the last reagent offers a means of separating beryllium (as $BeCl_2$) from boron (as diborane), for purposes of analysis.

Beryllium borohydride, BeB_2H_8, reacts with trimethylamine to form an addition product having the molecular formula $BeB_2H_8 \cdot N(CH_3)_3$ (extrapolated boiling point, 260°; m. p. near 35°). This reacts further with trimethylamine according to the equation $BeB_2H_8 \cdot N(CH_3)_3 + N(CH_3) \rightleftarrows BeBH_5 \cdot N(CH_3)_3 + (CH_3)_3NBH_3$. The beryllium product of this reaction tends to lose trimethylamine, producing an oily material, which reacts with diborane to give BeB_2H_8. The compound $BeB_2H_8 \cdot N(CH_3)_3$ 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,[1] led us to examine the possibility of preparing a similar derivative of an alkali metal.[2] 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° 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°, the material melts to a clear liquid which evolves hydrogen slowly.

The composition of this substance was established as $LiBH_4$ 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

$$\begin{tikzcd} \mathrm{LiBH_4 + 4CH_3OH} \arrow[r] & \mathrm{LiB(OCH_3)_4 + 4H_2} \arrow[d, "\Delta"] \\ & \mathrm{LiOCH_3 + B(OCH_3)_3} \end{tikzcd}$$

Like its previously discovered aluminum and beryllium analogs, lithium borohydride reacts readily with hydrogen chloride at temperatures as low as −80° to form hydrogen, diborane and lithium chloride as primary products

$$LiBH_4 + HCl \longrightarrow LiCl + H_2 + {}^1/_2B_2H_6$$

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° 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° and boils at 44.5°.

Perhaps the most significant difference between these compounds is the fact that trimethylamine, which removes borine groups in the form of borine trimethylammine, $H_3B:N(CH_3)_3$, with ease from aluminum borohydride and with slightly greater difficulty from beryllium borohydride, has no action on lithium borohydride.[3]

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

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(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 (BH_4^-) anion should be capable of existence. Attempts by Stock and Laudenklos (*Z. anorg. allgem. Chem.*, **228**, 178–192 (1936)) to prepare $K^+(BH_4)^-$ by the reaction of active hydrogen with potassium diborane. $K_2B_2H_6$. however. were unsuccessful.

(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

$$(CH_3)_3B:N(CH_3)_3 + C_5H_5N: \longrightarrow (CH_3)_3B:NC_6H_5 + (CH_3)_3N:$$

$$H_3B:N(CH_3)_3 + C_5H_5N: \longleftarrow H_3B:NC_6H_5 + (CH_3)_3N:$$

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

smooth rapid reaction with ethyllithium (in benzene solution) to yield lithium borohydride

$$3LiC_2H_5 + Al(BH_4)_3 \longrightarrow 3LiBH_4 + Al(C_2H_5)_3$$

This reaction indicates that the basic structures of the aluminum, beryllium and lithium borohydrides are closely related and that the differences in the chemical and physical properties of these compounds are probably due to minor differences in the degree of polarization or distortion of the BH_4 group. This point will be discussed in greater detail later in the paper.

The existence of the compound $LiBH_4$ led us to examine the possibility of preparing analogous quaternary organoboron derivatives, $Li(BR_4)$. We have found that trimethylboron either in the presence or absence of a solvent, is absorbed by ethyllithium at room temperature to form a white crystalline solid with the empirical composition $LiC_2H_5 \cdot B(CH_3)_3$. There is no reason to doubt that this substance is an example of a quaternary boron derivative $Li\left[B^{(CH_3)_3}_{C_2H_5}\right]$. The compound possesses an unexpected solubility in benzene and may be purified by crystallization from that solvent. The solid is stable toward dry air and dissolves in water to form a solution which slowly evolves a gas.[4] We are continuing the study of these quaternary organoboron salts.

Discussion of the Borohydrides

Comparison of the properties of diborane and of the three borohydrides described in this and the preceding papers of this series, reveals that there is a gradual transition from diborane to lithium borohydride. The data in Table I illustrate this transition in the physical properties.

TABLE I

COMPARISON OF CHEMICAL AND PHYSICAL PROPERTIES

	Diborane	Aluminum borohydride	Beryllium borohydride	Lithium borohydride
Anal. formula	B_2H_6	AlB_3H_{12}	BeB_2H_8	$LiBH_4$
	Increasing tendency to react as BH_4 derivatives $\longrightarrow$			
Reacn. formula	$(H_3B)_2$	$Al(BH_4)_3$	$Be(BH_4)_2$	$LiBH_4$
	$\longleftarrow$ Increasing tendency to react as BH_3 derivatives			
M. p., °C.	−165.5	−64.5	123°	+275°
B. p., °C.	− 92.5	44.5	91.3°	dec. 275°
V. p. at 0°, mm.	very high (>15,000)	119	0.5	very low ($<<10^{-5}$)

In its high volatility and very low freezing and boiling points, diborane displays properties characteristic of non-polar compounds. Lithium borohydride, with its relatively high melting point and extremely low volatility, as well as in the appearance of its crystals and in its insolubility in benzene, is far more polar in character. Aluminum and beryllium borohydride are intermediate in all of the physical properties mentioned, as well as in solubility. In these respects, the aluminum compound is more like diborane, the beryllium compound more like lithium borohydride.

Similar relationships exist in the chemical behavior. Diborane is very unstable, lithium borohydride relatively stable; diborane is very reactive toward air and oxygen, lithium borohydride does not react with dry air at ordinary temperature. Again the other borohydrides under discussion have properties intermediate between the extremes described, although judgment on these points must be qualitative only, since no reaction rates or equilibria have been measured.

Most striking, however, is the difference in the behavior of these substances toward trimethylamine. Lithium borohydride does not react at all. Beryllium borohydride gives borine trimethylammine when treated with trimethylamine but the reaction requires a temperature of about 90°. Furthermore, the reaction is reversible; *i. e.* the product of the reaction when treated with borine trimethylammine liberates trimethylamine. In other words, the borine group is very difficult to dislodge from beryllium borohydride.

In contrast to the preceding, the reaction of aluminum borohydride with trimethylamine occurs at temperatures between 0 and 25° and that of diborane proceeds rapidly at temperatures somewhat below −100°. Both of these reactions are irreversible.

The preceding survey of these compounds may be summarized by the statement that diborane behaves chemically toward many reagents as one might expect of a molecule consisting of two BH_3 groups not too firmly bound to each other; nothing in the chemical behavior of lithium borohydride is in any way suggestive of the presence of a BH_3 group. In terms of a descriptive and highly qualitative terminology, one might further state that the "BH_3 character" of the aluminum and beryllium borohydrides is less pronounced than in diborane, but is still definitely recognizable.

On the other hand, the whole behavior, chemical

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[4] Several years ago Thomas and Stevens, *J. Chem. Soc.*, 556 (1933), published a brief note in which they reported that they had treated trimethylboron with ethyllithium, phenyllithium, and benzylsodium in ligroin at varying temperatures up to 120°, but they had not observed the formation of any organoboron derivatives. No experimental details were given.

and physical, of lithium borohydride, so far as its properties have been studied, is that of a substance whose structure is represented by the formula $Li(BH_4)$; at present we can say no more than that it seems very probable that the two constituents of the compound, Li and BH_4, are probably ions. Nothing in the behavior of diborane would lead one to suspect that it could possibly yield a BH_4 group or ion, unless one were to use the relatively slow reaction of diborane with ethyllithium to produce lithium borohydride as the basis for such a conclusion. Again, the properties of the aluminum and beryllium compounds are intermediate in character; for example, although the physical properties of aluminum borohydride are those of a non-polar substance, it nevertheless reacts in benzene solution with ethyllithium to give lithium borohydride by a relatively rapid reaction very similar to an ionic double decomposition.

All of these facts seem to us most satisfactorily interpreted by considering lithium borohydride to be a polar compound consisting of a lithium and a borohydride ion. It is possible that the degree of ionization of the compound may not be so high as that of a typical salt because of slight deformation of the borohydride ion; decision on this question must await accumulation of further data. It is evident, however, that the smaller and more highly charged aluminum and beryllium ions would exert a much greater deforming influence on the BH_4^- ion. As a result, the polar character of the beryllium compound would become less than that of the lithium borohydride and still less in the aluminum compound, as is actually the case. Furthermore, the deformation of the BH_4^- would make it susceptible to disruption, an interpretation which explains why BH_3 groups are relatively readily "extracted" from the aluminum and beryllium compounds.

But by far the most pronounced deforming influence should be exerted by the very small, highly charged boron ion. Such an aggregate as $B\text{-}BH_4^{++}$ would not be expected to be capable of existence. Disruption into BH_3 groups should be essentially complete, and association of such groups to diborane molecules is then easily understood.

We cannot too strongly emphasize the fact that this interpretation does not visualize any of these compounds as representing a system of tautomers, such as might be represented by the equation: $AlH_3 \cdot 3BH_3 \rightleftarrows Al(BH_4)_3$. Instead, we look upon the molecules as being something intermediate between those represented by formulas like the one on the right-hand side of the preceding equation and the one on the left-hand side. This statement is particularly true of the aluminum and beryllium compounds; the lithium compound probably is almost completely like a true BH_4 salt, diborane essentially an aggregate of two BH_3 groups.

Furthermore, we wish to point out that the interpretation given is a qualitative one which does not enter into the question of the exact nature of the chemical bonds which hold together the atoms involved. The suggestion that diborane represents a resonating system involving singlet electron, doublet electron, quadruplet electron and no electron bonds, with a certain degree of ionic contribution, is not contradicted, nor indeed concerned, in the interpretation we have given. Furthermore, resonance of this type is probably involved in the bonds in the aluminum and beryllium compounds, but is probably less important in the lithium compound. Chemical evidence alone cannot decide these questions, and since ours is a chemical study of these compounds, we are not entering into a discussion of the problem the further elucidation of which requires many additional data.

Experimental Part[5]

Apparatus and Technique.—The apparatus and technical methods used in this investigation are, for the most part, similar to those described in previous publications of this series. In a number of instances, the low volatility and high reactivity of some of the substances used and studied in this research made it necessary to devise several modifications of the usual techniques. These modifications will be discussed as the individual experiments are described.

Preparation of Diethylmercury.—Diethylmercury was conveniently prepared by the action of ethylmagnesium bromide on ethylmercuric chloride. A supply of the latter substance was kindly furnished us by Professor M. S. Kharasch.

A solution of 0.1 mole of ethylmagnesium bromide in ether was added to a solution of 0.05 mole of ethylmercuric chloride, also in ether, and the mixture left at room temperature for two hours. The excess of the Grignard reagent was decomposed with ice and a dilute solution of hydrogen chloride, and the ether layer separated, dried and fractionated. There was obtained 9.2 g. of diethylmercury (b. p. 97–99° at 125 mm.), indicating a yield of 70%.

Preparation of Ethyllithium.—The tube shown in Fig. 1 was prepared and thoroughly swept clean of oxygen with

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[5] All volumes refer to gases at standard conditions. Quantities of reactants, originally measured either by volume or by weight, have been reduced to millimoles to facilitate direct comparisons.

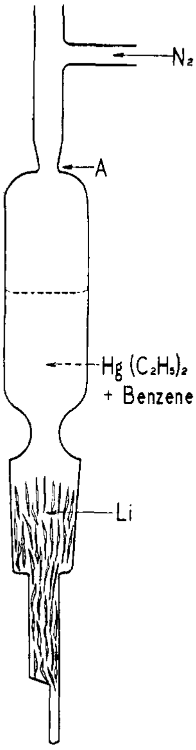

Fig. 1.

a stream of purified nitrogen.[6] In this tube were placed approximately 1 g. of lithium, freshly cut into long thin strips, 3.0 g. of diethylmercury, and 20 ml. of dry benzene. The tube was then sealed at A and heated in the vapors of boiling methyl alcohol (65°) for twenty-four hours. It was then connected to the filtering apparatus shown in Fig. 2. After this apparatus had been thoroughly evacuated, the stopcock B was closed, and the tip of the reaction tube broken at C by rotating the tube slightly. The warm benzene solution of ethyllithium passed through the porcelain filter[7] at D into the tube E. The stopcock, B, was then opened and the benzene distilled away into another section of the apparatus. The crude ethyllithium remaining in the tube was purified by sublimation under very low pressures (10^{-3} to 10^{-4} mm.). The apparatus was opened to the pump and the tube E immersed in a hot water-bath. As the temperature of the bath was slowly raised from 50 to 90°, the ethyllithium deposited on the walls of the tube just above the level of the water-bath as a coherent ring of white crystalline material.

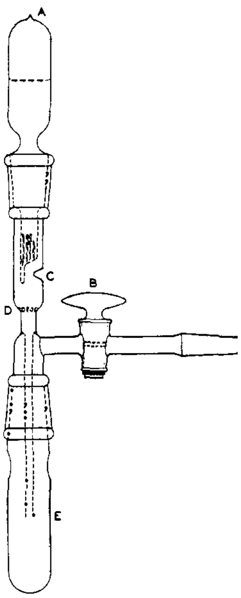

Fig. 2.

The yield of crude ethyllithium was almost quantitative (0.73 g., 93% of the calculated value). The yield of the pure sublimed material was somewhat less, averaging 60 to 70% of the crude. The purity of this sublimed ethyllithium was established by analysis.[8]

The tube was then filled with dry nitrogen, quickly closed in a rapid stream of nitrogen with the stopper F shown in Fig. 3, and placed in a box fitted with rubber gloves for operating in an atmosphere of nitrogen. After the box had been swept free of oxygen, the pure sublimed material was separated from the walls of the tube by means of a long spatula and samples of the material shaken out into small Pregl "piggies" (G, Fig. 3) which had been weighed previously. These samples were rapidly weighed and stored in a nitrogen-filled desiccator. In carrying out reactions with ethyllithium, a "piggy" containing a suitable quantity of ethyllithium was introduced into the reaction tube in a stream of nitrogen, and the body of the "piggy" holding the sample was then carefully shaken loose from the stopper.

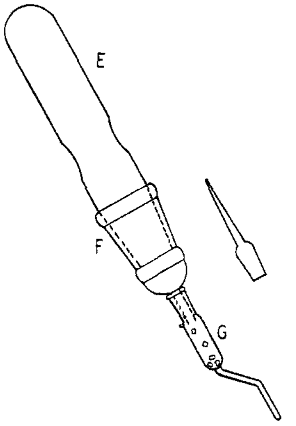

Fig. 3.

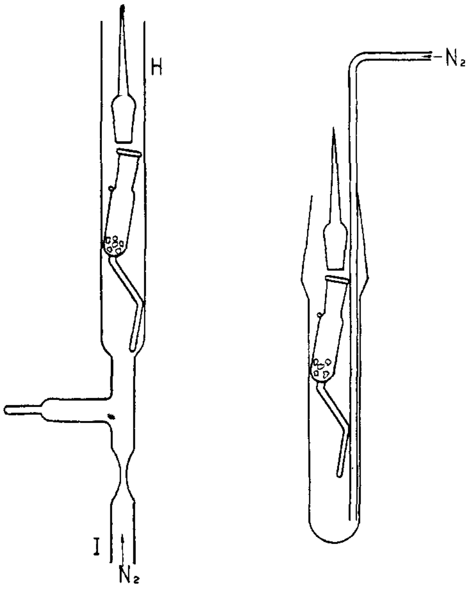

Fig. 4.

The reaction tube (Fig. 4) was then sealed (H) and connected to the apparatus in the usual manner with Picein (I) or attached by a standard ground glass joint, according to the type of reaction tube used in the experiment.

The same technique also was adopted for handling lithium borohydride.

Early attempts to transfer the samples of ethyllithium and lithium borohydride directly into the reaction tube were unsuccessful. The chief difficulty was the tendency of the smaller particles of the solid to cling to the walls of the reaction tube. This was particularly troublesome if it

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(6) Nitrogen from a tank was passed through a quartz tube containing copper (prepared by the reduction of copper oxide) maintained at 450°, and thoroughly dried with calcium chloride and fused sodium hydroxide.

(7) Unglazed porcelain disks, which can be sealed to Pyrex, are manufactured by the Selas Company, Philadelphia, and are an economical substitute for sintered glass filters.

(8) The analysis of this material was carried out conveniently by measuring the ethane liberated when a weighed sample was treated with methyl alcohol. Thus, 43.6 mg. of ethyllithium yielded 26.9 cc. of ethane; the calculated value is 27.13 cc.

was necessary (as it often was) to seal the tube. The procedure described above avoids this difficulty.

Preparation of Lithium Borohydride.—Diborane, 2.74 millimoles, was introduced into the reaction flask containing 6.80 millimoles of ethyllithium. The diborane was almost completely absorbed in two hours at room temperature. Another sample of diborane, 2.49 millimoles, was then added, and this also was taken up rapidly. After five hours, the volatile material was distilled away and condensed in another portion of the apparatus where it was subjected to a preliminary examination. This distillate appeared to be a mixture of the various ethyl derivatives of diborane containing only a trace of diborane itself. Both monoethyldiborane and diethyldiborane were separated by fractional distillation and condensation, and identified by their physical constants.[9]

The product remaining in the reaction flask was treated with a third sample of diborane, 2.65 millimoles, for sixteen hours; 2.06 millimoles excess diborane was separated from the less volatile ethyl derivatives by distillation from a U-tube at −140°. Thus a total of 5.82 millimoles of diborane had undergone reaction with the 6.80 millimoles of ethyllithium.

Since it did not seem advisable to attempt a quantitative separation of the ethyl diboranes present in the volatile reaction product, resort was had to an indirect procedure for determining the course of the reaction. Trimethylamine reacts with all of the ethyl diboranes in such a way that one mole of the former is absorbed per gram atomic weight of boron present (*e. g.*, $B_2H_5C_2H_5 + 2N(CH_3)_3 \longrightarrow BH_2(C_2H_5):N(CH_3)_3 + BH_3:N(CH_3)_3$, or $B_2H_4(C_2H_5)_2 + 2N(CH_3)_3 \longrightarrow 2BH_2(C_2H_5):N(CH_3)_3$).

Application of this procedure gave the following results. The various fractions of volatile reaction product were combined and treated with trimethylamine for two hours at 0°, after which time the excess of trimethylamine was removed. Since 4.99 millimoles of the latter were found to have been absorbed, the volatile reaction product must have contained 4.99 millimoles of atomic boron. But the total diborane entering the reaction (5.82 millimoles) had furnished 11.64 millimoles of atomic boron; hence the non-volatile reaction product must have contained 11.64–4.99, or *6.65 millimoles of atomic boron.*

Hydrolysis of the material obtained by interaction with trimethylamine yielded 8.24 millimoles of hydrogen, one-half of which came from the water. Since the 5.82 millimoles of diborane entering the reaction had contained 34.92 milliequivalents, the non-volatile residue must have contained 34.92 − 8.24, or *26.68 milliequivalents of hydrogen.*

From the amount of hydrogen evolved in the preceding treatment, it is possible also to determine what has happened to the ethyl radicals. The methylamine addition products have the composition, $BH_{(3-x)}(C_2H_5)_x:N(CH_3)_3$. It follows that the 4.99 millimoles of atomic boron found in the volatile reaction product must have been combined with a total of 3 × 4.99, or 14.97 milliequivalents of "hydrogen + ethyl." The amount of hydrogen obtained by hydrolysis of this material was 8.24 millimoles (of which one-half came from water); therefore the amount of "ethyl" in the volatile reaction product was 14.97 − 8.24, or 6.73 milliequivalents. But the amount of ethyllithium originally used was 6.80 millimoles; hence the non-volatile reaction product contained *no "ethyl."* Furthermore, since no volatile lithium compounds were obtained, the non-volatile reaction product must have contained *6.80 milliequivalents of lithium.*

Summing up these data, we see that the empirical formula of the non-volatile reaction product must have been $Li_{6.80}B_{6.65}H_{26.68}$, or $Li_{1.02}B_{1.00}H_{4.01}$.

Analysis of Lithium Borohydride.—An excess of methyl alcohol was condensed in a reaction tube with a weighed sample of lithium borohydride. As the alcohol melted, a vigorous reaction occurred with evolution of hydrogen. After the reaction mixture had stood for several hours at room temperature to ensure that the reaction had proceeded to completion, the hydrogen was removed and measured: 5.49 millimoles had been formed. Besides a small quantity of excess methyl alcohol which was obtained from the alcoholysis product in the reaction tube, no other volatile material could be recovered by distillation at room temperature. However, upon heating the non-volatile residue rather vigorously, methyl borate was obtained. This substance was not determined as such, but was treated with water and the boron estimated as boric acid: 40.6 cc. of 0.0365 *N* barium hydroxide was required, equivalent to 1.48 milliatoms of boron. The residue remaining in the flask was then titrated as lithium hydroxide: 4.40 cc. of 0.325 *N* hydrochloric acid was required, equivalent to 1.43 milliatoms of lithium. The final result showed that 31.6 mg. of lithium borohydride (1.45 millimoles) analyzed for $Li_{1.43}B_{1.47}H_{5.49}$ or $Li_{0.99}B_{1.02}H_{3.8}$.

The tenacity with which the methyl borate was held by the residue in the reaction flask was remarkable. We therefore investigated and traced the phenomenon to the formation of an intermediate compound, lithium boromethoxide, $LiB(OCH_3)_4$.[10]

Behavior toward Air.—A small sample of lithium borohydride was exposed to the atmosphere. No immediate change was observed. Within a few minutes, however, moisture was absorbed and hydrogen was evolved. In another experiment, dry air was placed in contact with a weighed sample of lithium borohydride for forty-eight hours. No reaction occurred.

Reaction with Hydrogen Chloride.—Hydrogen chloride, 2.02 millimoles, was condensed in a reaction flask containing 1.70 millimoles of lithium borohydride, and the mixture kept at −78° for sixteen hours. Analysis of the volatile products showed the presence of 1.80 millimoles of hydrogen and 24.2 cc. of a mixture of diborane, chlorodiborane, and hydrogen chloride. Had the reaction proceeded according to the equation, $LiBH_4 + HCl \longrightarrow LiCl + {}^1/_2H_2 + {}^1/_2B_2H_6$, without any side reaction of the

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[9] The main body of the distillate was trapped at −78°. The material which passed through a U-tube at this temperature consisted of two substances: traces of diborane, and monoethyldiborane. The diborane was separated by distillation from a U-tube immersed in an alcohol–ether bath at −140°: that fraction which passed through a U-tube at −78° but was trapped at −140° was identified as monoethyldiborane by its vapor tension, 7.0 mm. at −78°. The diethyldiborane was recovered by successive distillations through a U-tube at −50° and was identified by its vapor pressure of 42 mm. at 0° (Schlesinger, Horvitz and Burg, THIS JOURNAL, **58**, 407 (1936)).

By far the greater portion of the distillate consisted of less volatile material which must have been the more highly ethylated diboranes.

[10] Cambi, *Chem. Zentr.*, **85**, I, 1412 (1914).

excess hydrogen chloride with the diborane produced, the product would have consisted of 1.70 milliequivalents of hydrogen, and a mixture of 0.85 millimole of diborane and 0.32 millimole of hydrogen chloride (total volume of mixture, 26.2 cc.). The fact that the product actually contained 2.0 cc. of excess hydrogen and the volume of the hydrogen chloride–diborane mixture was 2.0 cc. less than that calculated, indicated that the reaction $B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$ had occurred to a slight extent. This conclusion was verified by hydrolysis of the mixture: 5.02 millimoles of hydrogen was obtained; calculated for 0.762 millimole of diborane plus 0.089 millimole of chlorodiborane, 5.02.

Pyrolysis.—Lithium borohydride, 0.28 millimole, in a reaction tube was heated slowly until the temperature reached 240°. The temperature was kept constant for one hour: a trace of non-condensable gas was formed, but no decomposition or other change could be observed. The tube was opened to the pump line for several minutes, but the material gave no indication of volatility even at this elevated temperature.

The temperature was then raised slowly. Between 275 and 280° the substance melted with slow evolution of hydrogen. Heating at 275–280° was continued. At the end of one hour and then at the end of a second hour the gas was removed with the aid of a Töpler pump and measured. A total of 0.21 millimole of hydrogen was obtained (the calculated value for the reaction $LiBH_4 \longrightarrow LiB + 2H_2$ is 0.56 millimole). No volatile material other than hydrogen was formed.

The residue in the flask was heated for two hours more: approximately 0.10 millimole of hydrogen was evolved. This was not removed from the reaction flask but was permitted to remain in contact with the solid residue for twenty hours at room temperature. The hydrogen was almost completely absorbed, the pressure in the reaction flask dropping from 22 mm. to less than 3 mm. Repetition of the heat treatment at 275–280° for two hours brought about the evolution of a similar quantity of hydrogen, but further evolution of gas became very slow. This is indicated by the tabulated results:

At end of 2 hours at 280°	0.21 millimole
At end of 4 hours at 280°	0.31 millimole
At end of 10 hours at 280°	0.35 millimole

Since the residue appeared to be attacking the glass tube, the experiment was discontinued.

Behavior toward Trimethylamine.—Efforts to remove borine groups from lithium borohydride with the aid of trimethylamine under various conditions were unsuccessful. The following experiment is typical of these attempts.

A sample of trimethylamine, 9.65 millimoles, was condensed in a tube containing 1.68 millimole of lithium borohydride and the mixture permitted to stand for twenty-four hours at 0°. No reaction occurred—all the trimethylamine could be recovered by distillation at room temperature. The trimethylamine was returned to the tube and the mixture heated at 100° for two hours. The formation of borine trimethylamine was not observed; the trimethylamine was recovered at room temperature.

Reaction of Trimethylboron with Ethyllithium.—A sample of ethyllithium, 3.08 millimoles, was placed in a reaction vessel with a manometer attached and 3.27 millimoles of trimethylboron added. After sixteen hours at room temperature, less than 0.35 millimole of trimethylboron had been absorbed (the pressure exerted by the trimethylboron in the tube was 600 mm.). After another reaction period of forty-eight hours, a further quantity of trimethylboron was absorbed, making a total of 0.95 millimole. The tube was then cooled to −80° and kept there for forty hours, but no addition under these conditions was observed.

It appeared likely that the slowness of the reaction at room temperature might be due to the poor contact between ethyllithium in the solid phase and trimethylboron in the gas phase, and that the reaction rate would be increased by the use of a solvent. Accordingly 5.0 ml. of dry benzene was distilled into the reaction mixture. There was a rapid absorption of trimethylboron (five to ten minutes) at room temperature. After ten hours, the benzene and excess trimethylboron was distilled away. There were recovered 0.35 millimole of trimethylboron, indicating that 2.92 millimoles of trimethylboron had been absorbed by 3.08 millimole of ethyllithium.

In another experiment in which no solvent was used, trimethylboron, liquefied at room temperature under its own vapor pressure in a sealed tube, reacted quantitatively with ethyllithium in less than twenty-four hours. A sample of 5.89 millimoles of trimethylboron was used; the excess was recovered by distillation from the tube kept at −80°. There was absorbed 1.43 millimoles of trimethylboron by 1.45 millimoles of ethyllithium. The material remaining in the tube was a white solid which did not exert any observable vapor pressure at room temperature. One ml. of benzene was distilled into the reaction tube, which was then sealed. On warming the mixture the solid lithium salt dissolved and, as the solution cooled, crystals in the form of long prisms separated. These crystals were examined under the polarizing microscope—they are anisotropic with parallel extinction.

The pure material was isolated by a modification of the method previously used for the preparation of ethyllithium. A small filter tube (similar to that shown in Fig. 2 but on a micro scale) was thoroughly flushed with nitrogen and connected to the sealed tube by a piece of rubber tubing. The lower part of the apparatus was evacuated, the crystals dissolved by warming the solvent, and the tip of the sealed tube broken by manual pressure. The filtered solution was cooled and the supernatant liquid separated from the crystals with a medicine dropper containing a tiny wad of glass wool in the tip, as a stream of nitrogen prevented access of the atmosphere. The crystals were washed twice with dry cyclohexane (also taken up with a medicine dropper) and the last traces of the solvent removed by a stream of the purified nitrogen. Several of the crystals were placed in a watch glass and exposed to the atmosphere. There was no change for several minutes; then it was observed that moisture had been absorbed.

A small portion of the material was added to several drops of distilled water. It dissolved immediately with the formation of a clear solution. After a few seconds a gas was evolved slowly.[11]

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(11) This description of the preparation and properties of this compound should be considered solely as a preliminary report. We are actively engaged in further study of these quaternary organoboron compounds.

Reaction of Ethyllithium with Aluminum Borohydride.—A solution of 0.403 millimole of ethyllithium in 2.0 ml. of benzene was treated with a slight excess of AlB_3H_{12}, 0.145 millimole. A white precipitate formed immediately. The reaction mixture was permitted to stand at room temperature for several hours to ensure complete reaction. The benzene and all the volatile products were distilled away from the reaction tube. The temperature was then raised to 100° and kept there for two hours in order to remove all traces of even only slightly volatile material.

The white solid remaining in the reaction tube was heated at 200° at 10^{-4} mm. without any noticeable effect. It melted at 270–275°, so there cannot be any doubt that lithium borohydride had been formed. Methyl alcohol was added to the reaction tube: 1.61 millimoles of hydrogen were obtained. The volatile products of the reaction were treated similarly, yielding 0.211 millimole of hydrogen and 0.400 millimole of ethane.

Summing up these results, it appears that a quantitative reaction between the ethyllithium and the aluminum borohydride had occurred: 0.403 millimole of ethyllithium had reacted with 0.135 millimole of $Al(BH_4)_3$ to produce 4.03 millimoles of lithium borohydride and 1.33 millimoles of triethylaluminum.[12]

Summary

1. A compound ($LiBH_4$) is formed by the action of diborane on ethyllithium. Its physical and chemical properties suggest that the compound is a salt with the structure $Li^+BH_4^-$ and the name lithium borohydride is proposed for this substance.

2. Lithium borohydride is stable to dry air, it melts at 275–280° with decomposition, and shows no evidence of volatility at temperatures at which it is undecomposed. Hydrogen chloride reacts to form hydrogen, diborane and lithium chloride. Methyl alcohol forms lithium boromethoxide, $LiB(OCH_3)_4$, and hydrogen. Trimethylamine does not react.

3. Ethyllithium undergoes what appears to be a metathetic reaction with aluminum borohydride in benzene solution: lithium borohydride is precipitated.

4. Ethyllithium adds trimethylboron (1:1 mole ratio) to form a white crystalline solid stable at ordinary temperatures. This substance $LiC_2H_5{\cdot}B(CH_3)_3$ appears to be representative of a new class of compound, $M^+(BR_4^-)$.

5. The physical and chemical properties of the lithium, beryllium, and aluminum borohydrides and of diborane are compared and discussed in the light of proposed structures for the compounds.

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[12] Since no attempt was made to isolate or identify any of the products of the reaction with the exception of lithium borohydride, it is possible that the excess aluminum borohydride and the triethylaluminum were not present as such in the volatile products of the reaction. Mixtures of the compounds of the type $C_2H_5Al(BH_4)_2$ would yield the same analytical results.

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

Reactions of Atoms and Free Radicals in Solution. I. A Study of the Substitution of Hydrogen on an Asymmetric Carbon Atom—The Chlorination of Primary Active Amyl Chloride

BY HERBERT C. BROWN, M. S. KHARASCH AND T. H. CHAO[1]

In the light of present knowledge, it appears that the substitution and displacement reactions of organic chemistry fall into two distinct groups: reactions that proceed by means of (A) an ionic or polar mechanism, and (B) atomic or free radical intermediates.

$$\text{(A)}\quad X{:} + Y\,\vert\,{:}Z \longrightarrow X{:}Y + Z{:}$$

$$\text{or}\quad W{:}\,\vert\,X + Y\,\vert\,{:}Z \longrightarrow W{:}Y + X{:}Z$$

$$\text{(B)}\quad X\cdot + Y\diagup\!{:}\!\diagup Z \longrightarrow X{:}Y + Z\cdot$$

Reactions involving bond scissions of the type indicated in A have been studied exhaustively from the standpoint of both synthetic utilization and reaction mechanisms.[2] The hypothesis that reactions in solution may proceed by way of an atomic or free radical mechanism, as indicated in B, has not as yet been comparably developed. Indeed, until very recently, the photochemical halogenation of organic substances was the only reaction commonly accepted as belonging to that class.

However, the number of examples bids fair to increase rapidly. Specifically, the addition of hydrogen bromide,[3] mercaptans[4] and sodium bisulfite[5] to olefins, the peroxide-catalyzed chlorination of aliphatic compounds with sulfuryl chlo-

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[1] Eli Lilly Fellow, 1939–1940.

[2] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapters V and VI.

[3] Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933); Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288, 400 (1937).

[4] Kharasch, Hammond, Melof and Mayo, unpublished work; Kharasch, Read and Mayo, *Chem. and Ind.*, **57**, 752 (1938).

[5] Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 175 (1938); Kharasch, Schenck and Mayo, THIS JOURNAL, **61**, 3092 (1939).