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Hydrides of Boron. V. The Ethyl and *n*-Propyl Diboranes

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

The ethyl and *n*-propyl diboranes were prepared, as part of general study[2] of the effect of substituents on the anomalous boron to boron linkage, to determine whether increase in the molecular weight of the radical replacing hydrogen in diborane is accompanied by marked changes in the stability of the compounds. Decrease in stability might shed light on the conditions favoring the formation of the boron to boron bond; the discovery of more stable derivatives, on the other hand, would have decreased the technical difficulties described in the next paper (VI) of this series.

The new compounds are, however, very similar to the methyl derivatives previously studied,[2] both in stability and in the reactions so far investigated. In diethyldiborane both ethyl groups appear to be attached to the same boron atom; in triethyldiborane, two of the ethyl radicals are bound to one boron atom and the third to the other, while tetraethyldiborane has a symmetrical structure with two ethyl groups attached to each boron atom. Just as among the methyl derivatives, there was no indication of the existence of a compound with more than four alkyl substituents nor any tendency toward a break of the boron to boron bond. Of the *n*-propyl compounds only the mono and di-*n*-propyl derivatives were isolated. There was evidence of the presence of heavier substances but, because of their very low volatility, they were not further investigated.

Experimental

A. **Apparatus.**—The apparatus and technical methods used in this investigation were similar to those described by Schlesinger and Walker in their study of the methyl diboranes[2] (p. 623).

B. **Analytical Methods.**—The procedure was identical with that described by Schlesinger and Walker[2] for the corresponding methyl derivatives except that it was considered unnecessary to isolate the ethyl and *n*-propyl boric acids produced by the action of water. Their isolation would have been very difficult because the acids are either not volatile enough to be handled in the vacuum apparatus or decompose when distillation is attempted.

Molecular weights of monoethyl, diethyl and mono-*n*-propyl diboranes were calculated from vapor densities. At temperatures at which they are stable triethyl, tetraethyl and di-*n*-propyl diboranes are not sufficiently volatile for molecular weight determinations by this method.

C. **Preparation of the Ethyl Derivatives of Diborane.**—When diborane and boron triethyl were mixed in the proportion of five moles to one and allowed to stand at room temperature for about ten hours, there was a decrease of about 10% in the volume of the vapor phase. Since the products of the reaction are liquid at room temperature, the volume change cannot be interpreted quantitatively. This reaction produced monoethyl and diethyldiboranes in predominating quantities and only small amounts of the heavier derivatives. A reaction mixture consisting of eight moles of boron triethyl and one mole of diborane produced triethyl and tetraethyl diboranes exclusively. In this reaction the volume of the vapor phase had decreased by about 50% after ten hours.

(1) **Isolation of Monoethyldiborane.**—The mixture resulting from the interaction of five moles of diborane and one mole of boron triethyl was partially condensed in a U-tube cooled to −140°, through which the excess of diborane passed to be condensed in a trap at liquid nitrogen temperature. The first condensate was then distilled through a U-tube cooled to −78.5° in which were condensed all materials except the monoethyldiborane. The fraction which passed through the latter tube was subjected to the same operations several times. As a result of these fractionations, the product of several reaction mixtures yielded samples all of which showed a vapor tension of 7 mm. at −78.5°, irrespective of the size of the vessel in which the measurement was made. The combined samples had a molecular weight of 56.1 (calcd. for $C_2H_5B_2H_5$, 55.8) and gave analyses in agreement with the formula. The melting point could not be determined since the liquid cooled to a glass instead of a crystalline product, nor was it possible, because of the instability of the compound, to measure the vapor tensions at higher temperatures. Warming the material to −30° for only thirty seconds raises the −78.5° tension from 7 to 12 mm.

ANALYSES.—$C_2H_5B_2H_5 + 5H_2O \longrightarrow B(OH)_3 + C_2H_5B(OH)_2 + 5H_2$

Sample	H_2 calcd.	H_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.395[3]	1.975	1.937	0.395	0.396
.580	2.900	2.908	...	...
.473[4]	2.365	2.376	...	...

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[1] This article represents 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] H. I. Schlesinger and A. O. Walker, THIS JOURNAL, **57**, 622 (1935). See also Burg and Schlesinger, *ibid.*, **55**, 4040 (1933).

[3] All quantities in this and subsequent analytical tables are expressed in millimoles.

[4] In this analysis after the hydrogen produced by hydrolysis was removed, the residue was oxidized by pure oxygen in the presence of nitric oxide instead of by nitric acid. The calculated values for carbon dioxide and for boric acid are based on the assumption that the original sample was completely hydrolyzed to boric and ethylboric acids.

$$C_2H_5B_2H_5 + 6O_2 \longrightarrow 2CO_2 + 2B(OH)_3 + 2H_2O$$

Sample	CO_2 calcd.	CO_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.327	0.654	0.652	0.654	0.653
.473[4]	.946	.929	.946	.981

(2) Isolation of Diethyldiborane.—The material condensed at −78.5° in the process of purification of the monoethyldiborane was fractionated further with traps at −60° and −196°. By repeating this process four times with the first condensate, a homogeneous material was obtained which exerted a vapor tension of 42 mm. at 0°. The observed molecular weights were 83.8 and 83.4; calculated for $(C_2H_5)_2B_2H_4$, 83.8. The melting point, as in the case of monoethyldiborane, could not be determined.

The vapor tensions of this substance were measured at several temperatures between −28 and 10.6°. Measurements covering larger temperature ranges could not be obtained because of the low volatility of the compound at lower temperatures and its rapid decomposition at higher ones. The values fit satisfactorily the equation $\log P = (1760/T) + 8.055$, as can be seen from the calculated temperatures given below. From the equation, the heat of vaporization is seen to be 8045 cal. The values for the boiling point, 67.1°, and for the Trouton constant, 23.6, must be considered only approximate, because of the large extrapolation involved.

V. t., mm.	7.4	10	20.5	42	51	72
T, °A., obsd.	245.1	249.9	261.1	273.1	277.5	283.7
T, °A., calcd.	244.9	249.5	261.0	273.6	277.3	284.0

ANALYSES.—$(C_2H_5)_2B_2H_4 + 4H_2O \longrightarrow (C_2H_5)_2BOH + B(OH)_3 + 4H_2$

Sample	H_2 calcd.	H_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.295	1.180	1.174	0.295	0.291
1.088	4.352	4.423	1.088	1.102

$$(C_2H_5)_2B_2H_4 + 9O_2 \longrightarrow 4CO_2 + 2B(OH)_3 + 4H_2O$$

Sample	CO_2 calcd.	CO_2 found
0.238	0.952	0.933
0.352	1.408	1.397

(3) Isolation of Triethyldiborane.—The mixture resulting from the reaction of eight moles of boron triethyl and one mole of diborane was passed through U-tubes surrounded by baths at −60 and −196°. The condensate in the tube at −196° was removed, and the material retained at −60° was passed through a series of U-tubes at −25, −60 and −196°. The distillation was then repeated with the −60° condensate until a substance having a uniform 0° tension of 4 mm. was obtained. Decomposition prevents the measurement of vapor tensions at higher temperatures. For the same reason, a reliable value for the molecular weight was not obtained and identification of the substance rests on analyses alone.

ANALYSES.—$(C_2H_5)_3B_2H_3 + 3H_2O \longrightarrow (C_2H_5)_2BOH + C_2H_5B(OH)_2 + 3H_2$

Sample	H_2 calcd.	H_2 found
0.142	0.426	0.421
0.203	0.609	0.594

$$(C_2H_5)_3B_2H_3 + 12O_2 \longrightarrow 6CO_2 + 2B(OH)_3 + 6H_2O$$

Sample	CO_2 calcd.	CO_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.475	2.850	2.767	0.950	0.915

(4) Isolation of Tetraethyldiborane.—The condensate obtained in the U-tube cooled to −25°, during the isolation of triethyldiborane, was pumped at that temperature for a short time. The material exhibited a 0° tension of 0.5 mm. The melting points of two different samples were −56.5 to −56°, and −56.5 to −56.3°.

ANALYSES.—$(C_2H_5)_4B_2H_2 + 2H_2O \longrightarrow 2H_2 + 2(C_2H_5)_2BOH$

Sample	H_2 calcd.	H_2 found
0.409	0.818	0.816
0.310	0.620	0.627

$$(C_2H_5)_4B_2H_2 + 15O_2 \longrightarrow 8CO_2 + 2B(OH)_3 + 8H_2O$$

Sample	CO_2 calcd.	CO_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.223	1.784	1.754	0.446	0.452

D. Preparation of the *n*-Propyl Derivatives of Diborane.—Mono-*n*-propyl and di-*n*-propyl diboranes were obtained by allowing a mixture of eight moles of diborane and one mole of boron tri-*n*-propyl[5] to stand at room temperature for about ten hours.

(1) Isolation of Mono-*n*-propyldiborane.—The reaction mixture was passed through a series of U-tubes at −80, −140 and −196°. The condensate in the −140° tube was subjected to several repetitions of this procedure until a substance was finally obtained that exhibited a vapor tension of 6.2 mm. at −60°. The molecular weight was found to be 71.1 while the theoretical value for $C_3H_7B_2H_5$ is 69.8.

ANALYSES.—$C_3H_7B_2H_5 + 5H_2 \longrightarrow 5H_2 + C_3H_7B(OH)_2 + B(OH)_3$[6]

Sample	H_2 calcd.	H_2 found
0.381	1.905	1.923
0.114	0.570	0.579

$$C_3H_7B_2H_5 + 7.5O_2 \longrightarrow 3CO_2 + 2B(OH)_3 + 3H_2O$$

Sample	CO_2 calcd.	CO_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.339	1.017	1.000	0.678	0.655
0.270	0.810	0.806	...	...

(2) Isolation of Di-*n*-propyldiborane.—The condensate obtained in the tube at −78.5° during the isolation of the mono-*n*-propyldiborane was distilled through U-tubes at −50, −78.5 and −196°. The condensate at −78.5° was passed through this same series until the main portion showed a vapor tension of 2.8 mm. at 0°.

ANALYSES.—$(C_3H_7)_2B_2H_4 + 4H_2O \longrightarrow 4H_2 + (C_3H_7)_2BOH + B(OH)_3$

Sample	H_2 calcd.	H_2 found
0.251	1.004	1.017

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[5] Boron tri-*n*-propyl was prepared by the interaction of a slight excess of boron trichloride and di-*n*-propyl zinc. The material was purified by fractional distillation.

[6] Determinations of boric acid in the presence of *n*-propylboric acid yielded high values, probably due to partial titrability of the latter.

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

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.

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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.

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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.

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

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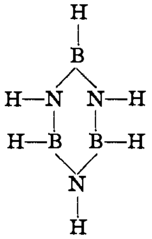
Stock and Pohland[2] have found that when the diammoniate of diborane, a salt-like substance first prepared by Stock and Kusz,[3] is rapidly heated to 200° in a closed tube the relatively stable, volatile compound $B_3N_3H_6$ is obtained. To this they assigned the ring structure



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.