[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Convenient Procedures for the Preparation of Alkyl Borate Esters[1-3]

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Primary, secondary and tertiary alkyl borate esters can be prepared conveniently and in good yield by the transesterification of methyl borate with the appropriate alcohol. The high volatility of the methanol-methyl borate azeotrope provides a means of driving the reaction to completion. In the presence of one equivalent of acetic acid, sodium borohydride reacts smoothly with primary and secondary alcohols at room temperature in accordance with the equation: $3ROH + NaBH_4 + HOAc \rightarrow (RO)_3B + NaOAc + 4H_2$. Under the same conditions, tertiary alcohols liberate but three moles of hydrogen, with the fourth mole being formed only at higher temperatures: $2ROH + NaBH_4 + HOAc \rightarrow (RO)_2BH + NaOAc + 3H_2$; $ROH + (RO)_2BH \rightarrow (RO)_3B + H_2$. This reaction provides a convenient general procedure for the synthesis of alkyl borates of all types.

In continuing our studies of alkoxy substituted borohydrides,[6] a convenient synthesis of secondary and tertiary alkyl borates became desirable.[7]

The transesterification of one alcohol with the borate ester of another alcohol was studied by Schiff.[8] This method has been recommended for cases where other methods fail.[9] Accordingly, the alcoholysis of a borate was selected for study.

Methyl borate is now readily available[10] and the low boiling point of the methanol—methyl borate azeotrope (b.p. 54.5°, nearly equimolar in the two components) provides a convenient means of shifting the reaction to completion

$$4(CH_3O)_3B + 3ROH \longrightarrow (RO)_3B + 3[CH_3OH, (CH_3O)_3B]$$

The transesterification of methyl borate was therefore examined as a synthetic route to the higher alkyl borates.

Addition of an equivalent of acid to mixtures of sodium borohydride and alcohol results in the evolution of hydrogen and the formation of the borate ester. Accordingly this reaction was also examined for its utility as a general procedure for the synthesis of alkyl borates.

Results and Discussion

The transesterification of methyl borate (in excess) by ethyl, isopropyl and *t*-butyl alcohols proceeded readily at the boiling points of the reaction mixtures. A fractionating column (15 theoretical plates) made it possible to remove the methyl borate–methyl alcohol azeotrope from the reaction mixture. The higher esters could be isolated by a simple distillation. Yields of 50–60% (based on alcohol) of ethyl, isopropyl and *t*-butyl borate were realized.[11]

Typical experimental results are summarized in Table I.

TABLE I

PREPARATION OF ALKYL BORATE ESTERS BY THE TRANSESTERIFICATION REACTION

Borate	Reaction mixture Methyl borate, moles	Alcohol, moles	Yield, %
Ethyl	2.07	1.70	62.5
Isopropyl	1.76	1.43	58.0
t-Butyl	1.92	1.60	54.5

The procedure based on sodium borohydride offered considerable advantage in yield, ease of operation and convenience. Consequently, major attention was devoted to the study of this synthetic route.

Sodium borohydride reacts readily with both methyl and ethyl alcohol at their boiling points.

$$4ROH + NaBH_4 \longrightarrow NaB(OR)_4 + 4H_2$$

Addition of an equivalent of acid results in the liberation of one mole of the corresponding alkyl borate. However, in the case of secondary and tertiary alcohols, such as isopropyl and *t*-butyl, no reaction is observed upon heating the alcohols under reflux with the borohydride for extended periods of time.[12]

The addition of an equivalent of acetic acid to a mixture of sodium borohydride and excess isopropyl alcohol results in evolution of four moles of hydrogen and formation of isopropyl borate. The ester is readily separated from the reaction mixture in yields of nearly 90%.

$$3(CH_3)_2CHOH + NaBH_4 + H^+ \longrightarrow [(CH_3)_2CHO]_3B + 4H_2 + Na^+$$

The reaction proceeds considerably more slowly in the case of the tertiary alcohols. In these cases only three equivalents of hydrogen are evolved at room temperature. The fourth equivalent of hydrogen forms only upon extended heating of the reaction mixture under reflux.

No difficulty was encountered in esterifying an unsaturated alcohol, such as allyl alcohol.

The results are summarized in Table II.

The results suggest that the equivalent of acid liberates borine from the borohydride. The hydride reacts rapidly at room temperature with the primary and secondary alcohols to liberate three equivalents of hydrogen and to form the desired

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(1) Addition Compounds of the Alkali Metal Hydrides. V.

(2) Based upon a thesis submitted by E. J. Mead in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Based upon a thesis submitted by C. J. Shoaf in partial fulfillment of the requirements for the degree of Master of Science.

(4) Research assistant on a National Science Foundation Grant, 1953–1954.

(5) Research assistant on Contract DA-33-008-ORD-992 supported by the Office of Ordnance Research, U. S. Army.

(6) H. C. Brown and E. J. Mead, THIS JOURNAL, **75**, 6263 (1953).

(7) For a discussion of the difficulties involved in applying literature methods to the synthesis of tertiary alkyl borates, together with pertinent literature references, see P. D. George and J. R. Ladd, THIS JOURNAL, **77**, 1900 (1955).

(8) H. Schiff, *Ann. Suppl.*, **5**, 154 (1867).

(9) M. H. Wuyts and A. Duquesne, *Bull. soc. chim. Belg.*, **48**, 77 (1939).

(10) H. I. Schlesinger, H. C. Brown, D. R. Mayfield and J. R. Gilbreath, THIS JOURNAL, **75**, 213 (1953).

(11) The preparation of *t*-butyl borate by the reaction of *t*-butyl alcohol with ethyl borate has recently been reported (ref. 7).

(12) H. C. Brown, E. J. Mead and B. C. Subba Rao, THIS JOURNAL, **77**, 6209 (1955).

TABLE II

PREPARATION OF ALKYL BORATE ESTERS BY THE SODIUM BOROHYDRIDE REACTION

Borate	Reaction mixture: Alcohol, ml.	Reaction mixture: Borohydride, moles	Reaction mixture: Acetic acid, moles	Hydrogen evolved, l. (S.T.P.)	Yield, %
Ethyl	250	0.201	0.220	18.4	93.1[a]
Isopropyl	250	.174	.191	15.6	88.5
t-Butyl	500	.448	.492	40.0	99.0
t-Amyl	250	.180	.198	16.2	85.6
Allyl	250	.197	.217	17.7	91.5

[a] Ethyl borate forms an azeotrope with ethanol and the product is obtained both in the form of ethyl borate (70%) and in the form of the azeotrope (30%). The yield includes ethyl borate recovered from the azeotrope by treatment with sulfuric acid.

ester.[13] In the case of *t*-butyl and *t*-amyl alcohols the reaction apparently stops at the di-*t*-alkoxyborine stage, with the last hydrogen atom undergoing replacement only at higher temperatures.

$$NaBH_4 + H^+ \longrightarrow Na^+ + H_2 + [BH_3]$$
$$2ROH + [BH_3] \longrightarrow (RO)_2BH + 2H_2$$
$$ROH + (RO)_2BH \longrightarrow (RO)_3B + H_2$$

The procedure offers a convenient general synthesis of borate esters in yields of approximately 90%.

Experimental Part

Materials.—Research grade ethyl, isopropyl, *t*-butyl and *t*-amyl alcohols were dried over calcium hydride. Allyl alcohol was dried over Drierite. The dried alcohols were distilled through fractionating columns until material of constant b.p. and $n^{20}D$ was obtained. Methyl borate (99%) and sodium borohydride (93%), both from Metal Hydrides, Inc., were utilized without further purification.

Preparation of *t*-Butyl Borate by the Transesterification Reaction.—Methyl borate (200 g., 1.92 moles) and *t*-butyl alcohol (118 g., 1.60 moles) were placed in a 500-ml., round-bottomed flask attached to a packed fractionating column. The column was brought to equilibrium and the methyl borate–methanol azeotrope removed (178 g.). The residue was flash distilled to yield 94 g. of crude product, b.p. 30–60° at 12 mm. On refractionation, *t*-butyl borate, b.p. 60.0–61.0° at 12 mm., was obtained in a yield of 54.5%.

Identical procedures were utilized for the preparation of ethyl and isopropyl borates.

Failure to achieve higher yields appeared to be due in part to the formation of mixed esters, as indicated by fractions having boiling points between those of the azeotrope and the ester product, and in part to some thermal decomposition of the product, as indicated by the formation of white, semi-solid residues. It is probable that these difficulties could be circumvented. However, the borohydride procedure proved so satisfactory that further study of the transesterification method was dropped.

Preparation of *t*-Amyl Borate by the Sodium Borohydride Procedure.—The following procedure is typical. In a carefully dried 500-ml. round-bottomed flask, equipped with a "Dry Ice" condenser (leading to a wet-test meter), a pressure equalized dropping funnel, and a magnetic stirrer, were placed 250 ml. of *t*-amyl alcohol and 6.84 g. (0.180 mole, corrected for impurity) of sodium borohydride. Acetic acid, 11.9 g. (0.198 mole), was added dropwise to the borohydride–alcohol slurry over a period of 11 minutes. The reaction mixture was then heated to reflux temperature for an additional 4 hours. Hydrogen evolved was 16.15 l. at S.T.P. (0.721 mole). The product was distilled through a modified Widmer column, the *t*-amyl alcohol being taken off at atmospheric pressure and the *t*-amyl borate being collected at 87° at 6 mm. The product weighed 42 g. (0.154 mole), a yield of 85.6% based on borohydride.

In ordinary preparations it is quite satisfactory to replace the "Dry Ice" condenser by a simple Vigreux column and distilling head, venting the hydrogen into a hood. The product can then be distilled directly from the reaction vessel.

Physical constants for the borate esters are summarized in Table III.

TABLE III

PHYSICAL CONSTANTS OF THE BORATE ESTERS

Borate	B.p. °C.	B.p. Mm.	$n^{20}D$	Anal.,[a] % B Calcd.	Anal.,[a] % B Found
Ethyl	118–119	743	1.3798	7.70	7.71
Isopropyl	90	120	1.3762	5.76	5.79
	75	76			
t-Butyl	53	9	1.3872	4.70	4.72
t-Amyl	105	13	1.4112	3.99	3.98
	87	6			
Allyl	42	7	1.4496	5.95	5.96

[a] By hydrolysis, followed by titration of the boric acid in the presence of mannitol.

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[13] The reaction of diborane with methanol to form dimethoxyborine and methyl borate was examined by A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **55**, 4020 (1933).

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The Preparation and Properties of Sodium Tetraalkoxyborohydrides[1,2]

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Sodium tetramethoxy-, tetraethoxy- and tetraisopropoxyborohydrides are conveniently prepared by the direct combination of the borate esters with the appropriate sodium alkoxide. However, no reaction was observed between sodium *t*-butoxide and tri-*t*-butyl borate. The thermal stabilities and solubilities of the tetraalkoxyborohydrides were examined.

Further study of the alkoxy substituted borohydrides[4] revealed that the products readily disproportionate. In investigating these reactions, information was required on the solubilities of the sodium tetraalkoxyborohydrides, one of the products of the disproportionation reaction. We undertook to prepare sodium tetramethoxy-, tetraethoxy-, tetraisopropoxy- and tetra-*t*-butoxyborohydrides and to determine their solubilities in a number of solvents.

Tetramethoxy- and tetraethoxyborohydrides of lithium, sodium, potassium, calcium, zinc and thallium have been prepared by direct combina-

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[2] Based upon a thesis submitted by E. J. Mead in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Research assistant on a National Science Foundation Grant, 1953–1954.

[4] H. C. Brown and E. J. Mead, THIS JOURNAL, **75**, 6263 (1953).