

methoxide in the solvents most favorable for the extraction of sodium borohydride. This fact explains why, in runs in which considerable amounts of sodium trimethoxyborohydride were found, not only the yield but also the purity was low.

#### D. Preparation of Lithium Borohydride from Lithium Hydride and Methyl Borate

The reaction between lithium hydride and methyl borate did not give as satisfactory results as the corresponding reaction with sodium hydride, although the same procedure was followed. Thus, the maximum yield was 70% as contrasted with 90-94%. A contributing factor in the low yields was caking of the reaction mixture so pronounced as to make stirring difficult, but not impossible. Variations in the experimental conditions were tried, such as preheating of the hydride and substitution of ethyl for methyl borate. These, and other factors which were helpful in eliminating the same difficulty in the sodium borohydride preparation, produced no effect in this case.

Removal of lithium borohydride from the crude mixture also presented unexpected difficulties. Since lithium borohydride is readily soluble in both ether and isopropylamine, it should have been easily extracted by these solvents. Nevertheless this did not prove to be the case. For example, in a typical experiment the amount of ether used

was twice that required to dissolve all of the lithium borohydride ultimately found to be present in the product. Yet a single extraction removed less than one-third of the borohydride, although repeated treatment with ether ultimately extracted most of the borohydride. Rapid stirring, use of still larger quantities of ether and raising the temperature to the boiling point of the latter, made little improvement in yield. On the other hand, extending the time of contact seemed effective. Thus, stirring the mixture of ether and the crude reaction product for six to eight hours before filtration, although it did not effect complete extraction, approximately doubled the quantity recovered by a single extraction when the contact time was only two hours. Although the yields were low and extraction difficult, purity of the final product was about 95% in all cases. Extraction by isopropylamine gave similar results. It is possible that lithium borohydride and lithium methoxide form mixed crystals and that both the extraction difficulties and the caking tendencies arise from this cause.

**Acknowledgment.**—The assistance of H. R. Hoekstra, J. R. Gilbreath and E. K. Hyde with individual experiments and preparations reported in this paper is gratefully acknowledged.

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

## The Preparation of Other Borohydrides by Metathetical Reactions Utilizing the Alkali Metal Borohydrides<sup>1</sup>

By H. I. SCHLESINGER, HERBERT C. BROWN AND EARL K. HYDE

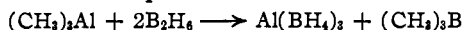
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Aluminum borohydride is prepared in excellent yield by the reaction of either sodium or lithium borohydride with aluminum chloride or bromide.  $AlX_3 + 3MBH_4 \rightarrow Al(BH_4)_3 \uparrow + 3MX$ . The aluminum borohydride, as the most volatile constituent of the reaction mixture is readily distilled away from the less volatile products and reactants. Beryllium borohydride is prepared by the analogous reaction of beryllium halides with lithium borohydride. Lithium borohydride may be prepared by metathesis between sodium borohydride and lithium chloride in isopropylamine solution.  $NaBH_4 + LiCl \rightarrow NaCl \downarrow + LiBH_4$ .

Aluminum borohydride, first prepared by the reaction between trimethylaluminum and diborane,<sup>2</sup> is required for the preparation of the borohydrides of heavy metals, such as uranium,<sup>3a</sup> thorium, hafnium, zirconium and titanium.<sup>3b</sup> It is of interest because of its extremely rapid reaction with water and it may be used in place of the alkali metal borohydrides when a volatile, liquid source of borohydride groups is desired, for example, in the study of organic reactions.<sup>4</sup>

The original preparative method was improved by the device of adding the diborane to the trimethylaluminum in small portions and removing all material volatile at  $-95^\circ$  after each addition. By this procedure the methyl groups are removed as trimethylboron, rather than as methylated diboranes, and a product almost free from methyl groups could be obtained. It was possible to attain yields as high as 80% of the aluminum

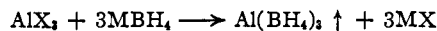
alkyl and 70% of the diborane, calculated according to the idealized equation



In spite of these improvements, the procedure remained a tedious one and required skillful manipulation. The discovery of methods by which alkali metal borohydrides could be conveniently prepared in any desired quantity<sup>5</sup> led to a satisfactory solution of the aluminum borohydride problem.

### Results and Discussion

The method developed consists of the metathesis between aluminum halides and alkali metal borohydrides, as represented by the equation



The reaction between lithium borohydride and aluminum chloride begins as soon as the reactants are mixed and continues at room temperature provided the aluminum borohydride is continuously removed by pumping. Completion of the reaction is accelerated by gradually raising the temperature to  $100^\circ$ . Purification of the product is readily effected by fractional distillation. Yields of 95% of pure aluminum borohydride have been

(1) New Developments in the Chemistry of Diborane and of the Borohydrides. VII. For an explanation of the nomenclature employed herein, see paper I of this series, *THIS JOURNAL*, **75**, 186 (1953).

(2) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *ibid.*, **62**, 3421 (1940).

(3) (a) H. I. Schlesinger and H. C. Brown, *ibid.*, **75**, 219 (1953); (b) H. Hoekstra and J. J. Katz, *ibid.*, **71**, 2488 (1949).

(4) Reactions of Aluminum Borohydride with Certain Organic Compounds, R. A. Lad, University of Chicago Thesis, 1946. It is anticipated that this article will soon be published in more accessible form.

(5) (a) H. I. Schlesinger, H. C. Brown and A. E. Finholt, *THIS JOURNAL*, **75**, 205 (1953); (b) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *ibid.*, **75**, 199 (1953).

obtained. Beryllium borohydride has been prepared in similar fashion.

Sodium borohydride reacts far more slowly at room temperature, even with continuous evacuation. Although the reaction is considerably faster at 100°, the mixture soon sinters to hard lumps and reaction virtually ceases. At about 110–130° melting occurs and production of aluminum borohydride continues satisfactorily. By operating from the start in the latter temperature range and by using a large excess of aluminum chloride, the major part of the reaction may be made to occur in 15 minutes and yields of 80% may be obtained in from 30–60 minutes. The reaction of potassium borohydride is even more sluggish than that of the sodium salt.

The fact that these reactions appear to cease, unless the aluminum borohydride is removed, suggests their reversibility. To test this possibility the pressures attained over mixtures of aluminum chloride and each of the three alkali metal borohydrides were observed. At 50° the pressure was 27 mm. in the case of the lithium salt, 2 mm. for the sodium salt and immeasurable for the potassium compound. Evidently the reverse reaction is favored in the last case and was tested by allowing aluminum borohydride to remain in contact with potassium chloride for 40 hours. The borohydride was absorbed to an extent which indicated that the reaction,  $\text{Al}(\text{BH}_4)_3 + 3 \text{KCl} \rightarrow 3 \text{KBH}_4 + \text{AlCl}_3$ , had proceeded about 59% to completion.

Because of the lower temperatures it requires and because its more favorable equilibrium permits a much smaller excess of aluminum chloride (the sublimation of which causes mechanical difficulties), the lithium borohydride is the most satisfactory of the three alkali metal borohydrides for small scale preparation of aluminum borohydride. Certain disadvantages of the lithium salt must, however, not be overlooked, especially when larger amounts are involved. Its cost is sure to be higher than that of the sodium salt and much greater care must be exercised to avoid explosions which may occur, owing to the immediate generation of aluminum borohydride when lithium borohydride and aluminum chloride are mixed.

Substitution of aluminum bromide for the corresponding chloride in the reaction with sodium borohydride produces slightly better results below 100°. At higher temperatures, however, the bromide is the less satisfactory. Comparison of the relative vapor tensions of the two halides suggests a possible explanation for the phenomenon. The bromide is more volatile than the chloride below 127°, the reverse is true at higher temperatures. If the reaction occurs between the vapor of the aluminum halide and the solid borohydride, it will be the slower, and will come to apparent cessation the sooner, the lower the vapor tension of the halide.

The reactions under discussion undoubtedly occur as stepwise replacements of halide by borohydride. In all of the reactions small quantities of slightly volatile materials are observed which may be mixed halide borohydrides, since they contain

active hydrogen but are much less volatile than aluminum borohydride. Attention is called to the fact that in the preparation of uranium(IV) borohydride by the action of aluminum borohydride on uranium(IV) fluoride, the non-volatile residue appears to be the compound  $\text{AlF}_2(\text{BH}_4)$ , as is described in paper X of this series.<sup>3a</sup>

Because of the ease with which sodium borohydride is prepared,<sup>5a</sup> it is of interest that the lithium salt may be prepared from the sodium salt by metathesis in solution. Addition of a small excess of lithium chloride to solutions of sodium borohydride in methylamine, ethylamine or isopropylamine causes the precipitation of sodium chloride. Evaporation of the filtered solution followed by a single extraction of the residue with ethyl ether, yields about 90–95% of lithium borohydride of 97–98% purity. Although the three solvents appear equally effective, isopropylamine, because of its higher boiling point, proved most convenient.

During the course of this work it was observed that aluminum borohydride at room temperature undergoes a decomposition by which hydrogen is evolved. The rate of decomposition, small at all times, gradually decreases until it becomes inappreciable. This retardation seems to be due to the accumulation of a glassy non-volatile decomposition product which is very soluble in the liquid borohydride and which acts as an inhibitor of the decomposition. Although neither the nature of the non-volatile material nor the mode of its action have been elucidated, the phenomenon has proved useful in making safer the storage of aluminum borohydride over longer periods of time, as is pointed out in the Experimental part.

#### Experimental Part

**Materials.**—Lithium borohydride and sodium borohydride were prepared by the methods previously described<sup>5</sup> and were recrystallized from ether and from isopropylamine, respectively. Commercially available reagent grade aluminum chloride was used. The material must not be partially hydrated, since otherwise the yield is decreased, and considerable quantities of hydrogen and diborane are formed. Aluminum bromide was prepared by the reaction of aluminum and bromine and sublimation of the product. Beryllium chloride and bromide were prepared by the action of the halogens on the metal; the products were sublimed.

**Hazards in Handling and Storage of Aluminum Borohydride. Stabilization of the Latter.**—Because aluminum borohydride is a hazardous material, its preparation is described in detail in the next section. One of the sources of the hazards is that the vapor of the compound detonates spontaneously and violently on contact with air containing only traces of moisture.<sup>6</sup>

As already pointed out in the discussion, a second hazard results from the decomposition of the borohydride to evolve hydrogen at room temperature. Even though the hydrogen evolution is slow, high pressures may develop in closed containers in the course of time. Because the reaction ultimately becomes so slow as to be practically negligible, the difficulty may be avoided by using containers the volumes of which are much greater than the volume of the stored liquid, or by providing the container with means by which the accumulated hydrogen may occasionally be removed without exposing the borohydride vapor to air.

Although these methods of avoiding the storage hazard are adequate when only small quantities are involved, they are not satisfactory for larger amounts. A different approach resulted from a study of the previously mentioned retardation in the rate of hydrogen evolution which is illustrated by the following example. A fresh sample of the

(6) The vapor seems not to react with extremely dry air. Furthermore, it is only the vapor which detonates in ordinary air.

liquid aluminum borohydride lost hydrogen at such a rate that in about 18 days at room temperature the hydrogen pressure in the storage vessel had risen from 0 to 300 mm. and at the end of 120 days to 540 mm. The accumulated hydrogen was removed and decomposition was allowed to continue. Now, in an additional 60 days, the hydrogen pressure rose to only about 20 mm. and further change was so slow that the experiment was discontinued.

The cause of the retardation appears to lie in the formation of a decomposition product which, in some as yet unknown way, acts as an inhibitor. When aluminum borohydride is evaporated after it has stood so long at room temperature that its rate of decomposition is very small, a glassy, non-volatile residue is left. This is so soluble in the borohydride that the latter cannot be completely removed by evacuation at room temperature. At somewhat higher temperatures, the residue undergoes a significant change, as made evident by the fact that it becomes insoluble and loses its inhibiting effect.<sup>7</sup> For these reasons it has been impossible to obtain a sample of the residue sufficiently well defined to warrant reporting analytical results. That the material contains aluminum, boron and active hydrogen has been established; it may be a solid solution of several substances in one another.

It will suffice to record only one of many experiments carried out to demonstrate that this residue actually acts as an inhibitor, rather than as a material, which, by being adsorbed on the vessel's glass walls, poisons a catalytic effect of the latter. A small amount of the residue, obtained by rapid evaporation at room temperature of an old sample of aluminum borohydride, was redissolved in a small amount of a freshly distilled sample of the latter and was rapidly transferred out of contact with air to a clean new container. Additional freshly distilled aluminum borohydride was added. Comparison of the rate of hydrogen evolution from this treated portion with an untreated portion of the sample of aluminum borohydride clearly demonstrated the same kind of stabilization as that described as resulting from long standing.

The inhibiting residue is, however, like aluminum borohydride itself, likely to detonate spontaneously in air and, being non-volatile, is even more difficult to handle. Its addition to aluminum borohydride is, therefore, troublesome. On the other hand, its rate of formation from the latter is accelerated by raising the temperature. Consequently, aluminum borohydride may be stabilized by heating it for 4 days at 40° in a closed vessel. Higher temperatures may not be used because they inactivate the inhibitor too rapidly; longer heating periods do not improve the results. These may be illustrated by recording the fact that a sample, heated as described, required 90 days to produce the same amount of hydrogen an untreated sample produced in 3 to 4 days. It must be mentioned, however, that this method of stabilization is *not* effective if the aluminum borohydride is to be stored at temperatures much above 25°; at 60°, for example, no method of decreasing the rate of hydrogen evolution has been found. Furthermore our results apply to storage in glass containers, although preliminary tests indicate that the observations are applicable to stainless steel containers also.

Aluminum borohydride thus treated may be safely stored at room temperatures for considerable periods. It is, nevertheless, desirable to vent accumulated hydrogen occasionally if larger amounts are stored for protracted periods (*e.g.*, more than a few months) or if the container has a relatively small gas space. If venting is not into a vacuum it must be carried out with due precautions (*e.g.*, low temperature of the borohydride, slow rate) to avoid escape of borohydride with the hydrogen or diffusion of air back into the container.

**Preparation of Aluminum Borohydride from Sodium Borohydride and Aluminum Chloride.**—The apparatus is shown in Fig. 1. Before undertaking a preparation, the entire system was dried by thorough evacuation. At the same time, the reaction vessel R was heated with a brush flame to aid in the removal of the last traces of moisture. R was flushed with oxygen-free nitrogen by closing stopcock (SC) 2 and slowly admitting nitrogen through SC 1, which

was then closed. R was re-evacuated and refilled with dry nitrogen as before. The cap of the slanting side arm was removed, and 190–195 g. of anhydrous aluminum chloride was poured in through a wide stem funnel. The reaction vessel was recapped and evacuated through SC 2 and SC 8 to remove air trapped in the powder.

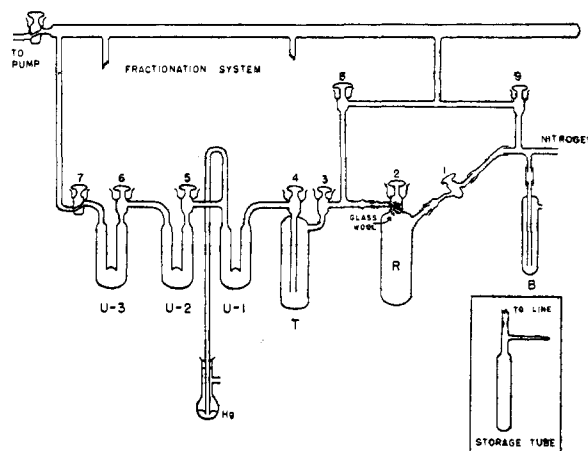


Fig. 1.—Apparatus for the preparation of aluminum borohydride.

SC 2 was closed, R was refilled with nitrogen and 35 g. of sodium borohydride was quickly introduced through the side-arm. R was recapped and re-evacuated. (The evacuation was started slowly to avoid carrying some of the finely divided borohydride out of the reaction flask; a glass wool plug in SC 2 reduced the danger of such loss.) After 10 minutes of evacuation nitrogen was again admitted into R. SC 1 and 2 were closed and the reaction vessel R was removed completely from the vacuum apparatus, capped and shaken to mix the reagents thoroughly. (Asbestos gloves and a safety mask should be worn during this operation.) The vessel R was replaced and the section of the apparatus between SC 2 and 3 was evacuated through SC 8.

Before removing the products, liquid nitrogen-baths were placed around the trap T and the U-tube, U-1. SC 2 was opened cautiously and the entire system was pumped down through SC 7. Then with SC 5 closed, the apparatus was slowly filled with nitrogen through SC 1 until the gas passed out through the mercury bubbler. A furnace was placed around the reaction vessel. The temperature was raised to 130° during a period of about 15 minutes. (Should the reaction mixture froth vigorously to the top of the vessel, the oven should be removed temporarily.) After one-half hour, the vigorous portion of the reaction was over. Then the nitrogen flow was stopped, a liquid nitrogen-bath was placed around U-2 and the entire system was pumped out through stopcocks 5, 6 and 7. After 10 minutes pumping, the oven was removed, but the pumping was continued for 20–30 minutes longer.

During the period the reaction was carried out in a vacuum, particularly during the time the reaction vessel was heated, large amounts of aluminum chloride sublimed out of the reaction vessel and condensed over the system up to the trap, T. This sublimation could be reduced by carrying the reaction out entirely in an atmosphere of nitrogen or by removing the furnace before evacuation. However, the evacuation and the heating were necessary to obtain the best yield. If the brief heating-vacuum treatment was eliminated, the yield was reduced 10–15%.

The residue in the reaction vessel may be disposed of by filling the latter with nitrogen, closing the stopcocks on the vessel, removing it from the line and cautiously shaking the contents into water through a 6-foot length of 30-mm. tubing. The reaction with the water is vigorous but not dangerous. The reactivity may be due to traces of aluminum borohydride adsorbed on some of the solids or to some unknown intermediate of low volatility.

Purification of the crude product was carried out as follows. SC 3 and 6 were closed and all the condensate in U-1 and U-2 was warmed and distilled back into the trap T. Then U-1 was cooled to –45° (solid-liquid chlorobenzene), U-2 to –140° (solid-liquid 40% ether–60% alcohol by

(7) These changes also occur, though more slowly, when removal of aluminum borohydride from the residue is attempted by prolonged evacuation at room temperature. No solvent for the residue other than the borohydride has been found.

volume), and U-3 to  $-196^{\circ}$ . With the system from SC 3 to 7 continuously evacuated through SC 7, the material in trap T was permitted to warm up slowly, to distil out and to be fractionally condensed in the U-tube system.

The material condensed in U-3 was diborane with a trace of aluminum borohydride. It was destroyed by reaction with methanol. The material in U-1 was aluminum chloride with some reactive material of unknown composition. It was treated with methanol and removed.

The aluminum borohydride, condensed in U-2, was re-fractionated through U-3 at  $-63.5^{\circ}$  (solid-liquid chloroform) and a liquid nitrogen-cooled U-tube on the vacuum line (not shown in Fig. 1) between SC 7 and the pump. The material collected in the  $-63.5^{\circ}$  bath was stored and combined with the products of later runs for re-fractionation.

The material passing through the  $-63.5^{\circ}$  bath was pure aluminum borohydride (v.t. 119.5 mm. at  $0^{\circ}$ ). It was stored in the vacuum apparatus or transferred to a sealed storage tube (Fig. 1, insert).

The yield of aluminum borohydride was 18 g. (33 ml. of liquid, density 0.55 g./ml.) or 80%.

**The Preparation of Aluminum Borohydride from Lithium Borohydride and Aluminum Chloride.**—The apparatus shown in Fig. 1 was used. The procedure was somewhat simpler than that described for sodium borohydride. Since the required excess of aluminum chloride was much smaller and the reaction temperature lower, there was little sublimation of aluminum chloride and the nitrogen atmosphere could be dispensed with. However, lithium borohydride and the aluminum halide react rapidly even at room temperatures. The original mixing of the reagents must be carried out with particular caution.

The system was dried and filled with dry nitrogen in the manner described previously. Vessel R was charged with 12.0 g. of lithium borohydride and a score of 6-mm. glass beads. (The latter aided in maintaining the reaction mass in a porous state.) The vessel was evacuated and again filled with nitrogen. A 10% excess of aluminum chloride, 31.0 g., was then quickly introduced while nitrogen continuously passed through to prevent diffusion of air into the vessel. (It proved convenient to add the reagents through a wide stem funnel. Different funnels were used for each of the reagents to avoid the latter coming into contact with each other in the presence of air.) The side tube was re-capped, the stopcock was closed, the reaction vessel was removed from the line and the reactants were thoroughly mixed by shaking. (Asbestos gloves and safety mask are recommended.)

The reaction vessel was then replaced on the line and evacuated through SC 2 to 7. SC 1, 8 and 9 were kept closed. During this operation trap T was cooled with a  $-63.5^{\circ}$  bath to condense traces of less volatile solids from the aluminum borohydride. The latter was condensed in U-1, cooled to  $-140^{\circ}$ , while small quantities of diborane passed through to U-2 at  $-196^{\circ}$ . When the initial reaction had subsided somewhat, a water-bath was placed around the reaction vessel and the temperature was gradually raised to  $100^{\circ}$  at a rate which avoided entrainment of the powders by the escaping gas.

After 2 to 4 hours, the reaction was virtually complete. Approximately 50–100 ml. of diborane was obtained. The aluminum borohydride in the  $-140^{\circ}$  bath was usually pure (v.t. 119.5 mm. at  $0^{\circ}$ ). When the material did not exhibit this vapor tension, it was purified by fractional condensation as previously described. The residue in R was disposed of as described for sodium borohydride.

The yield was 14.4 g. (22.5 ml. of liquid) of aluminum borohydride, or 95% of the theoretical.

**Aluminum Chloride-Borohydride Ratio.**—Excellent yields of aluminum borohydride were obtained from lithium borohydride with only a slight excess of aluminum chloride over the stoichiometric quantity. The preparation based on sodium borohydride required a large excess of the halide. A number of experiments were carried out to determine the effect of the  $\text{AlCl}_3/\text{NaBH}_4$  ratio on the yield. The data are summarized in Table I.

**Pressure of Aluminum Borohydride above Reaction Mixtures.**—A reaction vessel, similar to R (Fig. 1) but equipped with a short mercury manometer, was inserted in the system shown in Fig. 1. Alkali borohydride and a 50% excess aluminum chloride were added to the vessel and mixed as described in the preparation procedure. The vessel was replaced on the line, cooled to  $-196^{\circ}$  and evacuated. Then

TABLE I  
YIELD DATA FOR VARYING PROPORTIONS OF ALUMINUM CHLORIDE AND SODIUM BOROHYDRIDE

Mole ratio, <sup>a</sup> $\text{AlCl}_3/\text{NaBH}_4$	Time, hr.	Temp., $^{\circ}\text{C}$ .	Yield, % $\text{Al}(\text{BH}_4)_3$	Yield, % $\text{B}_2\text{H}_6$	Condi- tions <sup>b</sup>
0.094	1.5	25	0	0	
	6.5	100	0	0	P
.473	1	130	33.5	4.6	P
.57	12	100	56.8	...	P
.71	1	135	65.6	3.5	P
.85	4	100	59.7	...	P
1.0	1.5	120	47.6	3.1	N
1.7	0.5	130	67.8	...	N
2.0	2	125	81	4.3	N
2.3	0.75	115	73	9.2	N

<sup>a</sup> The stoichiometric mole ratio is 0.33. <sup>b</sup> P indicates that the reaction was carried out with constant pumping. N indicates that the reaction was carried out in a stream of nitrogen.

with SC 2 closed, the vessel was heated to the desired temperature. When the pressure had come to a constant value, the warm bath was replaced by one containing liquid nitrogen. Any pressure remaining at  $-196^{\circ}$  was ascribed to hydrogen, that remaining at  $-140^{\circ}$  to diborane and hydrogen. By subtracting the pressure of hydrogen and diborane from the total pressure, the partial pressure of aluminum borohydride was obtained. The value was checked by opening the vessel at  $-140^{\circ}$  to the pump for a short period and repeating the measurement of the pressure at the desired temperature. This procedure was repeated several times to determine that the results could be reproduced. The results are summarized in Table II.

TABLE II  
PRESSURES OF ALUMINUM BOROHYDRIDE ABOVE MIXTURES OF ALUMINUM CHLORIDE AND ALKALI BOROHYDRIDES

Alkali borohydride	Temp., $^{\circ}\text{C}$ .	Press., mm. $\text{Al}(\text{BH}_4)_3$	Notes
$\text{LiBH}_4$	23	6	11 mm. total pressure
	50	27	32 mm. total pressure
	100	150	Total pressure of hydrogen and diborane, 100 mm.
$\text{NaBH}_4$	23	<2	Aluminum borohydride pressure small and constant.
	50	2	
	75	3	Total pressure high, increasing with time
	100	3	

**B. Preparation of Beryllium Borohydride.**—The procedure is similar to that described for aluminum borohydride. A mixture of 7.0 g. of lithium borohydride and 40–45 g. of beryllium chloride was prepared in the reaction vessel and heated to  $90^{\circ}$ . The temperature was gradually raised to  $140^{\circ}$  over a period of 8 hours with continuous evacuation. Pure beryllium borohydride (v.t. 5.2 mm. at  $20^{\circ}$ ) was trapped at  $-80^{\circ}$  in 5.0 g. (80%) yield.

**C. Preparation of Lithium Borohydride by Metathesis.**—A sample of 9 g. of sodium borohydride (purity 89%) was dissolved in 350 ml. of isopropylamine (dried over sodium hydride). An aliquot of the solution was analyzed for active hydrogen. The remainder of the filtered solution containing 0.213 mole of borohydride was placed in a 1-l. flask and refluxed gently. An excess of lithium chloride, 11.4 g. (0.268 mole) was added in solid form through the top of the condenser.<sup>8</sup> (The lithium chloride had been dried in vacuum at  $190^{\circ}$ .) The mixture was refluxed 2.5 hours, and then filtered through a sintered glass funnel under pressure. The major portion of the solvent was removed from the filtrate by distillation at atmospheric pressure. The remainder was removed at low pressures as the temperature was raised to  $165^{\circ}$ .

The crude product was refluxed with 180 g. of dry ethyl

(8) Unless lithium chloride is used in slight excess, the sodium chloride is precipitated in difficultly filterable form.

ether and the solution passed through a sintered glass filter. The ether was removed from the clear filtrate as was the isopropylamine from the crude product. A yield of 4.5 g. of 97.6% lithium borohydride, corresponding to 94% of the theoretical, was obtained. Similar preparations in which methylamine or ethylamine were substituted for isopropylamine gave yields of 86–96%. The latter is more convenient for laboratory preparations.

**Acknowledgment.**—The assistance of H. R. Hoekstra, A. O. Walker, A. C. Bond, A. E. Finholt, D. F. Peppard and C. R. Witschonke with individual preparations and experiments in this study is gratefully acknowledged.

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

## Procedures for the Preparation of Methyl Borate<sup>1</sup>

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Simple procedures have been developed which permit the essentially quantitative conversion of boric oxide, boric acid or borax into the methyl borate-methanol azeotrope. The properties of this azeotrope have been investigated. We have re-examined methods for separating the ester from the azeotrope by procedures involving (1) washing the azeotrope with sulfuric acid, (2) azeotropic distillation with carbon disulfide and (3) treatment with salts. As a result of improvements in these procedures methyl borate can now be readily prepared by any one of them in yields of 90% or better.

Although methyl borate has been prepared by many workers, the procedures described are relatively complicated and the yields are relatively low.<sup>2</sup> Many have carried the reaction out in autoclaves under pressure<sup>2f,g,h</sup>; others have used concentrated sulfuric acid to facilitate the reaction.<sup>2k,l,m,n</sup>

Perhaps the most convenient procedure for the preparation of methyl borate in quantity is that of Webster and Dennis.<sup>2i</sup> They treated boric oxide with methanol and separated the ester from the methyl borate-methanol azeotrope by washing the latter with concentrated sulfuric acid. Their yield was only 42% on the basis of the equation and only 21% on the basis of the boron converted into ester. Since we required large quantities of methyl borate for our investigations, it was desirable to develop better synthetic procedures.

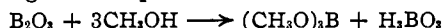
With the aid of the methods described in this paper it is now possible to obtain methyl borate by any one of several alternative routes in yields of 90% or better and of almost 100% purity.

### Results and Discussion

In the reaction of boric oxide and its derivatives with methanol, the product, methyl borate, is obtained in the form of its azeotrope with methanol. The pertinent boiling points are methanol 64°, methyl borate 68° and azeotrope (75.5% methyl borate by weight) 54.6°.<sup>3</sup> The problem therefore resolves itself into (1) the conversion of economical sources of boron to the azeotrope in high yield and

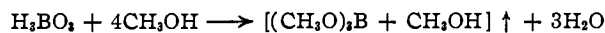
(2) the recovery of the methyl borate from the azeotrope.

It seemed possible that methyl borate free from the alcohol might be obtained by reaction of boric oxide with a quantity of methanol calculated according to the equation



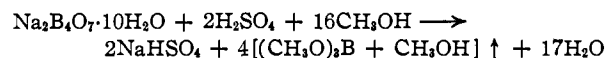
Actually, however, the distillate from this reaction mixture consisted of the azeotrope<sup>4</sup> in 71.6% yield. When four moles of methanol were used (3 moles for esterification, 1 mole for the azeotrope) per mole of boric oxide, the yield of methyl borate (as azeotrope) was 99.4%. In spite of the excellent yield, this reaction suffers from the disadvantage that only one-half of the boron is utilized.

This difficulty may be avoided since boric acid may be quantitatively converted to the ester by additional methanol.<sup>4</sup>



It has been recommended that sulfuric acid be used to drive the reaction to completion, but this procedure is unnecessary if the azeotrope is continuously bled off through an efficient column, used to separate the azeotrope from excess methanol. The use of sulfuric acid is actually harmful since it leads to considerable loss of methanol by ether formation.

Yields of methyl borate (as azeotrope) of from 92–93% may be obtained by the addition of methanol and sulfuric acid to borax, the cheapest of the three boron sources.



Although the equation calls for a methanol-to-boron ratio of 4:1, it is desirable to use an excess of methanol (8:1) to obtain better utilization of boron in a shorter reaction time.

Methanol may be fairly effectively extracted from the azeotrope by concentrated sulfuric acid, but numerous extractions are required and as much as about 15% of the methyl borate is lost by

(4) The composition of the azeotrope corresponds very closely to a mixture of one mole of ester and one mole of methanol. It will be convenient to refer to this azeotrope by the symbol  $[(\text{CH}_3\text{O})_2\text{B} + \text{CH}_3\text{OH}]$ .

(1) New Developments in the Chemistry of Diborane and the Borohydrides. VIII.

(2) (a) Ebelman and Bouquet, *Ann.*, **60**, 252 (1846); (b) V. Gassel, *Ann. chim. phys.*, [7] **3**, 22 (1894); (c) A. Pictet and G. Karl, *Bull. soc. chim.*, [4] **3**, 1123 (1908); (d) E. S. Khotinskii and S. L. Pupko, *Ukrainakii Khem. Zhur.*, **4**, Sci. Pt. 13 (1929); *C. A.*, **23**, 4441 (1929); (e) T. H. Vaughan, U. S. Patent 2,088,935; *C. A.*, **31**, 6875 (1937); (f) H. Schiff, *Ann. Suppl.*, **8**, 183 (1867); (g) H. Copeau, *Compt. rend.*, **127**, 721 (1898); (h) J. J. Etridge and S. Sugden, *J. Chem. Soc.*, 989 (1928); (i) S. H. Webster and L. M. Dennis, *THIS JOURNAL*, **55**, 3233 (1933); (j) E. Schulek and G. Vastagh, *Z. anal. Chem.*, **84**, 167 (1931); (k) M. Arquet, *Bull. soc. chim.*, [5] **3**, 1422 (1936); (l) R. P. Calvert and O. L. Thomas, U. S. Patent 1,308,576, *C. A.*, **13**, 2262 (1919); (m) F. J. Appel, U. S. Patent 2,217,354, *C. A.*, **35**, 1071 (1941); (n) G. Cohn, *Pharm. Zentr.*, **52**, 479 (1911).

(3) Other authors have reported compositions of 30% (ref. 2h) and 68% [M. Lecat, *Rec. trav. chim.*, **47**, 15 (1928)] of methyl borate.