occurred with evolution of heat when a mixture of 8.27 mmoles of sodium hydride and 22.5 mmoles of triethylboron was allowed to warm to room temperature, 14.5 mmoles of the latter was left unchanged. Hence 8.0 mmoles of the ester had reacted with 8.27 mmoles of the hydride as would be expected in the formation of an acid–base complex of the formula $NaBH(C_2H_5)_3$. The oily, non-volatile reaction product was not analyzed.

Heating of a mixture of trimethylboron (7.16 mmoles) and lithium hydride (1.52 mmoles) at 40° did not lead to an observable change within $^1/_2$ hour. Addition of 1.91 ml. of liquid diethyl ether followed by heating of the mixture to 100° for one hour caused the lithium hydride to dissolve.

The solid product which separated when the solution was cooled was recrystallized from ether. Attempts to remove the ether from the solid thus obtained failed, since melting accompanied by evolution of ether and of trimethylboron occurred when the solid was heated to 80°. When the melt was cooled to room temperature, solid material, presumbably lithium hydride, separated from the liquid. The solid absorbed trimethylboron rapidly and dissolved in the process. These observations point to the formation of a lithium hydride–trimethylboron addition compound stabilized by the formation of an etherate, but reversibly decomposed in the absence of ether.

Acknowledgment.—The assistance of Anthony M. Schwartz, L. R. Rapp, J. R. Gilbreath and A. E. Finholt in the preparation of intermediates and with individual experiments included in this paper is gratefully acknowledged.

CHICAGO, ILL.

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

Reaction of the Boron Halides with the Alkali Metal Hydrides and with Their Addition Compounds; A New Synthesis of Diborane[1]

BY H. I. SCHLESINGER, HERBERT C. BROWN, JAMES R. GILBREATH AND J. J. KATZ

RECEIVED MARCH 17, 1952

Gaseous boron fluoride and lithium hydride react only slightly at temperatures up to 180° to give compounds containing boron–hydrogen bonds. Boron fluoride ethyl etherate, on the other hand, reacts with either sodium or lithium hydride at temperatures up to 100° to form diborane in accordance with the equation $8(C_2H_5)_2O{:}BF_3 + 6LiH \rightarrow B_2H_6 + 6LiBF_4 + 8(C_2H_5)_2O$. The rate of reaction is markedly dependent upon the physical state of the metal hydride. In most cases the yield based upon the metal hydrides was no better than 40–60% unless very finely divided hydrides were used or the reaction was run in equipment providing a grinding action on the solid hydride. Sodium trimethoxyborohydride is far more reactive than the metal hydrides and affords a means of avoiding these difficulties. The reaction is $8(C_2H_5)_2O{:}BF_3 + 6NaBH(OCH_3)_3 \rightarrow B_2H_6 + 6NaBF_4 + 8(C_2H_5)_2O + 6B(OCH_3)_3$. Yields of diborane approaching the theoretical are readily obtained with short reaction times. The reaction has been developed into a convenient laboratory preparation of diborane.

In the past the boron hydrides were prepared by the hydrolysis of magnesium boride[2] or by the passage of a mixture of hydrogen and boron halide through an arc discharge.[3] As long as the interest in diborane was primarily theoretical and the requirements could be satisfied by relatively small quantities of the gas, these methods were adequate.

It has become apparent in recent years that diborane possesses possibilities as a useful chemical reagent and intermediate. Thus it acts on aldehydes and ketones at low temperatures to reduce them quantitatively to the corresponding alcohols.[4] It reacts with metal alkyls to form the corresponding borohydrides.[5] It has a large heat of combustion per gram (*ca.* 20 kcal.)[6] and unusual, interesting flame characteristics. Finally, at elevated temperatures, it decomposes cleanly to elementary boron, and, therefore, serves as a source of the element in high purity. These facts led us to undertake a study of the reaction of alkali metal hydrides with boron halides, since it offered promise of a more satisfactory method for the preparation of diborane than those hitherto available.

Results and Discussion

At temperatures of 100 to 180° boron halides, such as the bromide and fluoride, were found to react only superficially with lithium hydride. Although varying amounts of the halides were absorbed, the volatile products liberated only small quantities of hydrogen and contained no appreciable amounts of diborane.[7]

In contrast with the unsatisfactory results obtained with unsolvated boron halides, boron trifluoride–ethyl etherate reacted rapidly with lithium or sodium hydrides. Heat was evolved and both diborane and ether were liberated. Under the conditions employed, the main reaction may be represented by the over-all equation

$$6LiH + 8BF_3{:}O(C_2H_5)_2 \longrightarrow 6LiBF_4 + B_2H_6 + 8(C_2H_5)_2O$$

Sodium hydride reacted in analogous fashion.

In the more detailed experiments with lithium hydride it was observed that, even when an excess of the etherate was used, ether was frequently liberated before an appreciable amount of diborane had been produced. The solid product obtained did not give off any diborane even when heated to 200° but did so when treated with additional boron trifluoride etherate.

As suggested in the introductory paper of this

---

[1] New Developments in the Chemistry of Diborane and the Borohydrides. IV. For a theoretical discussion of some of the reactions described herein and for an explanation of the nomenclature employed, see paper I of this series, THIS JOURNAL, **75**, 186 (1953).

[2] A. Stock, E. Wiberg and H. Martini, *Z. anorg. allgem. Chem.*, **188**, 32 (1930), and earlier papers.

[3] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **53**, 4321 (1931); A. Stock and Sutterlein, *Ber.*, **67**, 407 (1934); H. I. Schlesinger, H. A. Brown, B. Abraham, N. R. Davidson, A. E. Finholt, R. Lad and J. Knight, THIS JOURNAL, **75**, 191 (1953).

[4] H. C. Brown, H. I. Schlesinger and A. B. Burg, *ibid.*, **61**, 673 (1939).

[5] H. I. Schlesinger and co-workers, *ibid.*, **62**, 3421, 3425, 3429 (1940).

[6] W. Eggersgluess, A. G. Monroe and W. G. Parker, *Trans. Faraday Soc.* **45**, 667 (1949).

[7] The lithium hydride, available to us at the time of these experiments, was relatively coarse and impure. Finely divided material of better quality might have behaved differently.

series,[1] this observation is readily interpreted on the assumption that the hydride initially undergoes an acid–base type reaction with boron fluoride, forming the intermediate, $LiBHF_3$, and that this then reacts with additional trifluoride to produce diborane[8,9]

$$3LiH + 3BF_3:O(C_2H_5)_2 \longrightarrow 3LiBHF_3 + 3(C_2H_5)_2O$$

$$3LiBHF_3 + BF_3:O(C_2H_5)_2 \longrightarrow {}^1/_2B_2H_6 + 3LiBF_4 + (C_2H_5)_2O$$

In these exploratory experiments it was convenient to operate with an excess of etherate. Consequently it is not surprising that lithium borofluoride was the end-product, since it was observed that boron trifluoride etherate reacts with either lithium or sodium fluorides under the conditions of the experiment.

$$MF + BF_3:O(C_2H_5)_2 \longrightarrow MBF_4 + (C_2H_5)_2O$$

Whether the simple fluoride would be formed in greater amount if the etherate were not present in excess was not determined.

In a typical experiment in which the theoretical amounts of sodium hydride and boron fluoride etherate were used ($6NaH + 8BF_3:(C_2H_5)_2O$), approximately 30% of the theoretical amount of diborane was produced in one hour. The rate of production then decreased markedly and only after several additional hours could yields of 40–60% be realized. It appeared probable that the reaction slowed down and essentially ceased primarily as the result of the formation of a coating of the alkali borofluoride (or of the alkali fluoride) on the relatively coarse particles of the hydride utilized in these experiments. Such a coating would prevent contact of the etherate with unchanged hydride.

This conclusion was supported by these observations. First, use of a large excess of the metal hydride led to quantitative utilization of a limited amount of boron fluoride etherate to form diborane. Additional etherate was utilized with greater and greater difficulty although analysis showed the presence of unchanged hydride in the reaction vessel. Second, the substitution of finely divided hydride for the coarser material originally available led to a greatly increased rate of reaction and improved utilization of the hydride. Finally, when the reaction was carried out in a vessel in which steel balls maintained a grinding action on the sodium hydride throughout the experiment, yields of diborane approximating 90% were obtained. Lithium hydride under all comparable conditions reacted more rapidly and more completely than sodium hydride.

The reaction of boron fluoride etherate on finely divided alkali metal hydrides is thus well suited for the preparation of diborane when a continuous supply of the latter is needed over an extended period of time. Nevertheless, the higher cost of lithium hydride and the technical difficulties and hazards of preparing and handling sodium hydride fine enough to react rapidly with boron fluoride etherate led us to seek a procedure which would avoid or minimize these objections and difficulties, especially for situations in which diborane is to be prepared only occasionally or in smaller amounts.

The development of the alternative procedure was based on the earlier observation that the action of methyl borate on sodium hydride produces sodium trimethoxyborohydride,[10] a white, finely divided solid which reacts as a convenient source of hydride ion. Its treatment with unsolvated boron fluoride led to the displacement and liberation of methyl borate without the formation of diborane, presumably according to the equation

$$NaBH(OCH_3)_3 + BF_3 \longrightarrow NaBHF_3 + B(OCH_3)_3$$

However, the use of the etherate of boron fluoride led to the desired reaction, *i.e.*, to the rapid evolution of diborane. An interpretation of this reaction in the light of the Lewis generalized acid–base concept was presented in the introductory paper of this series.[1]

In early experiments the quantity of etherate added to the reaction mixture was that called for by the equation

$$6NaBH(OCH_3)_3 + 8(C_2H_5)_2O:BF_3 \longrightarrow B_2H_6 + 6NaBF_4 + 6B(OCH_3)_3 + 8(C_2H_5)_2O$$

It was noted that the diborane collected after the first hour or two represented approximately 50–60% of the theoretical yield. Diborane continued to be evolved from the reaction mixture, but at an unsatisfactorily slow rate. The solid residue did not contain appreciable amounts of hydrolyzable hydrogen. The latter was, however, a component of a substance present in the liquid phase, which though volatile was less volatile than diborane. It was probably dimethoxyborine,[11] which could arise as a by-product from the reaction of diborane and methyl borate.

$$B_2H_6 + 4(CH_3O)_3B \rightleftarrows 6(CH_3O)_2BH$$

Fortunately, the difficulty was overcome by the simple expedient of using twice the theoretical quantity of the etherate. In this way yields of diborane approaching 100% were obtained and quantities as high as 20 l. have been synthesized in single preparations.

An explanation for the effect of an excess of the etherate may be found in the fact that boron fluoride reacts readily with methyl borate to form the compounds dimethoxyboron fluoride, $(CH_3O)_2BF$ and monomethoxyboron difluoride, CH_3OBF_2.[12] We observed that these substances are also rapidly formed from boron fluoride etherate and methyl borate.

$$(CH_3O)_3B + BF_3:O(C_2H_5)_2 \rightleftarrows (CH_3O)_2BF + CH_3OBF_2 + (C_2H_5)_2O$$

By removing methyl borate in the form of the fluoro

---

[8] The intermediate may produce a second intermediate, BHF_2, which then disproportionates to give diborane and boron trifluoride. In this connection, it is interesting that J. Goubeau and R. Bergmann [*Z. anorg. Chem.*, **263**, 69 (1950)] describe the formation of $NaBHF_3$ when boron fluoride and sodium hydride are heated to 200°. The compound was stable at that temperature.

[9] When the reaction was carried out at temperatures lower than usual, *e.g.*, at 10°, considerable amounts of lithium borohydride were formed. Whether this is due to the formation of the borohydride as an intermediate or whether it is a secondary reaction product resulting from the interaction of diborane and lithium hydride was not determined.

[10] H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, THIS JOURNAL, **75**, 192 (1953).

[11] A. B. Burg and H. I. Schlesinger, *ibid.*, **55**, 4020 (1933).

[12] M. V. Gasselin, *Ann. chim. phys.*, [7] **3**, 5 (1894).

derivatives, the excess of boron fluoride ethyl etherate may prevent the loss of diborane which otherwise might result from the formation of dimethoxyborine.

We also examined the use, in the reaction, of other boron halides such as boron bromide and boron chloride, of other etherates of boron fluoride such as the addition compounds with methyl ether, *n*-butyl ether and dioxane, and of other trialkoxyborohydrides such as the triethyl- and tributyl-compounds. In each case we were able to demonstrate the formation of at least small quantities of volatile boron compounds which gave hydrogen on treatment with water. Since in most instances the reactions appeared less favorable than that involving boron fluoride ethyl etherate and sodium trimethoxyborohydride, they were not investigated in any detail.

As pointed out in the introductory paper of the present series,[1] several convenient methods for preparing diborane have now been made available, *i.e.*, the reactions of boron fluoride etherates with lithium hydride, with the borohydrides of sodium or of lithium and with sodium trimethoxyborohydride. The procedure when the simple borohydrides are employed, is, in general, like those described herein for the use of the other two reagents. Which of the four reagents is to be used will depend on the quantity of diborane to be prepared and on the availability and relative costs of the starting materials. Lithium hydride is probably the most satisfactory for larger scale manufacture. Sodium borohydride, which is commercially available and avoids the hazards involved in handling finely divided lithium or sodium hydrides, is very convenient for laboratory scale preparations. Sodium trimethoxyborohydride has the advantage of ease of preparation; it has the minor disadvantage of large bulk and of the formation of relatively large amounts of methyl borate.

Experimental Part

Materials.—The lithium hydride, sodium hydride and sodium trimethoxyborohydride used in this work have been described in a preceding paper.[10]

The boron fluoride ethyl etherate was prepared by passing boron fluoride gas (Harshaw Chemical Co.) into anhydrous ethyl ether until the liquid was saturated. The product was distilled through a fractionating column packed with steel helices and rated at 25 theoretical plates. The fraction boiling between 124 and 125° was taken. The methyl etherate was prepared by the action of boron fluoride on methanol.[13] The product was distilled through the column and the fraction boiling between 125 and 126° was collected and used. The corresponding butyl etherate and dioxanate were prepared by passing boron fluoride into the corresponding ethers. They were used without further purification. The dioxanate is a solid; this fact necessitated the use of an excess of dioxane as a solvent.

The ethyl etherate slowly turned brown. During fractional distillation of the material a small amount of ethyl fluoride (b.p. −32°) collected in the −80° trap at the condenser outlet. Small quantities of water hastened the decomposition. Properly protected from moisture the etherate remains colorless for long periods.

In the following, volumes of gases or vapors are reduced to S.T.P.

The Reaction of Lithium Hydride and Boron Fluoride.—Boron fluoride (170 mmoles) was passed back and forth over 136 mmoles of lithium hydride maintained at 180°. Finally the remaining gas was removed and treated with water. Only 9 mmoles of hydrogen was obtained.[7]

The Reaction of Lithium Hydride and Boron Fluoride Ethyl Etherate.—A round-bottomed flask, fitted with a condenser and a mercury sealed stirrer, was connected through the condenser to two U-tubes in series, with stopcocks on each arm. The system was protected against development of excessive pressures by use of a mercury bubbler. Lithium hydride (3.6 g., *i.e.*, 4.8 g. of 75% LiH or 0.45 mole) was placed in the flask and the apparatus flushed out with nitrogen. The hydride was suspended in 140 g. of anhydrous ethyl ether, and to the stirred mixture 15.6 g. (0.110 mole) of boron fluoride ethyl etherate was added over a period of 30 minutes. The temperature of the reaction mixture rose to 35–40°, and the solid became light and fluffy. After all of the etherate had been added, the mixture was stirred for two hours and then heated at a gentle reflux for 14 hours while a gentle stream of nitrogen was maintained through the apparatus.

At the end of this time considerable solid had collected in the −195° U-tube, and several ml. of liquid was present in the −80° trap. The stopcocks on the side-arms of the two U-tubes were closed and the material was transferred to a high vacuum apparatus and there fractionated. A total of 269 ml. of diborane was obtained. Based on the equation $6LiH + 8BF_3{:}O(C_2H_5)_2 \rightarrow B_2H_6 + 6LiBF_4 + 8(C_2H_5)_2O$, and on the amount of the etherate used, the yield was 87%.

Several small scale experiments were carried out in which an excess of boron fluoride ethyl etherate was placed on lithium hydride in a reaction vessel connected to the high vacuum apparatus. After various intervals of time, the diborane and ethyl ether were recovered and measured and the etherate was returned for further reaction with the hydride. In the initial stages of the reaction, more ether was invariably recovered than could be accounted for on the basis of the diborane isolated, as discussed previously. However, in the later stages, the quantity of diborane and ether recovered corresponded closely to the 1:8 ratio of the equation

$$6LiH + 8BF_3{:}O(C_2H_5)_2 \longrightarrow B_2H_6 + 6LiBF_4 + 8(C_2H_5)_2O$$

The solid residue was dissolved in the minimum quantity of water and treated with a concentrated solution of potassium chloride. Potassium borofluoride precipitated. The weight of the precipitate indicated that the residue must have been predominantly lithium borofluoride with but small amounts of lithium fluoride.

A detailed description of the preparation of diborane in somewhat larger quantities is given in the section "Preparation of Diborane."

The Reaction of Sodium Hydride and Boron Fluoride Ethyl Etherate.—The reaction was carried out in the same manner as that previously described for lithium hydride. Sodium hydride, 2.40 g. (0.100 mole) was suspended in ether in the reaction flask, to which 19.2 g. (0.135 mole) of boron fluoride etherate was then added during 30 minutes. An immediate rise of temperature to about 60° and a marked increase in volume were observed. After the initial reaction had subsided, the flask was heated for eight hours at 110°. Diborane, 103 ml., was obtained. After several hours at room temperature, the flask was reheated for four hours at 110°. An additional 53 ml. of diborane was obtained, bringing the total yield to 42%.

In another larger scale experiment, a large excess of sodium hydride (1.01 moles) was allowed to react with 0.521 mole of boron fluoride etherate. After 7 hours, 0.7 l., and after 26 hours, 1.10 l. of diborane had been collected. The solid residue generated 14.2 l. of hydrogen by hydrolysis. This amount corresponds to 0.63 mole of sodium hydride on the assumption that no compound capable of generating hydrogen, other than sodium hydride, is present in the residue. On this assumption, the data indicate that 0.38 mole of the original 1.01 moles of the hydride had been used up. According to the equation

$$6NaH + 8BF_3{:}O(C_2H_5)_2 \longrightarrow 6NaBF_4 + B_2H_6 + 8(C_2H_5)_2O$$

0.38 mole of the hydride is equivalent to 0.504 mole of the etherate, an amount within a few per cent. of that contained in the original reaction mixture. In agreement with this calculation is the fact that practically none of the etherate was recovered. On the other hand, the amount of diborane obtained was only 70% of the calculated value. Neverthe-

---

[13] A. J. Kolka and R. R. Vogt, THIS JOURNAL, **61**, 1463 (1939).

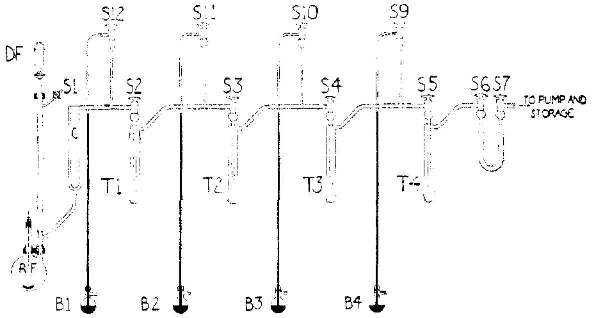

Fig. 1.—Apparatus for the preparation of diborane by the use of boron trifluoride etherate.

less, in view of the indirect character of the calculation, which is based on an assumption which does not consider the possibility that the solid residue might contain a sodium hydride–boron fluoride adduct, the agreement between the calculated and observed data is considered satisfactory confirmation of the postulated equation.

Numerous experiments were carried out to determine the effect of variables on the yield. The results support the conclusions: (1) Increased temperature increases the rate of production of diborane. (2) Stirring increases the rate of reaction. (3) A large excess of either sodium hydride or of boron fluoride ethyl etherate increases markedly the rate of generation.

From these studies it appears that the particle size of the sodium hydride and the coating of product on these particles were the primary causes of the slow rate of reaction and the low yield. To test this conclusion, a number of experiments, in which continuous grinding was effected, were carried out. In a typical experiment 0.672 g. of sodium hydride (28.0 mmoles) and 10.62 g. of boron fluoride ethyl etherate (74.8 mmoles) were introduced into a tube containing several steel balls. The sodium hydride was contained in a thin glass capsule to prevent premature reaction with the etherate. The tube was evacuated and sealed. The sodium hydride capsule was broken by shaking the tube, which was then attached to an inclined rotating device at an angle of approximately 70° from the vertical. The tube was maintained at 60° by an electrically heated mantle for 12 hours without rotating and for another 24 hours with rotating to produce a grinding action of the steel balls on the coated sodium hydride particles. At the end of the reaction period, the tube was attached to the high vacuum apparatus, opened and the diborane isolated. The 91.5 ml. obtained represents a yield of 87%. The ether isolated (834 ml. of gas or 37.2 mmoles) corresponded to a 99% utilization of the sodium hydride, as was also indicated by analysis of the solid residue by hydrolysis. It is probable that the conversion of the sodium hydride and boron fluoride to diborane was essentially quantitative, but that some of the latter was lost as a result of the extended exposure to 60°. It is known that diborane undergoes slow decomposition under these conditions.

The Reaction of Sodium Trimethoxyborohydride with Boron Fluoride Etherate.—The following two experiments, typical of a number carried out, illustrate the beneficial effect brought about on the yield of diborane by the use of an excess of boron trifluoride etherate in the reaction under discussion. Details of manipulation are omitted since the procedure for preparing diborane by the reaction is fully described later.

In the first of these experiments, 0.55 mole (69.9 g.) of sodium trimethoxyborohydride, suspended in 52 ml. of ether, was treated with 0.74 mole (105 g.) of boron fluoride etherate. The ratio, NaH:BF_3 thus was 1:1.42, or almost the theoretical 1:1.33. The reaction vessel was immersed in a 60° bath and the mixture was stirred for 2.5 hours. At the end of this time 1075 ml. of diborane had been generated. Continuation of the reaction under the same conditions for 2.5 hours longer brought the total diborane up to 1111 ml. (0.05 mole), a yield of only 54%.

In the second experiment the amounts of the trimethoxyborohydride and of the etherate were, respectively, 163.5 and 531.3 g., a molar ratio of 1:2.73 instead of the theoretical 1:1.33. No ether was added and the mixture, though maintained at 60° as in the preceding experiment, was not stirred. Nevertheless, in 4 hours, 4.48 l. of diborane was collected, a yield of 94%.

The Reaction of Sodium Trimethoxyborohydride and Boron Fluoride Methyl Etherate.—The trimethoxyborohydride was treated with the addition compounds of boron fluoride with *n*-butyl ether, with dioxane and with methyl ether. Yields of diborane of 60–80% were obtained. The preparation involving the methyl etherate is of particular interest because the dimethyl ether formed in the reaction is a gas; it thus acts as its own inert atmosphere for the reaction and carries the diborane out of the reaction flask. The reaction may have some advantage in experiments in which the diborane is not isolated but is passed directly into a reaction mixture.

Sodium trimethoxyborohydride, 0.104 mole, was treated with 0.161 mole of boron fluoride methyl etherate (16% excess which is a larger excess than was used in the first experiment with the ethyl etherate). The reaction was run for 45 minutes at 25–30° and for 30 minutes at 60°. The diborane was not isolated, but was passed through a weighed tube filled with sodium trimethoxyborohydride which absorbs the gas.[14] The yield was 80%.

Preparation of Diborane.—Although diborane, prepared by the reactions described herein, is not nearly so likely to inflame or to detonate spontaneously on contact with air as are the samples prepared by the older methods, it is, nevertheless, a substance which must be handled with due regard for the hazards involved. For this reason, a procedure used by us is described in considerable detail.

The type of apparatus schematically represented in Fig. 1 was found convenient both for the investigation of reactions involving the use of boron fluoride etherate to generate diborane, as well as for the preparation of the latter in quantities up to about 20 liters. The apparatus may be employed whether lithium or sodium hydrides, or lithium or sodium borohydrides, or sodium trimethoxyborohydride is to be used with the etherate. Because the description is a general one covering all of these reagents, specific quantities are not stated, except to point out that a considerable excess of the etherate (up to 100%) was used beyond that required for the conversion of the fluoride into borofluoride. It should also be mentioned that the etherate should be pure, *i.e.*, should be colorless.

The apparatus consisted of a 2-liter reaction flask equipped with a sturdy gland stirrer, a dropping funnel, an inlet for nitrogen, an outlet from the reaction flask through a cold finger condenser to a series of traps, and several open end mercury manometers for safety devices. The apparatus was connected through a vacuum line to a mercury condensation pump backed by a rotary oil pump. All stopcocks and ground joints were lubricated with Apiezon N and in most cases mercury seals were used.[15]

Before use, the system was flushed thoroughly with dry, purified nitrogen through stopcock S1 and flamed to remove traces of moisture. The alkali metal hydride or the desired derivative was then placed in the reaction flask, RF, and the entire apparatus was again flushed with nitrogen. At the same time the cold finger, C, was filled with a −80° mixture and was kept filled throughout the process. Trap T1 was cooled with a −80° bath and traps T2 and T3 with −196° baths. The nitrogen inlet S1 was closed and the stopcocks were so adjusted that non-condensable gases passed through the reaction flask through the traps and out through bubbler B4. The etherate was added at a rate slow enough to prevent undue rapidity of reaction. Stirring was continuous throughout the addition of the etherate and during the subsequent heating of the reaction flask to about, but not above, 60°. When no more gas was generated, nitrogen was admitted to sweep any traces of diborane from the flask into the traps. At this point, Trap T1 contained a small amount of ether and a trace of diborane; T2 contained the greater and T3 a smaller amount of diborane. Stopcock S2 was then closed to allow nitrogen to flow out through bubbler B1. Stopcock S3 was then also closed and the −80° bath around T1 was replaced by one at −196°. This trap was later used to collect residues from the purification process for ultimate disposal.

---

[14] H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, This Journal, **75**, 199 (1953).

[15] When reactions involving relatively small amounts of gases were to be studied quantitatively, mercury sealed joints were used and were lubricated with graphite to avoid loss of gas or generation of volatile impurities by contact with stopcock greases.

The rest of the apparatus was then evacuated to *ca.* 10^{-5} mm. through S7. Stopcock S6 was closed and all material in trap T3 was condensed in T2. For purification of the contents of what was then in T2, these were passed through trap T3 kept at −100° for this purpose and into T4 at −196°. The latter then contained diborane of fairly high purity as shown by the fact that its vapor tension at −112° usually was above 220 mm. For further purification, the residues in T3 may be distilled back into T1 and the diborane may be transferred from T4 back to T2. A second fractionation from T2 back through T3 and T4 may then be undertaken but this time T3 should be maintained at −140° rather than at −100°. The purified diborane may then be transferred to storage bulbs on the vacuum line or used directly for reaction studies.

Residues from the fractionation procedure were all distilled into T1 and the stopcocks adjusted to pass nitrogen through the reaction flask, the cold finger, T1 and out through bubbler B2. Methanol was then added slowly through the dropping funnel to destroy any hydrides remaining in the flask. The stopcocks were readjusted to allow nitrogen to pass out through B1 and T1 was allowed to warm to room temperature. The nitrogen stream carried with it sufficient methanol into T1 to render harmless any residues there remaining. After standing at room temperature for a short time, the reaction flask and T1 could be removed safely for cleaning.[16]

Acknowledgment.—The assistance of H. R. Hoekstra, A. E. Finholt, D. M. Ritter, L. R. Rapp and I. Sheft with individual experiments and preparations reported in this paper is gratefully acknowledged.

---

[16] This description follows, with a few modifications, one given in Atomic Energy Commission Document MDDC-1338, by H. I. Schlesinger, George W. Schaeffer and Glen D. Barbaras. The document entitled "The Deposition of Pure Boron, Part I" may be obtained by inquiry to the Technical Information Division, Atomic Energy Commission, P. O. Box E, Oak Ridge, Tenn.

CHICAGO, ILL.

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

Reactions of Diborane with Alkali Metal Hydrides and Their Addition Compounds. New Syntheses of Borohydrides. Sodium and Potassium Borohydrides[1]

BY H. I. SCHLESINGER, HERBERT C. BROWN, HENRY R. HOEKSTRA AND LOUIS R. RAPP

RECEIVED MARCH 17, 1952

In the presence of diethyl ether, lithium hydride reacts readily with diborane to form lithium borohydride: $LiH + {}^1/_2B_2H_6 \rightarrow LiBH_4$. The latter is also formed by reaction of diborane with either lithium ethoxide or lithium tetramethoxyborohydride: $2B_2H_6 + 3LiOC_2H_5 \rightarrow 3LiBH_4 + B(OC_2H_5)_3$, and $2B_2H_6 + 3LiB(OCH_3)_4 \rightarrow 3LiBH_4 + 4B(OCH_3)_3$. Lithium borohydride is readily purified by recrystallization from ethyl ether; the etherate, $LiBH_4 \cdot (C_2H_5)_2O$, is obtained, but the ether is removed easily. Attempts to bring about a direct reaction between sodium hydride and diborane have not succeeded. However, diborane is rapidly and quantitatively absorbed by sodium trimethoxyborohydride in accordance with the equation: ${}^1/_2B_2H_6 + NaBH(OCH_3)_3 \rightarrow NaBH_4 + B(OCH_3)_3$. Dimethoxyborine reacts in similar fashion with the trimethoxyborohydride. The new product, sodium borohydride, may also be prepared by the reaction of diborane with either sodium methoxide or sodium tetramethoxyborohydride. Potassium borohydride, also prepared for the first time, is obtained by the interaction of potassium tetramethoxyborohydride with diborane. These new methods, together with others described in other papers of this series, make the alkali metal borohydrides readily available. Sodium borohydride is a white crystalline solid of remarkable stability. It has been heated in air to 300° and in vacuum to 400° without apparent change. It dissolves in cold water without extensive reaction. From its aqueous solutions it may be recovered as the dihydrate. At 100° it reacts rapidly with water to liberate 4 moles of hydrogen, a reaction which also occurs rapidly at room temperature in the presence of acids or of certain catalysts. Boron fluoride liberates diborane quantitatively. The borohydride is a strong reducing agent both for organic and inorganic compounds. Potassium borohydride has properties similar to those of the sodium salt, but has not yet been investigated as thoroughly.

The borohydrides of aluminum,[2a] beryllium[2b] and lithium,[2c] have hitherto been prepared only by the action of diborane on the respective metal alkyls[3,4]

$$Al(CH_3)_3 + 2B_2H_6 \longrightarrow Al(BH_4)_3 + (CH_3)_3B$$
$$3Be(CH_3)_2 + 4B_2H_6 \longrightarrow 3Be(BH_4)_2 + 2(CH_3)_3B$$
$$3LiC_2H_5 + 2B_2H_6 \longrightarrow 3LiBH_4 + (C_2H_5)_3B$$

This type of reaction is unsatisfactory when borohydrides in even moderate amounts are desired. The metal alkyls, particularly the less volatile ones of the alkali metals, are themselves difficult to prepare and handle on any large scale. Also the reaction is slow and requires repeated treatment with a large excess of diborane to remove completely all alkyl groups from the reaction product.

As a result of an investigation of the reactions of diborane with alkali metal hydrides and with their derivatives, a more satisfactory synthesis of lithium borohydride and methods of preparing the hitherto unknown sodium and potassium borohydrides were discovered. It thus became possible to study the properties of alkali metal borohydrides in more detail than could previously be done.

The knowledge thus gained enabled us later to develop methods for the preparation of borohydrides which have the advantage of not requiring the use of diborane, as is described in subsequent papers of this series.[5]

Results and Discussion

In the absence of solvents no reaction between diborane and lithium hydride was observed, even at elevated temperatures and pressures. The solu-

---

[1] New Developments in the Chemistry of Diborane and the Borohydrides. V. For a theoretical discussion of the reactions described herein, and for an explanation of the nomenclature employed, see paper I of this series, THIS JOURNAL, **75**, 186 (1953). For the experimental work on the lithium and sodium compounds discussed herein, H. R. Hoekstra is largely responsible. The discussion of the potassium compounds is based on the experiments of L. R. Rapp.

[2] (a) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *ibid.*, **62**, 3421 (1940); (b) A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940); (c) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

[3] The formation of lithium borohydride in the reaction of aluminum borohydride with ethyllithium in benzene solution has been observed (ref. 2c), but is also not feasible for larger scale preparations.

[4] The equations are idealized; the alkyl groups are actually recovered as mixtures of the boron alkyl and alkyl derivatives of diborane.

[5] No. VI, H. I. Schlesinger, H. C. Brown and A. E. Finholt, THIS JOURNAL, **75**, 205 (1953), and No. VII, H. I. Schlesinger, H. C. Brown and E. K. Hyde, *ibid.*, **75**, 209 (1953).