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# The Preparation of Sodium Borohydride by the High Temperature Reaction of Sodium Hydride with Borate Esters[1]

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By disproportionation of sodium trimethoxyborohydride, $NaBH(OCH_3)_3$, at 230°, products richer in hydrogen than the parent compound, are obtained. But the reactions do not go completely to the formation of sodium borohydride unless methyl borate is continuously removed from the reaction mixture. Even under these conditions the reaction is not clean-cut, since some dimethoxyborine, $HB(OCH_3)_2$, is evolved along with the methyl borate and pure sodium borohydride is not obtained. A far simpler method of preparation of the latter is afforded by the rapid reaction at 225–275° of one mole of methyl borate with four moles of sodium hydride: $4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$. Isopropylamine extracts the sodium borohydride from the reaction product and nearly quantitative yields of essentially pure sodium borohydride are obtained. Sodium trimethoxyborohydride or tetramethoxyborohydride as well as esters, such as ethyl or *n*-butyl borates, also react with sodium hydride to produce sodium borohydride. Moreover, lithium hydride can be converted into lithium borohydride by similar reactions. At 330–350° sodium hydride and boric oxide react to produce up to 60% yields of sodium borohydride. The reaction, which appears to follow the course: $4NaH + 2B_2O_3 \rightarrow 3NaBO_2 + NaBH_4$, is relatively slow, and has thus far proved less satisfactory than the preparation based on sodium hydride and methyl borate. The reaction of hydrogen under pressure with sodium metal and methyl borate was observed to yield sodium trimethoxyborohydride and small quantities of sodium borohydride.

The reactions of diborane with lithium hydride and with sodium trimethoxyborohydride[2] constitute preparative methods for the simple borohydrides, far more satisfactory than the procedures by which such compounds were originally obtained.[3] Continuation of the line of work which resulted in these improvements has now made the borohydrides still more readily accessible by the development of methods of preparation which avoid the use of diborane. As a consequence interesting uses for them in organic and inorganic chemistry are being found.[2,4]

## Results and Discussion

Attempts to prepare sodium borohydride without the use of diborane began with a study of the disproportionation of sodium trimethoxyborohydride according to the equation

$$4NaBH(OCH_3)_3 \longrightarrow NaBH_4 + 3NaB(OCH_3)_4$$

Although the disproportionation occurred at the temperature employed (about 230°), the results were not satisfactory. Apparently equilibrium was established when the reaction had proceeded only partially in the desired direction.

The observation that sodium tetramethoxyborohydride has an appreciable dissociation pressure of methyl borate at the temperatures at which the disproportionation occurs, suggested that the latter might be driven to completion by continuous removal of methyl borate in vacuum

$$\left\{\begin{array}{l}4NaBH(OCH_3)_3 \longrightarrow NaBH_4 + 3NaB(OCH_3)_4\\ 3NaB(OCH_3)_4 \longrightarrow 3NaOCH_3 + 3B(OCH_3)_3\uparrow\end{array}\right.$$

This procedure greatly improved the results, but led to the liberation of only about 80% of the calculated amount of methyl borate. The remainder of the trimethoxyborohydride apparently decomposed by a side reaction, which produced dimethoxyborine according to the equation

$$NaBH(OCH_3)_3 \longrightarrow NaOCH_3 + (CH_3O)_2BH$$

Although sodium borohydride of 50% purity could be extracted from the reaction product by the use of liquid ammonia, efforts at improvement of the results were discontinued as a result of the observation that sodium hydride and methyl borate in the correct proportions undergo a rapid reaction at 225–275° to produce sodium borohydride of 90–96% purity, and in a yield as high as 94%, according to the equation

$$4NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3$$

Methyl borate may be replaced by either sodium trimethoxyborohydride or tetramethoxyborohydride.

$$3NaH + NaBH(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3$$
$$4NaH + NaB(OCH_3)_4 \longrightarrow NaBH_4 + 4NaOCH_3$$

The methyl borate also may be replaced by higher esters, such as ethyl and *n*-butyl borate.

$$4NaH + B(OC_2H_5)_3 \longrightarrow NaBH_4 + 3NaOC_2H_5$$

Attention is called to the fact that, in the reaction of methyl borate with certain grades of sodium hydride, difficulties were occasionally encountered. These seemed to be due to the formation of sodium trimethoxyborohydride under certain conditions and to its low melting point (230°). The difficulties and the methods of overcoming them are described in the Experimental part. These difficulties were not encountered when ethyl borate was used in place of methyl borate in the reaction with sodium hydride, probably because sodium triethoxyborohydride, even if formed, melts above 300°. However, the sodium ethoxide produced is much less stable than the methoxide; above 240° it undergoes relatively rapid decomposition according to the equations[5]

$$NaOC_2H_5 \longrightarrow NaOH + C_2H_4$$
$$NaOC_2H_5 \longrightarrow NaOH + 2C + 2H_2$$

To maintain an adequate reaction rate in the desired reactions, and yet to prevent decomposition of the sodium ethoxide, the temperature had to be

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

(2) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *ibid.*, **75**, 199 (1953).

(3) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

(4) (a) H. I. Schlesinger, H. C. Brown, *et al.*, *ibid.*, **75**, 215 (1953); (b) S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 122 (1949).

(5) J. F. Durand, *Compt. rend.*, **172**, 1504 (1921).

maintained within narrow limits. Since it could not rise above 240°, the reaction was slow and close control was required.

Fortunately, by preheating the hydride, operating at a somewhat higher temperature, and adding a small quantity of the crude product from a previous run, it was possible to utilize the less reactive hydrides with methyl borate to obtain excellent yields. Although reaction conditions may require slight modifications depending upon the nature of the hydride available, the procedure has proved satisfactory both on the laboratory and the pilot plant scale.

The reaction requires the ready availability of methyl borate. Conditions were found which permit its preparation in essentially quantitative yield from methanol and borax, boric acid or boric oxide.[6]

Treatment of metallic sodium with a mixture of hydrogen and methyl borate at 250° under pressure gave good yields of the trimethoxy derivative

$$2Na + H_2 + 2B(OCH_3)_3 \longrightarrow 2NaBH(OCH_3)_3$$

At somewhat higher temperatures and with the sodium and methyl borate in the approximate proportions required for the reaction

$$4Na + 2H_2 + B(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3$$

sodium borohydride was formed. The yields were relatively low. This result was considered to be due to the poor agitation effected by the only pieces of equipment available at the time and in all probability could be improved by adequate stirring.

In addition to the methods already mentioned, we observed that sodium hydride and boric oxide underwent reaction to yield sodium borohydride.

$$4NaH + 2B_2O_3 \longrightarrow 3NaBO_2 + NaBH_4$$

Yields of approximately 60% were obtained by grinding the reactants together in a small glass ball mill at 330–350° for 20 to 48 hours. The loss of boron in a product other than the borohydride, the low yields obtained in apparatus readily available for laboratory purposes, and the higher temperatures required are disadvantages of the method for small scale preparations. The fact that such a solid–solid reaction should occur at all with what must be an extensive rearrangement of atoms is exceedingly interesting.

Lithium borohydride can be similarly prepared

$$4LiH + B(OCH_3)_3 \longrightarrow LiBH_4 + 3LiOCH_3$$

The reaction was not quite as satisfactory as in the case of the sodium compound. In the first place the maximum yield obtained was 70% as contrasted with 90–94% in the case of the sodium borohydride; in the second place the extraction of the lithium borohydride from the crude reaction product offered difficulties. Nevertheless, the reaction constitutes a convenient one-step laboratory route to lithium borohydride.

In the course of this work it became necessary to determine the solubilities in various solvents of a number of the intermediates and products discussed in this paper. These data are summarized in the Experimental part.

## Experimental Part

**Materials.**—The sodium hydride used in this work consisted of two different products, obtained, respectively, from the Ethyl Corporation and from E. I. du Pont de Nemours and Co. The two hydrides were similar in chemical composition and general physical appearance. Analysis for sodium and hydrogen indicated that both materials were 97 to 99% pure; the remaining impurities were sodium metal and some unidentified materials. The particle size of both hydrides was between 80 and 200 mesh, although the Ethyl Corporation material was somewhat finer. Extraction of the hydrides with ligroin yielded no soluble organic material. Despite these similarities, there was a marked difference in reactivities. The du Pont product necessitated special precautions described below.

The lithium hydride was obtained from the Lithalloy Corporation.[7] Its analysis indicated a purity of 97%. It was a fine powder of 200 mesh.

The borate esters and the tri- and tetraalkoxyborohydrides were obtained as described elsewhere.[2,6] The boric oxide was the commercial product obtained from the Pacific Coast Borax Co.

### A. Disproportionation of Trialkoxyborohydrides

**Sodium Trimethoxyborohydride, $NaBH(OCH_3)_3$.**—In an experiment in which the volatile reaction products were not removed as formed, 5.63 g. of sodium trimethoxyborohydride was heated for 2 hours at 250–255° in the evacuated glass liner of a small Aminco hydrogenator. Extraction of a 1.32-g. sample of the product with liquid ammonia yielded 0.354 g. of a solid which liberated 118.5 ml. of hydrogen upon hydrolysis. This corresponds to a partially disproportionated product of the composition $NaBH_{1.75}(OCH_3)_{2.25}$.

Other experiments were carried out in a glass tube from which the volatile reaction products could be transferred to a vacuum system from time to time. A 6.39-g., or 50-mmole, sample was heated rapidly to its melting point (230°) and maintained at that temperature for 7 hours. The pressure rose gradually to a maximum of 10 mm. After removal of a part of the volatile products, the same pressure was re-established on continued heating. A second removal of the volatile material now resulted in solidification of the remaining contents of the tube within a few minutes. Heating was continued for 7 hours with continuous removal of volatile products. The total amount of methyl borate obtained (29.5 mmoles) corresponds to a conversion to sodium borohydride of about 39.3 mmoles of sodium trimethoxyborohydride according to the equation

$$4NaBH(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3 + 3B(OCH_3)_3$$

In addition, 9.6 mmoles of dimethoxyborine, identified by its vapor tension, was obtained. This quantity corresponds to an equal number of moles of the trimethoxy derivative, according to the equation

$$NaBH(OCH_3)_3 \longrightarrow NaOCH_3 + HB(OCH_3)_2$$

Thus, of the original 50 mmoles of sodium trimethoxyborohydride, a total of 48.9 mmoles had reacted, 39.3 mmoles or 78.6% to give sodium borohydride and 19.2% to give dimethoxyborine.

This conclusion was confirmed by the fact that a 0.370-g. sample of the solid residue generated 123.5 ml. of hydrogen, as compared with the value, 131 ml., calculated on the basis that the two postulated reactions occurred in the relative amounts indicated. In spite of this agreement, extraction of the solid residue yielded a product which gave only about one-half of the amount of hydrogen expected for pure sodium borohydride.

**Pyrolysis of Other Alkoxyborohydrides.**—Sodium triethoxyborohydride was pyrolyzed as described for the corresponding methyl derivative. The results were very similar, except that the ethoxy derivative did not melt at the temperature of the experiment and that the reaction proceeded somewhat more rapidly. Melting did not take place below 295°, but volatile products began to be evolved at 230°. From 29.95 mmoles of the ethoxy derivative, heated at 240° for 7 hours, 17.5 mmoles of ethyl borate and a trace of diethoxyborine (0.2 mmole) were obtained. The ethyl borate

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(6) H. I. Schlesinger, H. C. Brown, D. Mayfield and J. R. Gilbreath, This Journal, 75, 213 (1953).

(7) It is our understanding that lithium hydride of the necessary purity and fineness may be obtained from the Maywood Chemical Works, Maywood, N. J., or from Metalloy Corporation, Minneapolis, Minn.

TABLE I

SELECTED EXPERIMENTS ON THE REACTION OF SODIUM HYDRIDE WITH METHYL AND ETHYL BORATES

| Expt. | Source of sodium hydride | Ester used, borate | Addn. time (min.) and temp., (°C.) | Subsequent heating time (min.) and temp. (°C.) | Yield, % | Purity | Comments |
|---|---|---|---|---|---|---|---|
| 1 | Ethyl Corp. | Methyl | 20<br>230–270 | 10<br>270 | 87 | 93 | Dry powder |
| 2 | du Pont | Methyl | 20<br>230–270 | . . . | . . | . . | A mush formed. No preheating of hydride |
| 3 | du Pont | Methyl | 40<br>245–260 | 60<br>250–260 | 86 | 91 | Hydride was preheated at 250° for $1^1/_4$ hr. |
| 4 | du Pont + reaction product of a previous run | Methyl | 40<br>245–255 | 60<br>250–260 | 94 | 96 | Hydride was preheated at 250° for $1^1/_4$ hr. |
| 5 | Ethyl Corp. | Ethyl | 20<br>220 | 120<br>220 | 87 | 86 | Dry powder |
| 6 | Ethyl Corp. | Ethyl | 90<br>260 | 10<br>260 | 4 | 27 | Powder turned black |
| 7 | du Pont | Ethyl | 30<br>230 | 5<br>230–240 | 82–87 | 88 | Dry powder |

recovered indicated that the reaction had proceeded approximately 90% to completion.

The disproportionation of tri-*n*-butoxyborohydride was also studied. In this case it was hoped that the solubility of sodium tetra-*n*-butoxyborohydride in organic solvents might offer a means of driving the reaction toward completion. However, the results were no more favorable than those obtained with the simpler compounds.

## B. Preparation of Sodium Borohydride by High Temperature Reactions

**The Reaction of Sodium Hydride and Borate Esters.**—The preparations were carried out in a one-liter, 3-neck round-bottom flask, the center ground joint of which was fitted with a gland stirrer (Scientific Glass Co.). The arms of the stirrer were made of Monel metal, jointed at 5 places to permit entry through the 29/42 joint and shaped to the contour of the flask. It is important that the stirring is vigorous, but that relatively little material is thrown to the upper, cooler portions of the apparatus. A thermometer well was placed in one of the remaining necks, in the other, a condenser. The top of the condenser was fitted with a two-hole rubber stopper which held a soda-lime tube and a 100-ml. dropping funnel. The flask was heated by an electric furnace. With the heater in place, the top of the flask was covered with glass wool and with a fitted cover made of several layers of asbestos paper.

The flask and the attachments were flushed with nitrogen, the thermometer well was removed from the flask, Ethyl Corporation sodium hydride (50 g. was the usual charge) was poured through the opening as rapidly as possible by means of a funnel and the thermometer well was replaced. The calculated quantity of methyl borate was placed into the dropping funnel. Stirring and heating were started. When the temperature within the flask reached 220°, addition of methyl borate was begun at a uniform rate such that the addition was complete in 20–40 minutes. The temperature was maintained between 230 and 270° during the addition of the methyl borate and usually for 60 minutes thereafter. The furnace was then removed and, as the mixture cooled, air was allowed to enter the flask through the drying tube. Stirring was continued throughout these operations to keep the solid product in a finely-divided form.

Isopropylamine, dried over barium oxide and distilled from sodium hydride, was used to extract the borohydride from the reaction mixture. For this purpose the solid was poured from the reaction flask into a 1-l. round-bottom flask and 400 ml. of isopropylamine was added. The mixture was heated gently under reflux for a few minutes, then allowed to cool to room temperature. The slurry of solution and suspended sodium methoxide was then rapidly poured into a sintered glass filter funnel and the solution forced through the sintered glass disc by applying slight air pressure. The flask and the filter cake were washed with two small portions of isopropylamine. The filtrate and washings were combined. Most of the amine was removed by distillation at atmospheric pressure, but for the removal of the last traces of amine from the solid, reduced pressure was necessary. The sodium borohydride was obtained as a white, finely divided solid in yields of 86 to 94% and purities of 90 to 96%.

An alternative procedure for the extraction of the sodium borohydride was the addition of the reaction product to 200 ml. of liquid ammonia (dried with sodium) contained in a dewar vessel. The mixture was stirred for several minutes and the clear solution was forced through a filter stick into a flask where the ammonia was permitted to boil off. The last traces were removed under vacuum. Yields and purities were essentially the same as those obtained with isopropylamine.

Recrystallization from water as the dihydrate[2] or from isopropylamine yielded sodium borohydride in purity of better than 99%.

Attempts to utilize the du Pont hydride in this reaction led to the formation of partially melted mixtures which could not be stirred effectively and to low yields (75% or less) of products of very low purity (25–50%). The precautions and procedure necessary for utilizing the du Pont hydride in this reaction were (1) preheating of the sodium hydride to 250°, (2) regular addition rate of the methyl borate, (3) thorough stirring and (4) addition of 10–20% of the unextracted product of a previous successful run. Although the reaction proceeded at a slightly faster rate at temperatures above 250°, there was little difference in the results obtained at temperatures from 250 to 280°. It was not possible to go above 280° since sodium methoxide began to decompose at 290°.

The reason for the different action of the two hydrides was not discovered. Different methods of manufacture may have produced surfaces on the hydride particles which differ in their reactivity with methyl borate. The formation of the partially melted mixtures, which were so difficult to handle, was probably due to the intermediate formation and accumulation of sodium trimethoxyborohydride which, when pure, melts at 230° and which, when admixed with the other substances which may be present, melts at 190° or below.

The reaction of ethyl borate on sodium hydride proceeded in a manner entirely analogous to the reaction of methyl borate with sodium hydride. The yields and purity of the sodium borohydride were of the same order of magnitude in the two cases. Table I lists the results obtained in representative runs with methyl and with ethyl borate.

The difference in behavior of methyl and ethyl borates toward the less reactive hydride, which has already been discussed, is illustrated in experiments 2 and 7. The necessity of maintaining a relatively low temperature when ethyl borate is used is shown in experiment 6 and the relative slowness of the reaction of this borate under these conditions may be seen by comparing experiments 1 with 5, and 3 with 7.

**The Reaction of Sodium Hydride with Sodium Trimethoxyborohydride.**—A mixture of 0.40 mole of sodium trimethoxyborohydride and 1.20 moles of sodium hydride was stirred and heated. At 200° the mixture liquefied partially and formed a paste which soon became so hard that stirring was no longer possible. The temperature was then raised to 250–270° and there maintained for 30 minutes. The crude product was extracted with isopropylamine. The product analyzed 89% sodium borohydride, and the yield was 78%.

**The Reaction of Sodium Hydride with Sodium Tetramethoxyborohydride.**—The experiments and results were quite similar to those described in the preceding paragraph. A 66% yield of sodium borohydride of 91% purity was obtained.

**The Reaction of Sodium, Hydrogen and Methyl Borate.**—Experiments revealed that methyl borate is not appreciably attacked by sodium under the conditions (225–275°) utilized for the synthesis of sodium borohydride. It therefore appeared possible that the borohydride might be prepared in a single step from sodium, hydrogen and the ester.

$$4Na + 2H_2 + B(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3$$

Unfortunately the only apparatus, available at the time, by which the mixture of sodium and methyl borate could be stirred under hydrogen pressure, was a small Aminco hydrogenator. Its shaking action provided only moderate, evidently insufficient agitation. Nevertheless, the following results indicate that with suitable equipment success in the reaction might be achieved.

The glass liner of the hydrogenator was charged with 3.45 g. (0.150 mole) of sodium and 4.01 g. (0.0386 mole) of methyl borate under 1040 lb. pressure of hydrogen at 21°. The mixture was shaken for 24 hours at 240–250°, during which time the pressure dropped to 770 lb. at 21°. The material, then removed from the hydrogenator, consisted of a white powder together with lumps of unchanged sodium. Extraction of the former with pyridine gave a material which on hydrolysis generated an amount of hydrogen corresponding to a mixture of approximately 15% sodium borohydride and 85% sodium trimethoxyborohydride.[8]

**The Reaction of Sodium Hydride and Boric Oxide.**—Two typical experiments will be described. A thoroughly mixed sample containing 1.39 g. of boric oxide and 0.94 g. of sodium hydride was placed into a 15-cm. long Pyrex tube, sealed at one end and equipped with a 29/42 male joint at the open end.[9] By means of the joint, the tube was connected with a simple vacuum system containing a mercury manometer for following the pressure in the system and a stopcock leading to a pump. The system was evacuated and then closed off by shutting the stopcock. A tube furnace was used to heat the reactants to 350°. At the end of 17 hours, 0.7 atm. of hydrogen had developed. The powder, appearing little changed except for a dark brown film at the surface of the glass, was extracted with pyridine.[8] There was obtained 62 mg. of sodium borohydride, a yield of 16.7% calculated from the amount of sodium hydride used.

In the second type of experiment, 1.56 g. of boric oxide, 1.00 g. of sodium hydride[9] and 15 steel ball bearings (1/4") were placed into a 25-cm. long Pyrex tube closed at one end. The tube was evacuated, closed and heated to 340° for 20 hours while it was rapidly and continuously rotated along its longitudinal axis (slightly inclined to the horizontal). When the tube was opened the glass was found to be partially coated with a brown encrustation and to be extensively etched. By a pyridine extraction of the contents of the tube, 211 mg. of 96% sodium borohydride was obtained, a yield of 51% based on the amount of sodium hydride used.

TABLE II

REACTION OF SODIUM HYDRIDE AND BORIC OXIDE

| Time, hr. | Temp., °C. | Yield, % |
|---|---|---|
| A. Stationary tube experiments | | |
| 40 | 215–250 | 0 |
| 17 | 300–310 | 4.8 |
| 45 | 310–333 | 19.0 |
| 17 | 350 | 16.7 |
| B. Rotating tube experiments | | |
| 28 | 250 | 1.3 |
| 20 | 270 | 8.5 |
| 20 | 290–310 | 14.0 |
| 20 | 320–330 | 17.5 |
| 20 | 340 | 51 |
| 46 | 330–350 | 64 |

Representative results obtained by these two procedures are summarized in Table II. The data indicate clearly that good mixing and temperature above 300° are essential if acceptable yields are to be obtained in a reasonable time.

Three equations may be written for the reaction between sodium hydride and boric oxide

$$8NaH + 7B_2O_3 \longrightarrow 3Na_2B_4O_7 + 2NaBH_4$$
$$4NaH + 2B_2O_3 \longrightarrow 3NaBO_2 + NaBH_4$$
$$8NaH + B_2O_3 \longrightarrow 3Na_2O + 2NaBH_4$$

The yields in the most favorable experiment exceed 100% if calculated according to the first equation, which can, therefore, not represent the actual course of the reaction. The third equation seems unlikely, since it suggests that sodium hydride should be able to react with sodium metaborate to give sodium oxide and sodium borohydride, a reaction which was shown not to occur under the conditions of the experiments. For these reasons, the yields stated in Table II were calculated according to the second equation, even though the data are inadequate for a final decision on the actual course of the reaction.

It is apparent that this reaction could be developed into a satisfactory synthesis of sodium borohydride. However, the procedure would probably require far more elaborate equipment, longer reaction times and higher temperatures than are necessary in the process utilizing borate esters.

## Solubilities

In seeking solvents for the extraction of sodium borohydride from the reaction mixtures obtained by the disproportionation of sodium trialkoxyborohydrides and by the high temperature reaction of sodium hydride and borate esters, it was necessary to obtain solubility data for the various products and intermediates encountered in this study. Solubilities were roughly determined (±10%) by the procedure previously described.[3] The data are summarized in Table III.

TABLE III

APPROXIMATE SOLUBILITIES IN GRAMS PER 100 GRAMS OF SOLVENT

| Solvent and b.p., °C. | Temp., °C. | $NaBH_4$ | $NaOCH_3$ | $NaBH(OCH_3)$ |
|---|---|---|---|---|
| Ammonia (liq.), −33 | 25 | 104 | 0.4 | 5.6 |
| Methylamine, −6.5 | 20 | 28 | ... | ... |
| Ethylamine, 16.6 | 17 | 21 | ... | ... |
| *n*-Propylamine, 48.7 | 28 | 10 | ... | ... |
| Isopropylamine, 34.0 | 28 | 6 | 0.1 | 9.0 |
| *n*-Butylamine, 77.8 | 28 | 5 | 0.1 | ... |
| Pyridine, 115.3 | 0–75 | 3–3.5 | 0.2–0.3 | 0.4–3.0 |
| Morpholine, 128.3 | 25, 75 | 1.4, 2.5 | 0.3, 0.1 | 0.3–2.3 |
| Dioxane, 101.5 | 25, 75 | Insol. | Insol. | 1.6–4.5 |

In the following solvents sodium borohydride has a solubility of less than 1 g. per 100 g. of solvent: aniline, ethyl and diethyl cellosolve, acetonitrile, diethylamine, triethylamine, ethyl acetate, diethyl ether and methyl borate. A few measurements of the solubilities of sodium ethoxide and of sodium tetramethoxy-, triethoxy- and tetraethoxyborohydrides were also made. The results showed that the solvents effective for the extraction of sodium borohydride from the product obtained by the reaction of sodium hydride with methyl borate, are also effective if the reaction is carried out with ethyl borate.

Although sodium borohydride is more soluble in liquid ammonia and in methyl-, ethyl- and *n*-propylamine than in isopropylamine, the latter was chosen for the extraction of the salt from the reaction mixture, because its vapor tension is low enough to permit convenient handling of the solvent, and yet high enough to make easy its removal from the sodium borohydride. Table III also shows that sodium trimethoxyborohydride is much more soluble than sodium

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[8] The experiments in which pyridine was used for extraction were carried out before the advantages of isopropylamine had been discovered.

[9] Ethyl Corporation sodium hydride was used in these experiments.

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.

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# The Preparation of Other Borohydrides by Metathetical Reactions Utilizing the Alkali Metal Borohydrides[1]

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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,[2] is required for the preparation of the borohydrides of heavy metals, such as uranium,[3a] thorium, hafnium, zirconium and titanium.[3b] 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.[4]

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° 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

$$(CH_3)_3Al + 2B_2H_6 \longrightarrow Al(BH_4)_3 + (CH_3)_3B$$

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[5] 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

$$AlX_3 + 3MBH_4 \longrightarrow Al(BH_4)_3 \uparrow + 3MX$$

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°. Purification of the product is readily effected by fractional distillation. Yields of 95% of pure aluminum borohydride have been

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[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).