

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

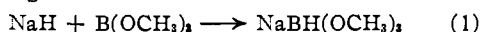
Addition Compounds of Alkali Metal Hydrides. Sodium Trimethoxyborohydride and Related Compounds<sup>1</sup>BY HERBERT C. BROWN,<sup>2</sup> H. I. SCHLESINGER, IRVING SHEFT AND D. M. RITTER

RECEIVED MARCH 17, 1952

Sodium hydride reacts readily at moderate temperatures with borate esters such as methyl, ethyl and *n*-butyl borate to form acid-base addition complexes. These new substances, Na[BH(OR)<sub>3</sub>], are stable white solids with strong reducing properties. The reactions of the sodium trimethoxyborohydride with water, alcohol, hydrogen chloride, boron fluoride and carbon dioxide are described. With boron fluoride etherate, diborane is obtained by a convenient reaction. Qualitative observations on the reducing properties of the compound in aqueous solution are noted. The corresponding reaction of methyl borate with lithium hydride does not proceed as smoothly because the addition compound appears to undergo decomposition and disproportionation fairly readily. Addition of other compounds of trivalent boron, *e.g.*, alkyl borons, to alkali metal hydrides is described.

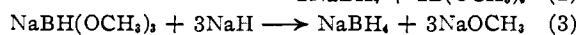
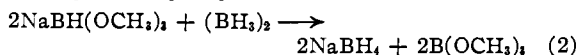
As pointed out in the introductory paper of this series,<sup>1</sup> the alkali metal hydrides as strong bases should be capable of adding to simple boron compounds such as the trialkyls, the trihalides and the alkyl borates. Several examples of such reactions are described in the present paper; the behavior of borate esters is taken up first and in the greatest detail because of their relationship to other aspects of this investigation.

Although other reactions of this type were examined the reaction between methyl borate and sodium hydride was most thoroughly studied. The possible significance of the fact that the reaction

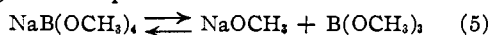


is accompanied by a large increase in the bulk of the solid and requires a relatively long time for its completion has already been discussed.<sup>1</sup> Details of the preparation are described in the Experimental part.

The particular significance of the compound to the larger investigation reported in this series of articles lies in its usefulness in the preparation of diborane and in its ready transformation to sodium borohydride by any one of the several reactions<sup>3</sup>



To drive reaction (4) to completion the sodium tetramethoxyborohydride must be decomposed according to the equation



and the methyl borate must be continuously removed by evacuation of the reaction vessel.

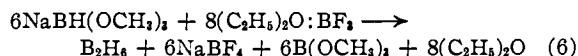
The preparation of diborane from the trimethoxyborohydride occurs according to the equation<sup>4</sup>

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

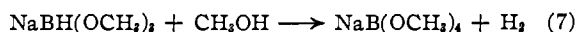
(2) Department of Chemistry, Purdue University.

(3) (a) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *THIS JOURNAL*, **75**, 199 (1953); (b) H. I. Schlesinger, H. C. Brown and A. E. Finholt, *ibid.*, **75**, 205 (1953); (c) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *ibid.*, **75**, 215 (1953). As explained in paper I, the formula (BH<sub>3</sub>)<sub>2</sub> is used for diborane.

(4) The several newly developed methods for the preparation of diborane are compared and evaluated in the next paper (No. IV) of this series: H. I. Schlesinger, H. C. Brown, J. R. Gilbreath and J. J. Katz, *ibid.*, **75**, 195 (1953).



Sodium trimethoxyborohydride has other properties of theoretical as well as of practical interest. Thus in cold water the salt dissolves with a short initial burst of hydrogen. Additional hydrogen is generated only slowly unless the solution is acidified. In hot water complete hydrolysis occurs rapidly with evolution of one mole of hydrogen per mole of the salt. With methanol, on the other hand, the compound reacts rapidly and completely even in the cold and without acidification

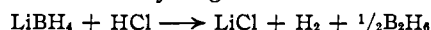


A possible explanation for these observations is found in the fact that the rate of hydrogen evolution by hydrolysis of borohydrides is markedly affected by the hydrogen ion concentration.<sup>5,6</sup> As the reaction proceeds the aqueous solution becomes strongly basic, since the product of the reaction, sodium borate, is extensively hydrolyzed. The increasing basicity of the solution rapidly decreases the reaction rate. In contrast thereto the product of the reaction with methanol, sodium tetramethoxyborohydride, is neutral in the alcoholic medium and does not appreciably alter the acidity of the mixture. The salt, therefore, reacts at a fairly steady rate with the alcohol to liberate hydrogen.

When hydrogen chloride is passed through sodium trimethoxyborohydride and the volatile products are immediately trapped at -80°, very little hydrogen is generated. The trapped material, however, when warmed to room temperature, does liberate hydrogen. No diborane is generated. These observations are in accord with the equation



This behavior is in marked contrast to that of borohydrides which liberate hydrogen immediately by treatment with hydrogen chloride.



The difference in the two reactions may be interpreted as involving the decomposition of the ions, BH<sub>4</sub><sup>-</sup> and BH(OCH<sub>3</sub>)<sub>2</sub><sup>-</sup>. In the simple borohydride the attack of the proton can only be on one of the four hydrogen atoms attached to boron. However, in the case of the trimethoxyborohydride,

(5) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *ibid.*, **75**, 215 (1953).

(6) M. Kilpatrick and C. D. McKinney, Jr., *ibid.*, **72**, 5474 (1950).



in portions of 200–300 g.<sup>16</sup> After all the methyl borate had been added, a drying tube was attached to the condenser and the flask was slowly warmed to reflux temperature of the methyl borate (68°) and there maintained for 5–6 hours. The solid gradually swelled to about 5 times its original volume and its color changed from gray to pure white. When no further volume increase was apparent, heating was discontinued, the reflux condenser was replaced by a downward one, and the excess of methyl borate was distilled away, the last traces under reduced pressure. The yield (2560 g.) was quantitative.

Owing to the variability in the behavior of commercial sodium hydride, it is recommended that each sample be tested in a small preparation to ascertain whether modifications in the procedure should be made to avoid unduly rapid reactions.

**Physical Properties and Analysis of Sodium Trimethoxyborohydride.**—The product, obtained as just described, was pure enough for most purposes. If desirable, it may be recrystallized from liquid ammonia or from isopropylamine. It was a fluffy white solid, stable in dry air and only slowly attacked by air of average humidity. Its decomposition at its melting point (230°) has already been discussed (equations (4) and (5) and reference 3b). The following approximate solubilities (g./100 g. solvent) were determined; pyridine, 0.4 (24°), 3.0 (75°); morpholine, 0.3 (24°), 2.3 (75°); dioxane, 1.6 (25°), 4.5 (75°); isopropylamine, 9.0 (25°); liquid ammonia, 5.6 (–33°).

The compound was analyzed for base and for boron by the usual titration of an aqueous solution, first by acid to the methyl red end-point and after addition of mannitol, to the phenolphthalein end-point by carbonate-free base. Active hydrogen was determined by hydrolysis of a separate sample.

*Anal.* Calcd. for 0.567-g. sample: Na, 0.102 g.; B, 0.479 g.; H<sub>2</sub> (for 1.930-g. sample), 338 ml. Found: Na, 0.101 g.; B, 0.482 g.; H<sub>2</sub>, 336 ml.

**Reaction with Hydrogen Chloride.**—The following results are typical of a number of experiments. A 0.420-g. sample of sodium trimethoxyborohydride (3.28 mmoles) was placed in a weighed U-tube, both ends of which contained glass wool plugs to contain the fine powder. One end of the tube was connected to a source of hydrogen chloride and the other end to a second U-tube maintained at –80°. The system was evacuated, the pump shut off and one equivalent of hydrogen chloride was slowly passed through the powder. Heat was evolved, the solid shrank markedly in volume and liquid collected in the –80° trap. At this stage of the experiment 20.6 ml. of hydrogen had been generated.

Removal of the –80° bath was followed within a few minutes by evolution of 28.3 ml. of additional hydrogen. The residual solid in the reaction chamber when hydrolyzed yielded 23.4 ml. of hydrogen, bringing the total collected (20.6 + 28.3 + 23.4) to 72.3 ml. or 3.22 mmoles. Since this quantity corresponds to 98% of that present in the original sample of the trimethoxyborohydride, it is evident that no diborane was formed.

The 23.4 ml. (1.04 mmoles) of hydrogen,<sup>17</sup> resulting from hydrolysis of the residue, indicates that only 68.1% of the original 3.28 mmoles of the trimethoxyborohydride had reacted with hydrogen chloride. Slower passage of the latter led to greater conversion, but also produced more hydrogen in the initial stage of the procedure and decreased the amount obtainable when the –80° condensate was warmed. More rapid passage of the hydrogen chloride had the opposite effects.

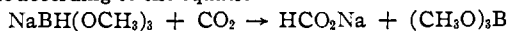
The differences just described were apparently due to the differences in the length of time elapsing between the generation of the volatile products of the reaction and their condensation at –80°. At that temperature hydrogen evolution did not occur at an appreciable rate, but set in again when the temperature was raised. These observations are in accord with the interpretation that the initial volatile products of the reaction were methanol and dimethoxyborine, which two substances did not react with each other at –80°, but produced hydrogen and methyl borate when the temperature was raised.<sup>18</sup>

(16) For smaller preparations, e.g., one mole of the compound, a 100% excess of methyl borate was found convenient.

(17) All volumes of gases and vapors are referred to standard temperature and pressure.

(18) A. B. Burg and H. I. Schlesinger, *THIS JOURNAL*, **55**, 4020 (1933).

**Reaction with Carbon Dioxide.**—In apparatus similar to that described above, carbon dioxide was slowly admitted to a sample of 0.457 g. (3.57 mmoles) of sodium trimethoxyborohydride. Heat was generated and the solid in the tube shrank in volume. Methyl borate collected in the –80° trap. Hydrolysis of the residue liberated 32 ml. of hydrogen showing that 60% (2.14 mmoles) of the trimethoxyborohydride had been utilized. The solution contained 2.23 mmoles of formate ion,<sup>19</sup> which is 96% of the amount to be expected from the reaction of 2.14 mmoles of the borohydride according to the equation



**Reaction with Boron Fluoride.**—Sodium trimethoxyborohydride, 0.358 g. (2.8 mmoles) was placed in a reaction tube (connected to a manometer and attached to the high vacuum apparatus) into which 65.8 ml. (2.9 mmoles) of boron fluoride was condensed by liquid nitrogen. When the mixture was permitted to warm to room temperature the pressure first rose to a maximum value as the boron fluoride vaporized, and then began to drop rapidly as it was absorbed. As soon as no further changes in pressure were observed, the volatile materials were removed and examined. No boron fluoride was found. A small more volatile fraction was isolated and identified as dimethoxyborine.<sup>18</sup> The bulk of the product was identified as methyl borate from its vapor pressure and melting point. The main reaction obviously was a simple displacement of methyl borate from the salt by boron fluoride.

**Reaction with Methanol.**—A sample of 3.56 g. (27.8 mmoles) of sodium trimethoxyborohydride was placed in a flask connected to a condenser and to a gas collection tube. An excess of methanol (20 ml. dried and distilled over sodium hydride) was admitted through the condenser. The heat evolved caused the methyl alcohol to reflux and in five minutes 620 ml. of hydrogen or 95% of that expected from equation (7) was evolved.

**Reaction of Sodium Hydride with Other Alkyl Borates.**—Sodium hydride reacted with ethyl and with butyl borates as it does with methyl borate, for which reason the reactions are not described in detail. It should be mentioned, however, that in the case of butyl borate it was found desirable to dilute the ester with dioxane. Even when this was done, a reaction vigorous enough to flood the condenser occurred after a few minutes of heating the reaction mixture to 100°. But after the initial reaction had been allowed to subside, the mixture could be warmed till it refluxed gently, under which conditions the desired reaction occurred.

**The Reaction of Lithium Hydride and Methyl Borate.**—A mixture of 0.162 g. of lithium hydride of ca. 75% purity (approximately 15 mmoles) with 3.755 g. (33 mmoles) of methyl borate was heated to 100° in a sealed tube. A vigorous reaction occurred and a gelatinous precipitate formed. The volatile products consisted of a considerable amount of hydrogen together with 344 ml. (15.3 mmoles) of methyl borate (vapor) contaminated with a trace of more volatile material, as evidenced by the fact that its vapor tension at –80° was 2 mm. instead of zero. Since approximately 17.3 mmoles of the ester had reacted with 15 mmoles of the hydride, the main reaction was evidently the formation of the 1:1 addition product, lithium trimethoxyborohydride. But that the reaction did not proceed uniquely in this direction was shown by the presence of hydrogen in the volatile reaction products.

The lithium salt thus obtained could not be readily purified. The initial product in reactions like the one described contained a small amount of material soluble in ether. After the material had been heated to 100° for 24 hours, about 20% of it could be extracted by ether showing that at least partial decomposition had occurred.<sup>20</sup> The decomposition could not be inhibited by the presence of excess methyl borate. At 200°, a temperature at which sodium trimethoxyborohydride disproportionates to the borohydride (equations (4) and (5)), the lithium compound produced methyl borate and dimethoxyborine by what must have been a relatively complex reaction.

**Reactions of Sodium and of Lithium Hydrides with Triethyl and Trimethylboron.**—In a vigorous reaction which

(19) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 560.

(20) An analysis of the ether-soluble material indicated that it had the composition  $\text{LiBH}_2(\text{OCH}_3)_2$ . It was, therefore, probably a product of disproportionation.

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  $\text{NaBH}(\text{C}_2\text{H}_5)_3$ . 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  $40^\circ$  did not lead to an observable change within  $\frac{1}{2}$  hour. Addition of 1.91 ml. of liquid diethyl ether followed by heating of the mixture to  $100^\circ$  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  $80^\circ$ . When the melt was cooled to room temperature, solid material, presumably 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.

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## Reaction of the Boron Halides with the Alkali Metal Hydrides and with Their Addition Compounds; A New Synthesis of Diborane<sup>1</sup>

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

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Gaseous boron fluoride and lithium hydride react only slightly at temperatures up to  $180^\circ$  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  $100^\circ$  to form diborane in accordance with the equation  $8(\text{C}_2\text{H}_5)_2\text{O}:\text{BF}_3 + 6\text{LiH} \rightarrow \text{B}_2\text{H}_6 + 6\text{LiBF}_4 + 8(\text{C}_2\text{H}_5)_2\text{O}$ . 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  $8(\text{C}_2\text{H}_5)_2\text{O}:\text{BF}_3 + 6\text{NaBH}(\text{OCH}_3)_2 \rightarrow \text{B}_2\text{H}_6 + 6\text{NaBF}_4 + 8(\text{C}_2\text{H}_5)_2\text{O} + 6\text{B}(\text{OCH}_3)_3$ . 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<sup>2</sup> or by the passage of a mixture of hydrogen and boron halide through an arc discharge.<sup>3</sup> 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.

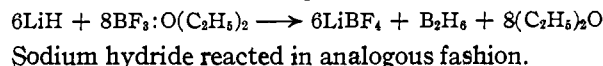
It has become apparent in recent years that diborane possesses possibilities as a useful chemical reagent and intermediate. Thus it acts on aldehydes and ketones at low temperatures to reduce them quantitatively to the corresponding alcohols.<sup>4</sup> It reacts with metal alkyls to form the corresponding borohydrides.<sup>5</sup> It has a large heat of combustion per gram (*ca.* 20 kcal.)<sup>6</sup> 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  $180^\circ$  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.<sup>7</sup>

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



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  $200^\circ$  but did so when treated with additional boron trifluoride etherate.

As suggested in the introductory paper of this

(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.

(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).