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.

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

Procedures for the Preparation of Methyl Borate[1]

BY H. I. SCHLESINGER, HERBERT C. BROWN, DARWIN L. MAYFIELD AND JAMES R. GILBREATH

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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 reexamined 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.[2] Many have carried the reaction out in autoclaves under pressure[2f,g,h]; others have used concentrated sulfuric acid to facilitate the reaction.[2k,l,m,n]

Perhaps the most convenient procedure for the preparation of methyl borate in quantity is that of Webster and Dennis.[2i] 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°.[3] 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

$$B_2O_3 + 3CH_3OH \longrightarrow (CH_3O)_3B + H_3BO_3$$

Actually, however, the distillate from this reaction mixture consisted of the azeotrope[4] 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.[4]

$$H_3BO_3 + 4CH_3OH \longrightarrow [(CH_3O)_3B + CH_3OH]\uparrow + 3H_2O$$

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.

$$\begin{aligned}&Na_2B_4O_7\cdot 10H_2O + 2H_2SO_4 + 16CH_3OH \longrightarrow \\ &\qquad 2NaHSO_4 + 4[(CH_3O)_3B + CH_3OH]\uparrow + 17H_2O\end{aligned}$$

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

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

(2) (a) Ebelman and Bouquet, *Ann.*, **60**, 252 (1846); (b) V. Gasselin, *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, *Ukrainskii 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**, 6675 (1937); (f) H. Schiff, *Ann. Supl.*, **5**, 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.

(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 $[(CH_3O)_3B + CH_3OH]$.

removal with the methanol. As described in the Experimental Part, the procedure may be improved by extracting the methanol from a mixture of the azeotrope and ligroin.

A second method of freeing the methyl borate from methanol is to add to the azeotropic mixture a substance which forms a second methanol azeotrope of boiling point lower than that of the methanol–methyl borate azeotrope. This lower boiling azeotrope is then distilled away from the methyl borate. Of the several azeotropes having the desired properties, the methanol–carbon disulfide one (14% methanol by weight) is the most satisfactory. As described in the Experimental Part, this procedure leads to the recovery of about 92% of the methyl borate.

A third and, in our opinion, the best method of separation consists of the addition of salts to the azeotrope. Calcium chloride has previously been used for this purpose,[2h] but we did not find it satisfactory. The salt swells greatly in the process and from the resulting large bulk of solid material the methyl borate is difficult to recover. Furthermore, only about 80% of the methanol was reclaimed.

Comparative results obtained with several salts are shown in Table IV, from which it may be seen that zinc chloride and lithium chloride are the most satisfactory. Of the two, the latter is to be preferred since less of it is needed and since recovery of the alcohol by simple distillation is more nearly complete than when zinc chloride is used. The details of this procedure are also described in the Experimental Part, where it is shown that a 96% yield of 99.6% pure methyl borate may be achieved.

Experimental Part

Materials.—Boric oxide, boric acid and borax were obtained from the Pacific Coast Borax Co. They were analyzed for boron content by titration in the presence of mannitol.[5] Yields were calculated on the basis of the boron content of the products. The methanol was a commercial product (99%) and was utilized without purification. All other chemicals were the usual C.P. reagents.

Properties of the Azeotrope.—The composition of the methyl borate–methanol azeotrope had not been accurately determined previously.[3] A sample of the azeotrope was distilled through a Podbielniak Heli-grid Column rated at 100 plates. The following data were obtained: b.p. 54° at 750 mm.; n^{20}_{D} 1.3488; 75.5% methyl borate by weight.

A. Preparation of Azeotrope

(1) **From Methanol and Boric Oxide or Boric Acid.**—Four moles of methanol was placed in a 5-l., 3-neck round-bottom flask fitted with a mercury sealed stirrer and a reflux condenser, the use of which was adequate because no attempt was made to separate the small excess of methanol from the azeotrope. Through the third neck, one mole of anhydrous boric oxide (99.5% purity) was introduced in small quantities at such a rate that the mixture refluxed gently. The reaction mixture was heated for an hour following completion of the addition. The reflux condenser was converted to a downward condenser and the material distilling up to 70° was collected in a flask protected from atmospheric moisture. The yield was essentially quantitative according to the equation $B_2O_3 + 4CH_3OH \rightarrow [B(OCH_3)_3CH_3OH] + H_3BO_3$. The effect of the methanol-boric oxide ratio on the yield of methyl borate as azeotrope is summarized in Table I.

TABLE I

EFFECT OF METHANOL–BORIC OXIDE RATIO ON YIELD OF METHYL BORATE

Boric oxide, G.	Boric oxide, Moles	Methanol G.	Methanol Moles	Mole ratio	Wt. of distillate, g.	Borate in distillate, %	Yield, %
1400	20	1920	60	3:1	1871	79.7	71.6
1400	20	2240	70	3.5:1	2353	79.6	89.9
1400	20	2560	80	4:1	2756	75.0	99.4
1400	20	3200	100	5:1	3279	63.5	100.0

When the methanol–boric oxide ratio was less than 4:1, the residual material was gummy and difficult to handle. Presumably, methyl metaborate,[2f] $(CH_3OBO)_x$, was present. When 12 moles of methanol instead of 4 were used per mole of boric oxide, 96.7% of the latter was converted to the azeotrope. Similarly, from 124 g. (2 moles) of boric acid and 512 g. (16 moles) of methanol, a 92.6% yield of azeotrope was obtained.

From Borax and Methanol.—A 1-l. round-bottom flask was attached to a column, 25 mm. i.d. by 75 cm. in length, packed with $^3/_{16}''$ stainless steel helices and rated at 15 theoretical plates. The flask was charged with 0.5 mole of borax ($Na_2B_4O_7 \cdot 10H_2O$; analysis for boron 99% of theoretical), 16 moles of methanol and 1 mole of sulfuric acid. The reaction mixture was slowly distilled. The major portion of the product was obtained as the azeotrope at 54°; a smaller fraction containing methyl borate was obtained at 54–62°. The yield was calculated on the total borate contained in both fractions. Data on the effect of methanol-borax ratio are summarized in Table II.

TABLE II

EFFECT OF METHANOL–BORAX RATIO ON YIELD OF METHYL BORATE

Borax[a] G.	Borax[a] Moles	Methanol G.	Methanol Moles	Mole ratio[b] MeOH: $Na_2B_4O_7 \cdot 10H_2O$	Time, hr.	Total yield ester, %
191	0.5	384	12	24:1	10	87.8
191	.5	512	16	32:1	9	92.9
191	.5	640	20	40:1	9	92.2

[a] Sulfuric acid–borax ratio: $2H_2SO_4 : 1Na_2B_4O_7 \cdot 10H_2O$. [b] Calculated ratio for azeotrope, 16:1.

When the quantity of sulfuric acid was reduced to the ratio of $1H_2SO_4 : 1Na_2B_4O_7$, the yields were identical with those reported in Table II, but the reaction was somewhat slower. In a typical experiment, instead of 9 hours, a reaction time of 16 hours was required to obtain an ester yield of 92.4%. It should be pointed out, however, that the reaction time is primarily dependent upon the efficiency and capacity of the column.

B. Separation of Azeotrope

(1) **Sulfuric Acid Separation.**—Data for a number of experiments utilizing concentrated sulfuric acid to extract the methanol from the azeotrope are listed in Table III. The acid was added in portions, the number and quantity of which are shown in the second and third columns. Comparison of these columns with the following ones shows that it was advantageous to use several small portions rather than a few larger ones.

TABLE III

EXTRACTION OF METHANOL FROM AZEOTROPE WITH SULFURIC ACID

Azeotrope, ml.	Sulfuric acid Portions	Sulfuric acid Ml.	Methanol in acid layers, %	Borate in acid layers,[a] %
3000	3	60, 40, 40	70	24
3000	5	60, 4 × 20	85	20.5
3000	10	60, 9 × 10	98	14.5
3000	10	60, 9 × 10	96.6	15.2
1000	10	20, 9 × 4	97.5	15.8

[a] The weight of the acid layer was determined. Since the weight of acid it contained was known and the quantity of methyl borate was obtained by a boric acid determination, the amount of methanol was determined by difference.

Distillation of the extracted borate ester yielded a small first fraction at 54° which contained the remaining methanol and a second fraction of practically pure methyl borate

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(5) J. A. M. van Liempt, *Rec. trav. chim.*, **39**, 358 (1920).

(b.p. 67.5–68° at 750 mm.). The over-all yield was 89%. The last column shows that even in the most favorable experiment 14.5% of the methyl borate was lost as part of the acid layer.

A mixture of 570 ml. (500 g.) of the azeotrope and 570 ml. of ligroin (b.p. 110°, previously washed with sulfuric acid) was treated with two portions of 20 ml. of sulfuric acid. Only 4.8% of the ester was lost and 98.1% of the methanol was removed. Distillation of the solvent led to 91.2% yield of ester boiling from 67.5–68.5°.

Azeotropic Separation.—A mixture of 2800 g. of the azeotrope and 1400 g. of carbon disulfide was fractionally distilled with the aid of the column employed for the preparation of the azeotrope. The carbon disulfide–methanol azeotrope distilled at 38°. The distillate separated into two layers, of which the lower one (97% carbon disulfide–3% methanol) was returned to the still. At the end of 45 hours of operation, methanol removal was complete, as indicated by the rise in boiling point to that of carbon disulfide, 46°. The products were a carbon disulfide–methanol fraction of 2105 g., a fraction from 46 to 67.5° of 88 g. (73% ester) and 1940 g. of pure methyl borate, b.p. 67.5–68.5°. The yield was 92.3%. The reaction time could probably be greatly decreased by the use of a more efficient column.[6]

Lithium Chloride Separation.—The effectiveness of a number of salts in separating the methanol from the azeotrope was studied. Data are summarized in Table IV.

The addition of 120 g. of anhydrous lithium chloride to 1000 g. of the azeotrope caused the mixture to separate into two layers.[7] The lower one consisted of a solution of lithium chloride in methanol plus some suspended salt and contained from 3.6 to 4.0% of the methyl borate present in the azeotrope. The upper layer contained about 96% of the methyl borate of from 99.5 to 99.7% purity; the slight contamination was methanol.

TABLE IV

EXTRACTION OF METHANOL FROM THE AZEOTROPE WITH SALTS

Salt used	LiCl	NaCl	$CaCl_2$	$Ca(NO_3)_2$	$AlCl_3$	$MgCl_2$	$ZnCl_2$
G. salt per 135 g. azeotrope	13	30	14	30	8.0	15	46
Purity of methyl borate, %	99.6	98.0	92.5	90	85	98.2	99.6

The methanol was recovered from the lower layer by distillation. Below 90°, the small quantity of the methyl borate present distilled as the azeotrope. At a pot temperature of from 95 to 115°, 96% of the methanol was recovered practically pure. At this stage the lithium chloride was obtained partly as a powder and partly as readily powdered lumps.

By raising the temperature to 160°, the remaining 4% of the methanol could be recovered. When that was done, the lithium chloride was obtained as a hard cake which, though usable, was inconvenient to handle. It is, therefore, recommended that heating the residue above 115° be avoided if the lithium chloride is to be re-used in subsequent separations.

Acknowledgment.—The assistance of Anthony M. Schwartz and E. K. Hyde with individual experiments and preparations described in this paper, is gratefully acknowledged.

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(6) The advantage of recycling a portion of the carbon disulfide is lost if the carbon disulfide–methanol mixture contains as little as 1.5% of methyl borate, for then separation into two layers does not occur. This difficulty is avoided by use of a good fractionating column.

(7) Although a smaller amount (80 g.) of the salt seems to saturate the solution, the larger quantity gives somewhat better results.

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

Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen[1]

BY H. I. SCHLESINGER, HERBERT C. BROWN, A. E. FINHOLT, JAMES R. GILBREATH, HENRY R. HOEKSTRA AND EARL K. HYDE

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Sodium borohydride reacts slowly with water ultimately to liberate 4 moles of hydrogen per mole of the compound at room temperature, or 2.4 l. per gram. The reaction is greatly accelerated by rise of temperature or by the addition of acidic substances, for which latter purpose boric oxide is convenient and effective when the objective is the generation of hydrogen. Particularly striking is the catalytic effect of certain metal salts, especially that of cobalt(II) chloride. Thus pellets of sodium borohydride containing only 5% of the cobalt salt react as rapidly as those containing 10 times that amount of boric oxide. The effect of the cobalt salt is ascribed to the catalytic action of a material of empirical composition, Co_2B, which is formed in the initial stages of the reaction.

The hydrolysis of sodium borohydride is of interest in connection with the use of the compound as a reducing agent in aqueous solutions[2] and because of its potential usefulness for the generation of hydrogen whenever or wherever the use of the compressed gas is inconvenient. Under appropriate conditions, 2.37 l. of hydrogen (gas at S.T.P.) are liberated per mole of the compound, as compared with 1.1 l. for calcium hydride and 2.8 l. for lithium hydride. At ordinary temperatures, however, only a very small percentage of the theoretical amount of hydrogen is liberated at an appreciable rate, since the initial moderately rapid rate soon decreases after the borohydride and the water have been mixed. As a result, not only may the aqueous solution of the compound be effectively used as a chemical reagent, but a large part of the salt may actually be recovered unchanged from such solutions by removal of water *in vacuo*.[3]

It is evident that the decrease in the initial rate of hydrogen evolution is due to the increasing *p*H of the solution[4] which in turn is caused by the formation of the strongly basic metaborate ion

$$BH_4^- + 2H_2O \longrightarrow BO_2^- + 4H_2$$

Thus the initial generation of hydrogen may be

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

(2) (a) H. I. Schlesinger, H. C. Brown and A. E. Finholt, *ibid.*, **75**, 205 (1953). (b) S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 122 (1949); unpublished work of G. W. Schaeffer and A. Stewart. (c) A. Stewart, Master's Thesis, University of Chicago (1948).

(3) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, THIS JOURNAL, **75**, 199 (1953).

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