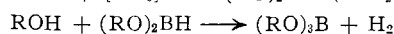
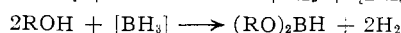
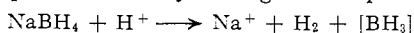


TABLE II  
PREPARATION OF ALKYL BORATE ESTERS BY THE SODIUM BOROHYDRIDE REACTION

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

<sup>a</sup> 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.<sup>13</sup> 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.



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  $n_D^{20}$  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-

(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).

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

<sup>a</sup> By hydrolysis, followed by titration of the boric acid in the presence of mannitol.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

## The Preparation and Properties of Sodium Tetraalkoxyborohydrides<sup>1,2</sup>

BY HERBERT C. BROWN AND EDWARD J. MEAD<sup>3</sup>

RECEIVED NOVEMBER 25, 1955

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<sup>4</sup> 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-

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

(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**, 6283 (1953).

tion of the borate ester and the metal alkoxide,<sup>5-7</sup> by metathesis between the tetraalkoxyborohydrides and metal halides,<sup>6</sup> and by reaction of sodium borohydride with methanol and ethanol.<sup>8</sup>

Neither isopropyl alcohol nor *t*-butyl alcohol reacts with sodium borohydride to form the corresponding tetraalkoxyborohydride.<sup>9</sup> The reactions of isopropyl borate with sodium isopropoxide and of *t*-butyl borate with sodium *t*-butoxide were investigated as a route to these tetraalkoxyborohydrides.

### Results and Discussion

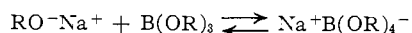
Equimolar amounts of the borate esters were mixed with the corresponding sodium alkoxides in the alcohol as solvent. At the end of the reaction the alcohol and unreacted borate ester were removed by volatilization. The results revealed that methyl, ethyl and isopropyl borates react with the corresponding sodium alkoxide in a 1:1 molar ratio to form white crystalline products whose analysis corresponded to the composition NaB(OR)<sub>4</sub>.

Treatment of sodium *t*-butoxide in *t*-butyl alcohol with excess *t*-butyl borate led to no observable reaction. Removal of the volatile components at 60–70° led to quantitative separation of the sodium *t*-butoxide and borate ester.

The possible formation of an unstable product at room temperature was investigated by examining the solubility of sodium *t*-butoxide in *t*-butyl alcohol in the presence and absence of *t*-butyl borate. Thus sodium *t*-butoxide exhibits a solubility of 0.21 mole per liter in pure *t*-butyl alcohol at 30°. In the *t*-butyl alcohol containing *t*-butyl borate (0.46 *M*), the solubility was slightly lower, 0.17 mole per liter. It was concluded that the two components do not react even at room temperature.

The failure of the two components to react is presumably due to steric difficulties. It is impossible to construct the tetra-*t*-butoxyborohydride ion with the usual Fisher–Hirschfelder–Taylor molecular models.

Quantitative data on the relative tendency for the different neutralization reactions to proceed was sought by titrating the four alkyl borates with standard solutions of sodium alkoxide in the appropriate alcohols as solvents.



However, both phenolphthalein and Alizarin Yellow R changed color long before the stoichiometric quantity of base had been added, even in the case of the methyl system. This observation is puzzling in view of the stability of the neutralization products, but the phenomenon was not investigated further.

The tetraalkoxyborohydrides are stable *in vacuo* up to temperatures of approximately 250°, but

(5) H. Copeau, *Compt. rend.*, **127**, 721 (1898).

(6) L. Cambi, *Atti acad. Lincei*, **23**, I, 244 (1914); *C. A.*, **8**, 2371 (1914).

(7) H. Meerwein and T. Bersin, *Ann.*, **476**, 113 (1929).

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

(9) H. C. Brown, E. J. Mead and B. C. Subba Rao, *ibid.*, **77**, 6209 (1955).

decompose above these temperatures. The approximate decomposition temperatures are: sodium tetramethoxyborohydride, 260–265°; sodium tetraethoxyborohydride, 340–345°; sodium tetraisopropoxyborohydride, 265–270°. All of the alkoxy borohydrides are highly sensitive toward hydrolysis, but the tetraisopropoxy derivative proved to be particularly susceptible and had to be handled with unusual precautions.

The solubilities of the tetraalkoxyborohydrides were determined in acetonitrile, benzene, diethyl ether, tetrahydrofuran, dimethyl ether of triethylene glycol (triglyme) and tetrahydrofuran. The results are summarized in Table I.

TABLE I  
SOLUBILITY OF SODIUM TETRAALKOXYBOROHYDRIDES

Solvent	Temp., °C.	Sodium tetraalkoxyborohydride <sup>a</sup>		
		Methyl	Ethyl	Isopropyl
Benzene	70	0	0	0
Ethyl ether	25	0	0	0
Acetonitrile	70	0	0	0
Methyl alcohol	0	272		
	25	334		
Ethyl alcohol	0		96	
	25		113	
Isopropyl alcohol	0			24
	25			29
Triglyme	25			5.4
Tetrahydrofuran	0	v.s. <sup>b</sup>	v.s. <sup>b</sup>	7
	25	467	v.s. <sup>b</sup>	10

<sup>a</sup> Solubility in g. per l. of solution. <sup>b</sup> Very soluble. Solution too viscous to handle.

### Experimental Part

**Materials.**—Methyl borate was a commercial product supplied by Metal Hydrides, Inc. It was purified by fractionation in a column rated at 50 theoretical plates. The remaining esters were prepared and purified as previously described.<sup>10</sup> The alcohols were the best available commercial materials, dried over calcium hydride and distilled from fresh calcium hydride through a packed column.

**Preparation of Sodium Tetraalkoxyborohydrides.**—Sodium metal, 4.64 g. (0.202 mole), was dissolved in 200 ml. of isopropyl alcohol under a nitrogen atmosphere. Isopropyl borate, 41.0 g. (0.226 mole), was added at a rate slow enough to avoid sharp rises in temperature. An immediate dense white precipitate was observed. All volatile materials were removed under reduced pressure. The product, 54 g. (0.20 mole), was quickly powdered and bottled.

*Anal.* Calcd. for C<sub>12</sub>H<sub>28</sub>BO<sub>4</sub>Na: Na, 8.52; B, 4.01. Found: Na, 8.69; B, 4.00.

Identical procedures were used for the preparation of the sodium tetramethoxy- and tetraethoxyborohydrides. In an attempt to prepare the tetra-*t*-butoxyborohydride, 16.6 g. (72.4 mmoles) of *t*-butyl borate was added to a solution of 1.32 g. (57.3 mmoles) of sodium in 75 ml. of *t*-butyl alcohol. The reaction mixture was refluxed for 15 min. with no noticeable change in the clear solution. The volatile components were removed at 1 mm., with the temperature maintained at 60–70°. The weight of the residue, 6.65 g., corresponded to that of the sodium *t*-butoxide in the reaction mixture.

**Investigation of the Possible Formation of Sodium Tetra-*t*-butoxyborohydride at Lower Temperatures.**—An attempt was made to titrate the alkyl borates in the alcohol as solvent by standard solutions of the sodium alkoxides in the corresponding alcohols. Both phenolphthalein and Alizarin Yellow R were used as indicators. The indicators changed color when 90% of the theoretical quantity of methyl borate had been added. However, in the case of the remaining esters, the indicators changed color after the addition of a

(10) H. C. Brown, E. J. Mead and C. J. Shoaf, *ibid.*, **78**, 3618 (1956).

small quantity of the alkoxide base.<sup>7</sup> In view of the stability of the ethoxy and isopropoxyborohydrides, it does not appear reasonable to attribute the effect to a considerable dissociation of the products,  $\text{NaOC}_2\text{H}_5 + \text{B}(\text{OC}_2\text{H}_5)_3 \rightleftharpoons \text{NaB}(\text{OC}_2\text{H}_5)_4$ . We did not attempt to examine the phenomenon further.

Sodium, 1.05 g. (0.0456 mole), was dissolved in 75 ml. of *t*-butyl alcohol in a nitrogen atmosphere. The flask was maintained at  $30.2 (\pm 0.1)^\circ$  for 4 hours and samples were removed from the supernatant liquid and titrated for base in order to determine the solubility of sodium *t*-butoxide. A similar measurement was made at  $60^\circ$ . The solubilities were determined to be  $0.208 M$  at  $30.2^\circ$ ,  $0.382 M$  at  $60^\circ$ .

To a clear solution of sodium *t*-butoxide ( $0.27 M$ ) in *t*-butyl alcohol at  $60^\circ$  there was added sufficient *t*-butyl borate to make the solution  $0.46 M$  in this component. After 2 hours at  $60^\circ$ , the reaction mixture was cooled slowly to  $30.2^\circ$ . Samples of the supernatant liquid were taken and analyzed for sodium alkoxide and for boric acid (after hydrolysis). The results,  $0.46 M$  in boric acid and  $0.17 M$  in sodium *t*-

butoxide, indicate that no measurable reaction had occurred.

**Decomposition Temperatures of the Tetraalkoxyborohydrides.**—Samples of the compounds were sealed in small glass tubes under vacuum. The samples were heated in a metal melting point block until rapid volatilization from the sample was observed.

**Solubilities of the Sodium Tetraalkoxyborohydrides.**—The solvent and sufficient tetraalkoxyborohydride were placed in 15-ml. centrifuge tubes. Sufficient salt was used to provide an undissolved solid phase. These mixtures were maintained at a constant temperature with frequent shaking. At intervals of time the tubes were centrifuged and samples of the clear supernatant liquid removed for sodium analysis. The solubilities measured in this way were reproducible to  $\pm 10\%$ . The determinations were complicated by the high viscosities of the solutions and the marked sensitivity of the materials to hydrolytic decomposition. The results are summarized in Table I.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

## The Preparation of Sodium Triisopropoxyborohydride and Tri-*t*-butoxyborohydride. The Effect of Alkoxy Substituents on the Reducing Properties of Borohydride Ion<sup>1,2</sup>

BY HERBERT C. BROWN, EDWARD J. MEAD<sup>3</sup> AND CHARLES J. SHOAF<sup>4</sup>

RECEIVED MARCH 7, 1956

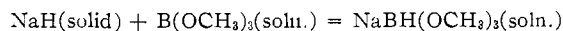
In refluxing tetrahydrofuran the rate of reaction of sodium hydride with borate esters decreases sharply in the order methyl > ethyl >> isopropyl >> *t*-butyl. The time required to achieve reaction in the case of isopropyl and *t*-butyl borates can be greatly reduced by operating in the dimethyl ethers of di- and triethylene glycol at  $130$ – $150^\circ$ . Sodium trimethoxyborohydride and triethoxyborohydride undergo disproportionation in tetrahydrofuran solution, whereas the isopropoxy and *t*-butoxy derivatives appear to be stable to this reaction. In contrast to sodium borohydride, sodium triisopropoxyborohydride reacts with isopropyl alcohol to liberate hydrogen, reacts very rapidly with acetone, and reduces ethyl benzoate at a moderate rate. The stability of the triisopropoxy- and tri-*t*-butoxyborohydrides toward disproportionation is attributed to the strain in the corresponding tetraalkoxyborohydrides, a necessary product of the disproportionation. The higher reactivity of the trialkoxyborohydrides as compared to the parent compound is attributed to the greater ease of removing hydride ion from a weak Lewis acid, alkyl borate, as compared to the removal from a strong Lewis acid, borane.

Preliminary results indicated that sodium trimethoxyborohydride is a more powerful reducing agent than sodium borohydride itself.<sup>3,6</sup> It appeared desirable to obtain quantitative data on the effect of the alkoxy substituents on the reducing potential of the borohydride ion. Accordingly, we undertook to prepare four typical trialkoxyborohydrides by the reaction of methyl, ethyl, isopropyl and *t*-butyl borates with sodium hydride in tetrahydrofuran solution<sup>6</sup> and to examine their behavior as reducing agents.<sup>7</sup>

### Results

As previously reported, methyl borate in tetrahydrofuran solution reacts vigorously with sodium hydride.<sup>6</sup> We attempted to follow the course of

the reaction by removing aliquots of the clear supernatant liquid and analyzing it for sodium (as base), boron (as boric acid) and hydrogen (as active hydride). Had the reaction followed the course expected, the analysis at the end of the reaction would have been 1.00 Na, 1.00 B, 1.00 H, corresponding to the reaction



Shortly after the exothermic reaction had ceased, the analysis corresponded closely to the 1:00 Na/1.00 B expected. However, the solutions were poorer in soluble hydride than that expected. At first we suspected that impurities were reacting with the "active hydrogen," but the rigorous purification of the reagents and detailed precautions in performing the experiments failed to alter the result. We concluded that the sodium trimethoxyborohydride must be undergoing a disproportionation into sodium tetramethoxyborohydride and materials richer in active hydrogen than the trimethoxyborohydride. The tetramethoxyborohydride is highly soluble in tetrahydrofuran,<sup>8</sup> but the other product or products must be less soluble and lost thereby from the solution, leading to a decrease in its active hydride content. The point was

- (1) Addition Compounds of the Alkali Metal Hydrides. VII.
- (2) Based upon theses submitted by E. J. Mead and C. J. Shoaf 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) Research assistant on Contract DA-33-008-ORD-992 supported by the Office of Ordnance Research, U. S. Army.
- (5) H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, *THIS JOURNAL*, **75**, 192 (1953).
- (6) H. C. Brown and E. J. Mead, *ibid.*, **75**, 6263 (1953).
- (7) The preparation of lithium tri-*n*-butoxyborohydride and its utilization as a reducing agent has been reported: G. Wittig and P. Hornberger, *Ann.*, **577**, 11 (1952).

- (8) H. C. Brown and E. J. Mead, *THIS JOURNAL*, **78**, 3614 (1956).