

behavior of aluminum borohydride, its reaction with ethyllithium to form lithium borohydride,  $\text{LiBH}_4$ , is mentioned, as is also the existence of the beryllium borohydride,  $\text{BeB}_2\text{H}_3$ , although detailed discussion of these substances is deferred to papers about to be published.

6. The possible structure of aluminum borohydride is discussed in preliminary fashion in the light of the facts presented. More detailed discussion of this matter is likewise deferred to the later papers to which reference has been made.

CHICAGO, ILLINOIS

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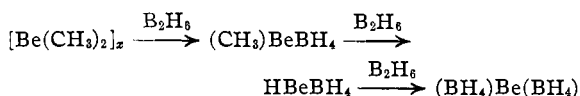
## Metallo Borohydrides. II. Beryllium Borohydride

BY ANTON B. BURG<sup>1</sup> AND H. I. SCHLESINGER

The similarity between aluminum and beryllium suggests that diborane, which reacts with trimethylaluminum to produce aluminum borohydride,  $\text{AlB}_3\text{H}_{12}$ , might behave in similar fashion toward dimethylberyllium. Not only does the reaction in question actually lead to the formation of a stable compound of molecular formula  $\text{BeB}_2\text{H}_3$ , but it proceeds in such a way that it is possible to recognize the existence of intermediate steps and to isolate by-products which are of importance in elucidating the chemical character of these metallo borohydrides.

The first product of the reaction between diborane and dimethylberyllium is a glassy material rich in methyl groups. The next stage is a non-volatile, mobile liquid. Further treatment with diborane leads to an unstable, easily sublimable solid which has a composition approximating the formula  $\text{CH}_3\text{BeBH}_4$ . This material reacts vigorously with additional diborane to give the volatile final product  $\text{BeB}_2\text{H}_3$  and a small amount of a non-volatile by-product which appears to be  $(\text{BeBH}_5)_x$ . In addition to these substances, boron trimethyl or methyl derivatives of diborane (or both) are obtained.

One might represent the series of reactions by the scheme



This scheme, however, is merely a summary of products obtained, and is not intended to suggest either a mechanism of the reaction or structures of the compounds involved.

The final product of the reaction, beryllium borohydride,  $\text{BeB}_2\text{H}_3$ , exhibits many properties which indicate its close relationship to aluminum

borohydride. Like the latter, the beryllium compound inflames violently in air and reacts vigorously with water. Its reaction with hydrogen chloride, to give hydrogen, diborane, and beryllium chloride, is rapid even at  $-80^\circ$ , and was found useful for analytical purposes. In physical properties it differs more decidedly from the aluminum compound; although both are readily vaporized at room temperatures, the beryllium compound is less volatile than the aluminum compound and its melting point is at least  $180^\circ$  higher. These differences suggest that the beryllium compound may be more highly polar in character than the aluminum compound. It should be mentioned also that the beryllium compound may be obtained as an unstable glass by rapid condensation at low temperatures. Possibly the crystalline variety of high melting point may represent a polymeric modification.

Of particular interest is the reaction of  $\text{BeB}_2\text{H}_3$  with trimethylamine. In this respect also the beryllium compound shows marked similarity with the aluminum analog, except that the results with beryllium borohydride are more clearly interpretable. At  $-80^\circ$  beryllium borohydride reacts with trimethylamine to form the relatively stable substance,  $\text{BeB}_2\text{H}_3 \cdot \text{N}(\text{CH}_3)_3$ . Although the substance begins to decompose irreversibly at  $140^\circ$ , it is sufficiently volatile that its purity can be demonstrated by measurement of its vapor tensions in the range  $65$ – $140^\circ$ , and that its molecular weight can be confirmed by a determination of its vapor density.

On heating it to  $100^\circ$  with trimethylamine (present in excess) the compound  $\text{BeB}_2\text{H}_3 \cdot \text{N}(\text{CH}_3)_3$  reacts further, yielding borine trimethylamine,  $\text{BH}_3\text{N}(\text{CH}_3)_3$ , and the compound  $\text{BeBH}_5 \cdot \text{N}(\text{CH}_3)_3$ . The latter is a solid which loses trimethylamine reversibly. It was not possible, however, to re-

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move all of the trimethylamine; all that can be said of the material obtained by partial removal of the amine is that it is capable of reabsorbing the amine and that it also reacts with diborane, to reproduce  $\text{BeB}_2\text{H}_3$  and presumably its trimethylamine addition product.

At present the most satisfactory formula for beryllium borohydride seems to be  $\text{Be}(\text{BH}_4)_2$ . The two  $\text{BH}_4$  groups are to be considered so highly deformed by the small, relatively highly charged beryllium that not only does the compound possess little, if any, real ionic character, but that it behaves, *e. g.*, toward the trimethylamine, as if it contained  $\text{BH}_3$  groups. This point will be more fully discussed in the next paper of this series on the metallo borohydrides, and has already been mentioned in the preceding paper.

### Experimental Part<sup>2</sup>

**Preparation of Dimethylberyllium.**—Dimethylberyllium was prepared by the reaction of metallic beryllium with dimethylmercury as originally suggested by Lavroff.<sup>3</sup> Approximately one gram of the metal, in the form of small lumps, was placed in a  $20 \times 1.3$  cm. Pyrex tube, toward one end of which there was provided a closed in-sealed spiral, later to be opened in vacuum by magnetic means. For the preparation of dimethylberyllium, the lower end of the tube (labeled Be in Fig. 1) was sealed to the high-vacuum apparatus, and the tube was evacuated at a temperature near the collapse point of the glass. After cooling, the tube was wrapped in cotton soaked in liquid nitrogen, and approximately 3 g. of liquid dimethylmercury was condensed upon the interior wall. Then the tube was sealed off from the apparatus and heated in an oil-bath at  $120$ – $125^\circ$ . The dimethylberyllium soon began to collect in the cooler part of the tube; after twenty-four hours, the reaction seemed to have ceased. The reaction tube now was sealed to the vacuum apparatus in the manner shown in Fig. 1, and opened by dropping a magnetically controlled steel ball upon the in-sealed spiral. The residual dimethylmercury was recovered by direct distillation, and then the dimethylberyllium was sublimed away from the unused metal, and caught in the

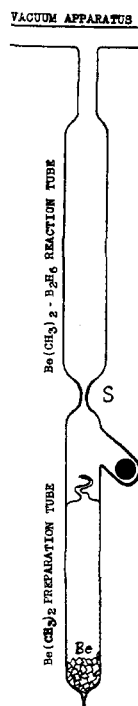


Fig. 1.

limited away from the unused metal, and caught in the

(2) The high-vacuum technique here employed was that developed chiefly by Stock, *Ber.*, **54A**, 142 (1921); "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, pp. 173–205. Important later developments are mentioned in the appropriate places. In this paper, the abbreviation *cc.* always designates the volume of a gas or vapor (calculated to standard conditions) or the normal-gas equivalent of a non-volatile substance.

(3) Lavroff, *J. Russ. Phys.-Chem. Soc.*, **16**, 93 (1884); *Bull. soc. chim.*, **41**, 548 (1884).

wide tube above. Finally, the preparation tube was sealed off at the point S, leaving the dimethylberyllium in a position convenient for treatment with diborane.

**The Reaction of Dimethylberyllium with Diborane.**—The product was treated with 92 cc. of diborane, which failed to react during a half hour at  $70^\circ$ , but was satisfactorily absorbed during ninety minutes at  $95^\circ$ . The reaction evolved 63 cc. of boron trimethyl, whose presence prevented 33 cc. of the diborane from reaching the reaction zone.<sup>4</sup> The other products of the reaction were a glassy material and a trace of a sublimable solid; the latter decomposed readily to yield a non-volatile solid and a gas having the properties of a mixture of mono- and dimethyldiboranes. On further treatment with 30 and 50 cc. portions of diborane, the glassy material changed to a non-volatile, mobile liquid, and finally into the rather unstable sublimable substance having a composition approximately represented by the formula  $(\text{CH}_3\text{BeBH}_4)_2$ .

**Analysis of  $(\text{CH}_3\text{BeBH}_4)_2$ .**—A small sample of the unstable sublimate was treated with 38.9 cc. of hydrogen chloride at  $-80^\circ$ . The evolution of non-condensable gases began rapidly, but soon slowed down markedly. Nevertheless, all of the boron was released, in the form of gaseous hydrogen compounds, during ten hours. These gases were hydrolyzed, yielding 22.4 cc. of pure hydrogen and 0.388 millimole of boric acid (free of  $\text{CH}_3\text{-B}$  compounds). Further treatment of the residue (containing all of the beryllium) with hydrogen chloride, finally at  $+80^\circ$ , brought the total of non-condensable gases so produced to 15.70 cc.; combustion analysis showed that 3.4 cc. of this was methane. Hydrolysis of the residue now yielded 0.9 cc. of hydrogen and 4.0 cc. of methane. The entire yield of hydrogen amounted to 35.6 cc., or 1.588 millimoles; the 7.4 cc. of methane is equivalent to 0.330 millimole. The beryllium was converted to 36.2 mg. of  $\text{Be}_2\text{P}_2\text{O}_7$ <sup>5</sup> representing 0.377 milligram-atom of beryllium.

Taking beryllium as unity, these results are summarized by the formula  $(\text{CH}_3)_{0.83}\text{BeB}_{1.03}\text{H}_{4.21}$ , approximating  $\text{CH}_3\text{-BeBH}_4$ . The sample probably contained a small proportion of  $\text{BeB}_2\text{H}_3$ , which has almost the same volatility. The production of 4.0 cc. of methane from the boron-free residue (during the final hydrolysis), demonstrates that the methyl groups in this compound are attached to beryllium.

**Further Reaction of  $\text{CH}_3\text{BeBH}_4$  with Diborane.**—A large portion of the  $\text{CH}_3\text{BeBH}_4$  described above was treated with diborane under a pressure somewhat above one atmosphere; as the reactants were warmed to room temperature, a violent fuming occurred, and the solid became fusible at  $50^\circ$ . After a half-hour at  $60^\circ$ , the material could be cooled to room temperature without solidifying, but it became a solid (infusible at temperatures below  $100^\circ$ ) after remaining for ten hours in the atmosphere of diborane at  $50^\circ$ . After removal of the unused diborane and the methyldiboranes (by distilling from the reaction tube at  $-80^\circ$ ), the solid reaction product was treated repeatedly with fresh samples of diborane,

(4) The absence of methyl derivatives of diborane here may have been due to lack of adequate mixing of the boron trimethyl with the diborane not used in the reaction.

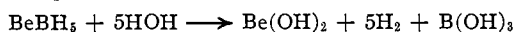
(5) Produced by the method of Čupr, *Z. anal. Chem.*, **76**, 184 (1929).

TABLE I  
 VAPOR TENSIONS OF  $\text{BeB}_2\text{H}_8$ 

$t$ , °C.	16.9	20.4	26.3	29.9	34.4	39.9	45.0	49.0	55.3	58.0	60.2	69.0
$p_{\text{mm.}}$ (obsd.)	4.2	5.4	8.3	11.6	17.4	25.9	37.1	51.2	81.0	96.3	112.8	199.8
$p_{\text{mm.}}$ (calcd.)	4.0	5.4	8.9	12.0	17.2	26.3	38.5	51.6	80.5	96.8	112.5	200.0

until the formation of the methylboranes no longer could be observed. The main product was the very stable, sublimable white solid later shown to be beryllium borohydride,  $\text{BeB}_2\text{H}_8$ . A small quantity of non-volatile white solid also was obtained.

The non-volatile by-product was hydrolyzed, to produce 38 cc. (1.70 millimoles) of pure hydrogen (analyzed by combustion). The subsequent determination of beryllium gave 32.0 mg. of  $\text{Be}_2\text{P}_2\text{O}_7$ , corresponding to 0.333 millimole of atomic beryllium. The ratio of hydrogen to beryllium is thus only slightly in excess of five to one, a result explained by the assumption that the non-volatile solid is  $(\text{BeBH}_3)_2$ , which should be hydrolyzed according to the equation



This assumption also makes it easy to understand why the substance reacts further with diborane to form  $\text{BeB}_2\text{H}_8$ .

**Analysis of Beryllium Borohydride,  $\text{BeB}_2\text{H}_8$ .**—Beryllium borohydride, obtained as in the preceding section, reacts rapidly with dry hydrogen chloride, even at temperatures as low as  $-80^\circ$ , to produce hydrogen, diborane, and chlorodiborane as volatile products. The ideal equation is  $\text{BeB}_2\text{H}_8 + 2\text{HCl} \longrightarrow \text{BeCl}_2 + 2\text{H}_2 + \text{B}_2\text{H}_6$ , but it is difficult to complete this reaction at low temperatures. It was possible, however, by successive treatments of the residue with small samples of hydrogen chloride at temperatures as high as  $100^\circ$ , to achieve an analytically adequate separation of boron from beryllium by this reaction. After the treatment with hydrogen chloride, the residue and the volatile products were hydrolyzed separately.

Thus a 9.2-cc. (0.410 millimole) sample of the stable sublimate gave a total of 73.4 cc. (3.28 millimoles) of hydrogen, 0.817 millimole of boric acid and 37.5 mg. of beryllium pyrophosphate, corresponding to 0.391 millimole of atomic beryllium. Per mole of the compound there are thus 7.98 moles of hydrogen, 1.99 moles of boron and 0.95 mole of beryllium, in accordance with the molecular formula  $\text{BeB}_2\text{H}_8$ .

This molecular formula was checked by a determination of the vapor density: 26.2 cc. of the vapor weighed 44.5 mg. The molecular weight therefore was 38.0 (calcd., 38.7). Check results were 38.5 and 39.0.

On account of the vigorous reaction of the compound with stopcock grease (even with Apiezon L, which does not react with diborane), it was necessary to employ a special weighing bulb having a mercury float-valve, as shown in Fig. 2, for weighing samples of this substance. Even with this device, some difficulty was experienced in obtaining complete transfer of the sample into the weighing bulb, evidently because of the production of a slight trace of non-condensable gas by attack upon the thin and distant layer of Picein in the ground joint.

#### Physical Properties of Beryllium Borohydride.

—The vapor tensions of  $\text{BeB}_2\text{H}_8$ , measured by the

aid of the completely immersed bulb described in an earlier paper,<sup>6</sup> are given in Table I. The results determine the equation:  $\log_{10} p_{\text{mm.}} = 11.772 - (3240/T)$ , from which the check values in Table I were calculated. The normal sublimation temperature is calculated to be  $91.3^\circ$ , and the heat of vaporization, 14,810 cal./mole.

The melting point could not be observed, for the compound began to decompose slightly (at  $123^\circ$ ) before any definite fusion could be recognized. At this temperature, the pressure is computed to be five atmospheres.

**The Compound  $\text{BeB}_2\text{H}_8 \cdot \text{N}(\text{CH}_3)_3$ .**—A mixture containing 0.482 millimole (10.8 cc.) of beryllium borohydride and an excess of trimethylamine (3.049 millimoles) was kept for sixteen hours at  $-80^\circ$  in a simple reaction tube.<sup>7</sup> From the reaction mixture, a total of 2.678 millimoles (60 cc.) of trimethylamine could be removed (most at  $-80^\circ$  and the rest at  $-45^\circ$ ); from the resulting glassy residue, 0.103 millimole (2.30 cc.) of beryllium borohydride could be removed by sublimation at  $35^\circ$  (softening point of the residue). The product thus purified contained 0.371 millimole of the amine and 0.379 millimole of the borohydride, corresponding to the formula  $\text{BeB}_2\text{H}_8 \cdot \text{N}(\text{CH}_3)_3$ . On exposure to air, this material burst into a brilliant blue-white flame. This flash was repeated when water was poured into the open tube.

The 1:1 addition reaction occurred without use of an excess of the amine; thus a mixture prepared from 5.4 cc. (0.241 millimole) of beryllium borohydride and 5.7 cc. (0.254 millimole) of the amine, lost only 0.3 cc. (0.013 millimole) of the latter when warmed for a short time to  $35^\circ$ .

The latter sample was used to determine the vapor tensions of the compound from  $65$  to  $140^\circ$ . The results shown in Table II determine the equation

$$\log_{10} p_{\text{mm.}} = 8.353 - (2909/T)$$

from which the check values were calculated. From this equation the extrapolated boiling point is found to be  $260^\circ$ , the molar heat of vaporization 13,300 cal. and the Trouton constant, 25.0

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

(7) Fig. 2a, Schlesinger and Burg, *ibid.*, **60**, 293 (1938).

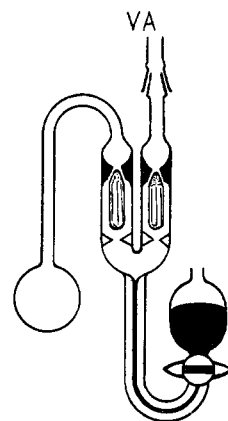


Fig. 2.

TABLE II  
 VAPOR TENSIONS OF  $\text{BeB}_2\text{H}_3\text{N}(\text{CH}_3)_3$ 

$t$ , °C.	65.0	75.2	80.8	85.6	92.5	100.5	110.3	119.9	125.3	131.3	139.8
$p_{\text{mm.}}$ (obsd.)	0.52	1.00	1.33	1.72	2.50	3.64	5.80	9.00	11.30	14.50	20.1
$p_{\text{mm.}}$ (calcd.)	0.56	1.00	1.36	1.75	2.49	3.69	5.83	8.93	11.25	14.45	20.3

cal./deg. mole. The high value of this constant is usual for such a low region of the vapor tension curve as was obtained in this case.

For the determination of the **molecular weight** of the addition compound, the material was synthesized from nearly equal volumes of its immediate constituents: 1.07 cc. of beryllium borohydride and 1.00 cc. of trimethylamine.

The product was heated in the completely immersed bulb to 128°, a temperature at which the sample appeared to be wholly vaporized, for the pressure, 11.37 mm.,<sup>8</sup> was about 10% lower than the vapor tension of the compound. As the bulb capacity was 118.2 cc., the volume of vapor at standard conditions amounted to 1.15 cc., whereas the value expected on the basis of the formula  $\text{BeB}_2\text{H}_3\text{N}(\text{CH}_3)_3$  is 1.07 cc.

That the trimethylamine is held very firmly in the compound is shown by the fact that the latter does not react with diborane to give borine trimethylamine even at 70°.

**The Compound  $\text{BeBH}_5\text{N}(\text{CH}_3)_3$ .**—A 5.4 cc. sample of the addition compound was treated with 2.71 cc. of trimethylamine, acting during thirty hours at 95°. The borine trimethylamine formed during this period was removed, and the residue was heated further with the unchanged trimethylamine, first for eighteen hours at 100° and then twelve hours at 90°. The result of this procedure was the formation of a total of 5.4 cc. of borine trimethylamine, with the accompanying absorption of 5.5 cc. of trimethylamine. A final heating of the residue with 21.2 cc. of trimethylamine for thirty-six hours at 100° had no effect; evidently the reaction had gone to completion according to the equation:  $\text{BeB}_2\text{H}_3\text{N}(\text{CH}_3)_3 + \text{N}(\text{CH}_3)_3 \longrightarrow \text{BeBH}_5\text{N}(\text{CH}_3)_3 + (\text{CH}_3)_3\text{N}\cdot\text{BH}_3$ .

The final residue presented the appearance of foliate frost-patterns: main stems striated, with side branches shooting off at 60° angles. Although the material appeared to be entirely uniform, it was not possible to observe a definite melting point: *in vacuo*, the range was 60–70°, but in an atmosphere of trimethylamine, it was 92–97°. The difference is to be explained in terms of the tendency of the substance to lose trimethylamine when heated *in vacuo*; the resulting oily material probably dissolves the undissociated solid, at a temperature far below the true melting point. Trimethylamine suppresses the dissociation; hence the melting range is higher.

**Removal of Trimethylamine from  $\text{BeBH}_5\text{N}(\text{CH}_3)_3$ .**—The compound  $\text{BeBH}_5\text{N}(\text{CH}_3)_3$  could be denuded of one-

(8) Corrected for the expansion of mercury, but not for the pressure of mercury vapor, since the conditions were such that very little of that vapor should have been mixed with the sample.

third of its trimethylamine, by a process of heating at 100°, sudden chilling, and immediate removal of the liberated amine.<sup>9</sup> Four such treatments of the 5.4-cc. sample of  $\text{BeBH}_5\text{N}(\text{CH}_3)_3$  yielded 1.6 cc. of trimethylamine, but this was the practical limit of the process. The residue seemed to be capable of liberating more trimethylamine, for its vapor tension varied from 0.2 mm. at 100° to 6 mm. at 120°, but it was not feasible to isolate the amine whose presence was indicated by the sharp rise of pressure. Since the product of removing trimethylamine was an oily liquid rather than a solid, it scarcely can have been  $\text{BeBH}_5$ , which previously was indicated to be a non-volatile solid. Since the actual limit of removal of trimethylamine might fairly be estimated at 50% of the original amine content, it might be reasonable to suspect that the final product of the de-amination of  $\text{BeBH}_5\text{N}(\text{CH}_3)_3$  is a compound of that substance with  $\text{BeBH}_5$ . However, the matter will need fuller investigation.

The residue now was allowed to react with diborane (2.9 cc.) during twelve hours at 80°. All but 0.75 cc. of the diborane was absorbed, and 0.51 cc. of pure  $\text{BeB}_2\text{H}_3$  (vapor tension 6 mm. at 23°) was obtained. Confirmation of the identity of this tiny sample was found in its behavior in condensation: it showed its characteristic tendency to condense as an invisible film at low temperatures, and then turn white when warmed. It is to be noted that the quantity of diborane absorbed was very nearly enough to convert all of the material from the  $\text{BeBH}_5$ -composition to the  $\text{BeB}_2\text{H}_3$  composition.

**Treatment of  $\text{BeB}_2\text{H}_3\text{N}(\text{CH}_3)_3$  with Diborane.**—Following the demonstration of the monomeric character of the addition compound, came an attempt to remove trimethylamine from this material by the action of diborane. The 1-cc. sample of  $\text{BeB}_2\text{H}_3\text{N}(\text{CH}_3)_3$  was exposed to 1.75 cc. of diborane, during six hours at 70°. The diborane then was completely regained; no reaction had occurred. It is therefore evident that the attachment of trimethylamine to  $\text{BeB}_2\text{H}_3$  is far stronger than its attachment to a  $\text{BH}_3$  group, strong as the latter bond is known to be.

### Summary

Dimethylberyllium reacts with diborane to produce a new compound having the molecular formula  $\text{BeB}_2\text{H}_3$  (normal sublimation temperature, 91.3°; m. p. not observable), and methylboron compounds. The reaction involves several intermediate stages, one of which is represented by a substance which seems to be  $\text{CH}_3\text{BeBH}_4$ . A non-volatile by-product evidently is  $(\text{BeBH}_5)_x$ .

These new beryllium compounds react vigorously with air, moisture, and hydrogen chloride;

(9) Direct heating *in vacuo* could not be used, because some of the beryllium material was sufficiently volatile to diffuse away into the cooler parts of the vacuum apparatus.

the last reagent offers a means of separating beryllium (as  $\text{BeCl}_2$ ) from boron (as diborane), for purposes of analysis.

Beryllium borohydride,  $\text{BeB}_2\text{H}_8$ , reacts with trimethylamine to form an addition product having the molecular formula  $\text{BeB}_2\text{H}_8 \cdot \text{N}(\text{CH}_3)_3$  (extrapolated boiling point,  $260^\circ$ ; m. p. near  $35^\circ$ ). This reacts further with trimethylamine according to the equation  $\text{BeB}_2\text{H}_8 \cdot \text{N}(\text{CH}_3)_3 + \text{N}(\text{CH}_3)_3 \rightleftharpoons$

$\text{BeBH}_5 \cdot \text{N}(\text{CH}_3)_3 + (\text{CH}_3)_3\text{NBH}_3$ . The beryllium product of this reaction tends to lose trimethylamine, producing an oily material, which reacts with diborane to give  $\text{BeB}_2\text{H}_8$ . The compound  $\text{BeB}_2\text{H}_8 \cdot \text{N}(\text{CH}_3)_3$  does not lose trimethylamine when it is heated with diborane.

The question of the structure of the beryllium borohydride is briefly discussed.

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

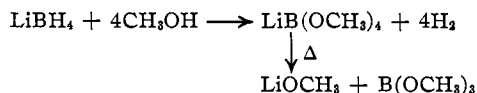
### Metallo Borohydrides. III. Lithium Borohydride

BY H. I. SCHLESINGER AND HERBERT C. BROWN

The reactions of the methyl derivatives of aluminum and beryllium to form the interesting aluminum and beryllium borohydrides,<sup>1</sup> led us to examine the possibility of preparing a similar derivative of an alkali metal.<sup>2</sup> Since ethyllithium is easy to prepare and to purify, we used it as the starting material.

At room temperature, gaseous diborane is absorbed rapidly by ethyllithium with the formation of the various ethyl derivatives of diborane and a white solid which is remarkably stable and non-volatile; it can be heated at  $240^\circ$  under pressures as low as  $10^{-4}$  to  $10^{-5}$  mm. without the slightest evidence of either decomposition or volatilization. Upon raising the temperature to  $275$ – $280^\circ$ , the material melts to a clear liquid which evolves hydrogen slowly.

The composition of this substance was established as  $\text{LiBH}_4$  in two ways: indirectly, by comparing the composition of the volatile products with that of the starting materials; and directly, by treatment of the compound with methyl alcohol. The latter reaction proceeds smoothly at all temperatures at which the alcohol is liquid, in accordance with the equation

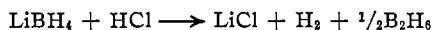


Like its previously discovered aluminum and beryllium analogs, lithium borohydride reacts

(1) Schlesinger, Sanderson and Burg, *THIS JOURNAL*, **61**, 536 (1939); **62**, 3421 (1940); Burg and Schlesinger, *ibid.*, **62**, 3425 (1940).

(2) It has long been postulated that salts with the  $(\text{BH}_4^-)$  anion should be capable of existence. Attempts by Stock and Laudenklos (*Z. anorg. allgem. Chem.*, **228**, 178–192 (1936)) to prepare  $\text{K}^+(\text{BH}_4^-)$  by the reaction of active hydrogen with potassium diborane,  $\text{K}_2\text{B}_2\text{H}_6$ , however, were unsuccessful.

readily with hydrogen chloride at temperatures as low as  $-80^\circ$  to form hydrogen, diborane and lithium chloride as primary products

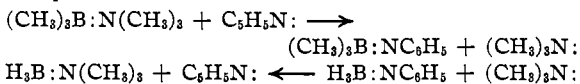


On the other hand, lithium borohydride differs markedly from the aluminum and beryllium derivatives in a number of respects. For example, both the aluminum and the beryllium compounds are spontaneously inflammable, while the lithium derivative is unaffected by dry air. Its salt-like character (it melts at  $275$ – $280^\circ$  with decomposition and exerts no appreciable vapor pressure at temperatures up to this point) is still another striking difference—the aluminum derivative, it may be recalled, melts at  $-64.5^\circ$  and boils at  $44.5^\circ$ .

Perhaps the most significant difference between these compounds is the fact that trimethylamine, which removes borine groups in the form of borine trimethylamine,  $\text{H}_3\text{B} \cdot \text{N}(\text{CH}_3)_3$ , with ease from aluminum borohydride and with slightly greater difficulty from beryllium borohydride, has no action on lithium borohydride.<sup>3</sup>

In view of these differences, it is of considerable interest that aluminum borohydride undergoes a

(3) In the course of attempts to determine whether pyridine could accomplish the removal of borine groups more readily than does trimethylamine, the compounds trimethylborine pyridine and borine pyridine were prepared and characterized. During this study, an unusual observation was made. Toward trimethylboron, pyridine acts as a stronger base than trimethylamine, whereas toward borine, pyridine acts as a weaker base than trimethylamine, as shown by the equations



This anomalous result is being investigated; the results will be reported shortly.