

## Syntheses of the alkali metal borodeuterides<sup>1</sup>

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A synthesis of sodium borodeuteride on a molar scale has been developed. Trimethylamineborane was exchanged (6) with deuteriosulfuric acid in deuterium oxide to obtain trimethylamineborane- $d_3$  of a high isotopic purity. Reaction of trimethylamineborane- $d_3$  with sodium methoxide in diglyme at 120–150 °C yielded sodium borodeuteride, which, after purification, was obtained in a 40–50% overall yield. The conditions for obtaining material of a high isotopic and chemical purity were found to be rather stringent but, once worked out, were easily reproducible.

Lithium borodeuteride and potassium borodeuteride were also prepared from trimethylamineborane- $d_3$  and the corresponding methoxide salts. An alternative synthesis of lithium borodeuteride, involving the reaction between lithium deuteride and boron trifluoride etherate, was found to be more satisfactory, since it avoided the formation of stable 1:1 solvent complexes with lithium borodeuteride.

The products that were obtained had a chemical purity of 97%, and contained 98–99 atom % deuterium. The deuterium analyses were performed by reducing a series of ketones containing no  $\alpha$  hydrogens and analyzing the secondary alcohol by nuclear magnetic resonance for residual hydrogen on the alcohol carbon.

Une synthèse du deutériure de bore et de sodium à une échelle molaire a été développée. Le triméthylamineborane est échangé (6) avec l'acide deutériosulfurique dans l'oxyde de deutérium, permettant l'obtention de triméthylamineborane- $d_3$  d'une pureté isotopique très élevée. La réaction du triméthylamineborane- $d_3$  et du méthylate de sodium dans le diglyme à 120–150 °C conduit au deutériure de bore et de sodium, lequel, après purification, est obtenu avec un rendement global de 40–50%. Les conditions pour préparer un produit d'une haute pureté isotopique et chimique sont assez rigoureuses mais, une fois développées, peuvent être facilement reproduites.

Le deutériure de bore et de lithium et le deutériure de bore et de potassium sont aussi préparés à partir du triméthylamineborane- $d_3$  et des méthylates correspondants. Cependant le deutériure de bore et de lithium forme un complexe stable avec les solvants éthers et il est plus convenablement préparé à partir du deutériure de lithium et l'éthérate du trifluorure de bore.

Les deutériures ainsi préparés ont une pureté chimique de 97% et une pureté isotopique de 98–99%. Le contenu de deutérium est déterminé par la réduction de cétones ne possédant aucun proton en position  $\alpha$ , suivi d'une analyse quantitative par résonance magnétique nucléaire.

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### INTRODUCTION

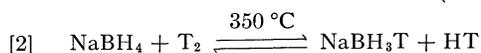
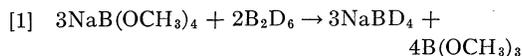
Sodium borohydride is widely used as a selective, relatively mild chemical reducing agent for organic functional groups (1). It is often used as a complement to the much more powerful reagent, lithium aluminium hydride, which reduces a wide range of functional groups rapidly and nonselectively. Thus, sodium borohydride will ordinarily reduce aldehydes and ketones to the corresponding alcohols without affecting carboxylic acid groups or their derivatives. A particular advantage of sodium

borohydride is its greater resistance to hydrolysis, which permits reductions to be performed in aqueous or alcoholic media.

Because of their wide applicability as reducing agents, the deuterium analogues of lithium aluminium hydride and sodium borohydride are very useful reagents for the selective introduction of deuterium into organic compounds. There are literature preparations for lithium aluminium deuteride which allow its preparation from inexpensive starting materials. Holding and Ross (2) have described the preparation of lithium deuteride from the elements and its subsequent transformation into lithium aluminium deuteride. The compound is also commercially available.

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There are isolated reports of the synthesis of sodium borodeuteride, but none of them can be adapted readily to routine preparation. Davis *et al.* (3) have prepared it on a small scale from sodium tetramethoxyborohydride and diborane- $d_6$  (eq. [1]), but the use of molar quantities of diborane is obviously undesirable. Wilzbach (4) has found that tritium gas exchanges with sodium borohydride at 350 °C (eq. [2]). This synthesis could be applied to the deuterio compound, but the use of the isotope is relatively inefficient and there is the technical disadvantage of working at high temperatures and pressures. Another synthesis of sodium and other metal borodeuterides has been disclosed briefly in a patent (5) and may offer a reasonable synthesis if magnesium boride of the right composition can be obtained readily. In this paper we describe a new, convenient synthesis of lithium, sodium, and potassium borodeuterides from readily available starting materials.

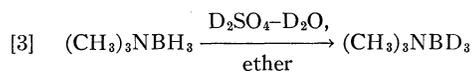


### RESULTS

In a brief communication, Davis *et al.* (6) describe the rapid exchange of the boron hydrogens of trimethylamineborane with deuterium when the amineborane is stirred with acidic heavy water. In the same communication it was mentioned that sodium borodeuteride could be made from the deuterated amineborane, but neither were details given nor was the product analyzed or identified.

We have reinvestigated the reaction from a preparative point of view and have confirmed the ready exchange of the boron hydrogens for deuterium when an ether solution of trimethylamineborane is stirred with acidic heavy water. Methylene chloride serves equally well as a solvent for the amineborane, and presumably any other solvent which would permit easy isolation of the product could be used. The previous workers (6) employed DCl as a catalyst for the exchange. We have also found  $\text{D}_2\text{SO}_4$  to catalyze the exchange readily and have

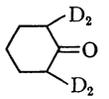
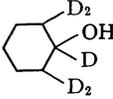
used it routinely in this work (eq. [3]). The product from the exchange reaction was identified as trimethylamineborane- $d_3$  by melting point and mixture melting point (94–95 °C) with starting material; the product sublimes easily and can be transferred on a vacuum line.



Exchanges were performed with up to 6 moles of amineborane, using 0.5 *N*  $\text{D}_2\text{SO}_4$  in  $\text{D}_2\text{O}$  as catalyst. In general, equilibrium was reached after 24 h of vigorous stirring at room temperature, after which the depleted heavy water was replaced by fresh acidic heavy water. The exchange was conveniently followed by withdrawing aliquots, removing the solvent, and comparing infrared spectra recorded in tetrachloroethylene. The strong, broad band at 2 300  $\text{cm}^{-1}$  from trimethylamineborane was seen to disappear almost completely, being replaced by a broad doublet at 1 740  $\text{cm}^{-1}$  from the deuterated compound. Tetrachloroethylene was used as solvent because it does not absorb in the 2 250 – 2 400  $\text{cm}^{-1}$  range. Accurate mass spectral analysis was difficult because of the low intensity of the parent peak, and nuclear magnetic resonance (n.m.r.) analysis for residual hydrogen on boron is made impossible by the line broadening of the boron nuclei (7). Yields of trimethylamineborane- $d_3$  of 60–65% were usually obtained, the losses being due to hydrolysis.

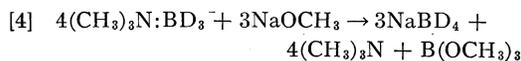
The reaction between trimethylamineborane and sodium methoxide was then investigated with purified diglyme as solvent. No reaction was observed until the temperature reached 120 °C; at this point trimethylamine was evolved and the reaction proceeded smoothly between 130 and 150 °C. Various methods were tried in order to obtain a chemically pure product. Purification by recrystallization from diglyme gave pure material, but the recovery was only 60%. The most effective procedure involved complete removal of the solvent from the crude material under vacuum. This crude product had a chemical purity of 75–90%. Extraction of the above residue with *n*-propylamine and evapora-

TABLE I  
Reduction of ketones with sodium borodeuteride

Ketone	Alcohol	Deuterium content (by n.m.r)
PhCOPh	$\begin{array}{c} \text{OH} \\   \\ \text{PhCDPh} \end{array}$	>99%
PhCOCD <sub>3</sub>	$\begin{array}{c} \text{OH} \\   \\ \text{PhCDCD}_3 \end{array}$	98%
		96.3%
CD <sub>3</sub> COCD <sub>3</sub>	$\begin{array}{c} \text{OH} \\   \\ \text{CD}_3\text{CDCD}_3 \end{array}$	97.2%
CD <sub>3</sub> COCD <sub>3</sub>	$\begin{array}{c} \text{OH} \\   \\ \text{CD}_3\text{CDCD}_3^* \end{array}$	94.2%

\*Commercial sodium borodeuteride was used.

tion of the solvent yielded material of greater than 97% chemical purity. The final yield of purified sodium borodeuteride was 70–80% of the theoretical yield based on eq. [4].

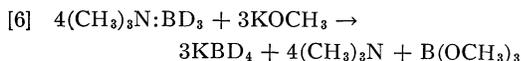
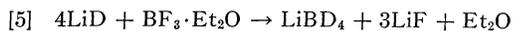


The isotopic purity of the product was most rapidly and conveniently checked by reducing a ketone containing no  $\alpha$  hydrogens and determining the residual hydrogen in the alcohol by n.m.r. Several ketones were reduced and analyzed (Table I). The results of these analyses showed that the products contained 97–98 atom % deuterium. A commercial sample of sodium borodeuteride from Czechoslovakia was found to contain 94–95 atom % deuterium by this method.

Sodium borodeuteride was hydrolyzed with acid and the resulting HD or D<sub>2</sub> was analyzed, but erratic results were obtained. Thus, one sample hydrolyzed with D<sub>2</sub>SO<sub>4</sub>–D<sub>2</sub>O gave deuterium gas containing 88% D<sub>2</sub> and 12% HD, whereas hydrolysis with H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O gave hydrogen containing 81% HD and 19% H<sub>2</sub>. The compound was fully characterized by sodium and boron analyses, the details of which are given in the Experimental.

The preparation of lithium borodeuteride and potassium borodeuteride from trimethylamineborane-*d*<sub>3</sub> was then investigated. Lithium borohydride is a more powerful reducing agent than the sodium or potassium compound and has been used for the reduction of esters (11, 12). It has been prepared by metathesis from sodium borohydride and lithium chloride (13); a number of other preparations are described by Gaylord (1). Potassium borohydride has chemical properties very similar to those of sodium borohydride, although it is not as hygroscopic as the latter, and has a lower solubility in most organic solvents (8); it has also been prepared by metathesis from sodium borohydride and potassium hydroxide (14).

The reaction between lithium methoxide and trimethylamineborane under the same conditions as used for the preparation of sodium borodeuteride yielded 83% of the theoretical amount of trimethylamine (as the hydrochloride) and a 1:1 solvate of lithium borohydride (or deuteride) and diglyme in a 70% yield. Since it was rather difficult to obtain a pure product from the stable solvate, a number of other approaches were investigated (Table II); the most successful synthesis is based on the reaction between lithium deuteride and boron trifluoride etherate (eq. [5]) as described by Wittig and Hornberger (17). This gave a 57% yield of lithium borodeuteride of a high isotopic purity.



The direct synthesis of potassium borodeuteride from potassium methoxide and trimethylamineborane-*d*<sub>3</sub> in diglyme (eq. [6]) proved to be a straightforward reaction. The product, isolated in over a 70% yield, had a chemical purity of 94% and an isotopic purity of 98%.

#### DISCUSSION

The present synthesis of the alkali metal borodeuterides makes it possible to prepare these compounds in molar quantities from readily available starting materials by

TABLE II  
 Syntheses of lithium borodeuteride

Reagents	Solvent	Conditions	Product*
NaBD <sub>4</sub> , LiCl	<i>n</i> -PrNH <sub>2</sub>	Reflux	LiBD <sub>4</sub> (53% yield, 91.6% D)†
NaBD <sub>4</sub> , LiCl	<i>n</i> -PrNH <sub>2</sub>	Reflux, NaOH	LiBD <sub>4</sub> (80% D)
NaBD <sub>4</sub> , LiCl	EtNH <sub>2</sub>	Reflux	LiBD <sub>4</sub> (95% D)†
LiOCH <sub>3</sub> , Me <sub>3</sub> N:BD <sub>3</sub>	Diglyme	140 °C	1:1 complex
LiOCH <sub>3</sub> , Me <sub>3</sub> N:BD <sub>3</sub>	Dimethoxyethane	140 °C	Viscous liquid
LiD, Me <sub>3</sub> N:BD <sub>3</sub>	Ether	130 °C	Starting material (90%)‡
LiD, BF <sub>3</sub> ·Et <sub>2</sub> O	Ether	140 °C	LiBD <sub>4</sub> (57% yield, >98% D)§

\*The figures in parentheses refer to the chemical yield and (or) the deuterium content.

†Reference 13.

‡Reference 18.

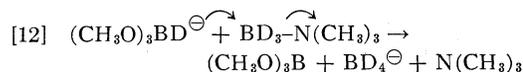
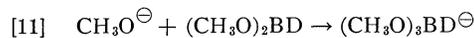
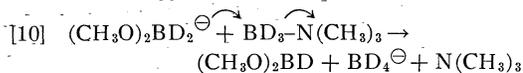
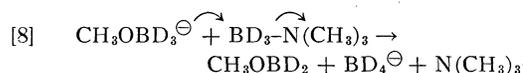
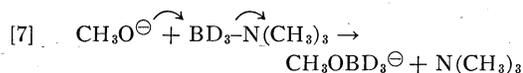
§Reference 17.

using standard laboratory procedures. In one experiment, sodium borodeuteride was prepared from trimethylamineborane-*d*<sub>3</sub> and sodium methoxide containing 20% sodium hydroxide. The isolated product contained 98.5 atom % deuterium. This result is in agreement with general experience in these laboratories and others (15) that boron hydrides (or deuterides) do not undergo base-catalyzed exchange of hydridic hydrogen. It also has the added advantage that it is not necessary to take extreme precautions to keep the sodium methoxide anhydrous. However, it was found that commercial sodium methoxide gave very low yields of sodium borodeuteride, apparently because of the presence of free methanol. No reaction was observed between commercial sodium oxide and trimethylamineborane in diglyme at 160 °C. In a large number of preparations, the sodium borodeuteride obtained by this synthesis has been found routinely to contain 98–99 atom % deuterium.

Several solvents other than diglyme were used in an effort to find one which did not require such careful purification before use. Butyl ether, veratrole, and decalin were tried, but none of these gave product yields as high as those obtained with diglyme.

In one of the preparations of sodium borodeuteride, trimethyl borate was isolated from the diglyme filtrate by distillation and identified by comparison of its infrared spectrum with that of an authentic sample. This served to confirm, qualitatively, the stoichiometry of eq. [4].

Brown *et al.* (16) have shown that alkoxyborohydrides are more powerful hydride transfer agents than borohydride itself. The sequence of reactions shown in eqs. [7]–[12] would then provide a qualitative mechanism for the reaction between sodium methoxide and trimethylamineborane-*d*<sub>3</sub> to form sodium borodeuteride and trimethylborate.



#### EXPERIMENTAL

The infrared spectra were recorded on a Perkin-Elmer 21 spectrophotometer, and the n.m.r. spectra on a Varian A-60 instrument. The melting points were determined on a Fisher-Johns apparatus and are uncorrected.

##### Trimethylamineborane-*d*<sub>3</sub>

The procedure of Davis *et al.* (6) was modified as follows. A solution of 400 g of commercial trimethylamineborane (Callery Company, Callery, Pennsylvania) in 4 l of dry diethyl ether was filtered through a plug of glass wool. The solution was stirred vigorously for 24 h with 500 ml of 0.5 *N* deuterio-sulfuric acid in deuterium oxide, in a flask with an outlet for the deuterium gas that was evolved. The

TABLE III  
Analysis of sodium borodeuteride

Method	Calculated	Found	% of theoretical
1. Acid titration for potential base (methyl red)	—	—	98.6, 98.5, 98.3
2. Deuteride (hydrolysis of a 20 mg sample)	42.8 ml of gas	41.7 ml of gas	97.4
3. Sodium (flame photometric determination)	54.9% Na	53.7% Na	97.8
4. Boron (mannitol titration)	25.80% B	25.22% B	97.7

used deuteriosulfuric acid was replaced with 500 ml of fresh 0.5 *N* deuteriosulfuric acid, which was stirred as before for 24 h. The exchange was continued with a total of ten 500 ml portions of acid. The ethereal solution was then washed once with 200 ml of deuterium oxide and dried over anhydrous granulated sodium carbonate, which was filtered off through a glass wool plug. The ether was evaporated at reduced pressure, leaving 240 g of white crystals, m.p. 94–95 °C (undepressed on admixture with starting material).

To follow the exchange, aliquots of the ethereal solution were withdrawn, dried over anhydrous sodium carbonate, and evaporated. The infrared spectra of the residues dissolved in tetrachloroethylene showed the gradual disappearance of the 2300  $\text{cm}^{-1}$  B—H band, and the appearance of a strong broad doublet at 1740  $\text{cm}^{-1}$  attributable to B—D bonds.

The used exchange waters were re-used in later preparations, immediately after the addition of a further 12.4 g (250 meq) of 98% deuteriosulfuric acid to each 500 ml.

#### Sodium Borodeuteride

A 1 l flask was fitted with a mechanical stirrer, dry-nitrogen inlet, and cold-water condenser. A mixture of 122 g (1.61 moles) of trimethylamineborane- $d_3$ , 65 g (1.20 moles) of alcohol-free sodium methoxide, and 400 ml of diglyme (redistilled under reduced pressure from sodium borohydride) was stirred under an atmosphere of dry nitrogen while the temperature was slowly increased from 70 to 150 °C (wax bath). The trimethylamine that was evolved was allowed to pass through the condenser, a drying tube containing calcium sulfate, and a small oil bubbler, and then was absorbed in concentrated hydrochloric acid. The recovery of trimethylamine hydrochloride was almost theoretical. The temperature was held at 150 °C until amine evolution ceased (about 4 h). The reaction mixture was filtered under suction while hot, and insoluble material was pumped to constant weight on the steam bath to yield 51 g of a white powder. This sodium borodeuteride was 88% chemically pure, as determined by the volume of hydrogen evolved on hydrolysis with acid. Similar results were obtained by iodate-thiosulfate titration (9). The crude product was stirred with 550 ml of *n*-propylamine (redistilled from calcium hydride) for  $\frac{1}{2}$  h and centrifuged, and the clear supernatant liquid was separated. Evaporation and drying *in vacuo* on the steam

bath gave 37 g (0.88 mole, 74% of theoretical) of sodium borodeuteride of 97% chemical purity.

#### Analysis of Sodium Borodeuteride

In addition to the deuterium content obtained from the reductions listed in Table I, independent chemical analyses were carried out to establish the identity and purity of the product.

Qualitative spectrographic emission analysis showed that sodium and boron were the only metals present to an extent greater than 0.1%. A 500 mg sample, when held at 100 °C for 3 h *in vacuo*, lost 0.04% by weight.

The results of the elemental analyses are summarized in Table III.

#### Lithium Borodeuteride (17)

Lithium deuteride (5 g, 560 mmoles) and diethyl ether (40 ml) were placed in a steel bomb and cooled in a Dry Ice–Freon bath. To the cooled mixture was added 14.9 g (105 mmoles) of boron trifluoride etherate, also precooled to –60 °C. The bomb was sealed immediately and warmed to room temperature; an extremely exothermic reaction occurred. When the initial reaction had subsided, the bomb was shaken at 140 °C for 17 h, cooled to room temperature, and opened cautiously. Only a very slight positive pressure was observed. The contents of the bomb were decanted into a centrifuge tube along with the ether rinsings of the bomb. After centrifugation, the clear supernatant liquid was placed in the refrigerator overnight to yield a mass of long white needles, which, when pumped to dryness, yielded 590 mg of product. Complete evaporation of the filtrate yielded a further 955 mg (total yield, 1.55 g or 57% based on boron trifluoride etherate).

After reduction of a sample of benzophenone, no benzylic hydrogen could be detected by n.m.r. analysis of the resulting benzhydrol (see below).

#### Potassium Borodeuteride

By using the procedure described for sodium borodeuteride, trimethylamineborane- $d_3$  (11.7 g, 154 mmoles) and potassium methoxide (8.4 g, 120 mmoles) were reacted in 40 ml of diglyme. The crude material was extracted three times with 150 ml of cold ethanol, the insoluble potassium borodeuteride being separated by centrifugation and dried *in vacuo*. The yield of 94% pure potassium borodeuteride was 6.0 g (97 mmoles, 80% yield based on trimethylamineborane- $d_3$ ). The isotopic purity was found to be 98% (see below).

*Isopropyl-d<sub>7</sub> Alcohol (10)*

Acetone-d<sub>6</sub> (4 g, 62 mmoles) was transferred on a vacuum line onto 0.8 g (19 mmoles) of sodium borodeuteride. When allowed to warm to room temperature, the reaction mixture swelled to a fluffy mass and heat was evolved. After the mixture was left for 2 h at room temperature, any unreacted acetone-d<sub>6</sub> was pumped away and 11 g of deuterium oxide was added. The alcohol was distilled off at atmospheric pressure, redistilled from 20 ml of water, and dried over sodium hydroxide. The n.m.r. spectrum showed 2.8% hydrogen on carbon 2 of the alcohol (evaluated by comparison with the hydrogen remaining in positions 1 and 3, previously determined by mass spectral analysis of the acetone-d<sub>6</sub>).

*Benzhydrol-α-d<sub>1</sub>**From Lithium Borodeuteride*

To a 200 ml, three-necked, round-bottomed flask fitted with a dropping funnel, reflux condenser, and dry-nitrogen source was added 35 ml of ether and 260 mg (40 meq) of lithium borodeuteride. The mixture was refluxed for 1 h to effect solution, and cooled; then 3.6 g (20 meq) of benzophenone in 25 ml of ether was added over 15 min, with no visible evidence of heat evolution or reaction. After being heated to reflux for 2.5 h, the reaction mixture was left at room temperature for 16 h. The excess deuteride was then destroyed with dilute aqueous sulfuric acid, the ether layer was separated, washed with dilute sodium bicarbonate, dried (CaCl<sub>2</sub>), and filtered, and the solvent was evaporated to give 3.3 g of a crude white crystalline product showing no carbonyl band in its infrared spectrum. Crystallization from 35 ml of ligroin (b.p. 65–110 °C) yielded 2.8 g (15 mmoles, 75%) of long white needles, m.p. 66–67 °C (lit. m.p. 68–69 °C). An n.m.r. analysis showed that there was less than 2% hydrogen on the carbinolic carbon atom.

*From Potassium Borodeuteride*

To a solution of 600 mg (10 mmoles) of potassium borodeuteride in 20 ml of ethylenediamine was added 1.8 g (10 mmoles) of benzophenone all at once. The reaction was heated and stirred at 60 °C for 1.5 h and at room temperature overnight; then it was poured into 200 ml of ice-cold water and the product extracted with ether (50, 50, and 100 ml). The ether extracts were washed with 2 N HCl solution and with cold water, dried, and taken to dryness. An infrared spectrum of the crude product showed that both hydroxyl and carbonyl groups were present. Crystallization from 15 ml of hot ligroin (b.p. 60–110 °C) yielded 1.0 g (5.4 mmoles, 54%) of long white needles, m.p. 66–67 °C.

An n.m.r. analysis indicated less than 2% hydrogen on the carbinolic carbon atom.

The reduction was also attempted in an aqueous system at 60–70 °C and in *N,N*-dimethylformamide solution, but the product was largely unreacted benzophenone.

## ACKNOWLEDGMENTS

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