuric Acid and Hydrogen Azide<sup>1</sup>

BY H. E. M. SPECHT, A. W. BROWNE AND K. W. SHERK

It has been found that hydrazine sulfate is formed when anhydrous hydrogen azide is condensed upon concentrated sulfuric acid,<sup>2</sup> and that the sulfates of both hydrazine and ammonia are obtained when hydrogen azide vapor is bubbled either through concentrated sulfuric acid<sup>3</sup> or

(1) This article is in part based upon the thesis presented to the Faculty of the Graduate School of Cornell University by H. E. M. Specht in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work of K. W. Sherk has been supported through the personal generosity of Mr. Haymo V. Pfister of the Pfister Chemical Company.

(2) A. E. McKinney, Ph.D. Thesis, Cornell University, 1923.

(3) Dennis and Isham, *THIS JOURNAL*, **29**, 218 (1907).

through an ethereal solution of 100% sulfuric acid.<sup>4</sup> In the presence of water, Schmidt<sup>5</sup> obtained hydroxylammonium sulfate, but found that hydrogen azide acted as an *aminating agent* toward benzene in hot sulfuric acid, with formation of aniline sulfate as the principal product.

On the assumption that the formation of hydrazine, ammonia, and hydroxylamine from hydrogen azide in these experiments may have been due to the decomposition of an intermediate product

(4) H. S. Bennett, Ph.D. Thesis, Cornell University, 1917.

(5) Schmidt, *Ber.*, **57**, 704 (1924); **58**, 2413 (1925).