small quantity of the alkoxide base.[7] 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, $NaOC_2H_5 + B(OC_2H_5)_3 \rightleftarrows NaB(OC_2H_5)_4$. 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 (±0.1°) 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°. The solubilities were determined to be 0.208 *M* at 30.2°, 0.382 *M* at 60°.

To a clear solution of sodium *t*-butoxide (0.27 *M*) in *t*-butyl alcohol at 60° there was added sufficient *t*-butyl borate to make the solution 0.46 *M* in this component. After 2 hours at 60°, the reaction mixture was cooled slowly to 30.2°. 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 ±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.

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[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[1,2]

BY HERBERT C. BROWN, EDWARD J. MEAD[3] AND CHARLES J. SHOAF[4]

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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°. 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.[5,6] 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[6] and to examine their behavior as reducing agents.[7]

Results

As previously reported, methyl borate in tetrahydrofuran solution reacts vigorously with sodium hydride.[6] 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

$$NaH(solid) + B(OCH_3)_3(soln.) = NaBH(OCH_3)_3(soln.)$$

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,[8] 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

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(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).

confirmed by adding ether in small portions to a solution of sodium trimethoxyborohydride in tetrahydrofuran, causing a fractional precipitation of the material in solution. It was observed that the materials precipitated were richer in hydride than the trimethoxy derivative, and the solvent soluble products poorer.

In the reaction of lithium hydride with methyl borate, it was observed that the product was not homogeneous and a disproportionation to dimethoxyborohydride and tetramethoxyborohydride was postulated.[5]

$$\mathrm{LiBH(OCH_3)_3} \longrightarrow \mathrm{LiBH_2(OCH_3)_2} + \mathrm{LiB(OCH_3)_4}$$

Presumably, a similar disproportionation reaction is involved in the present case. We plan to investigate the precise nature of this disproportionation reaction at a later date.

The reaction of ethyl borate with sodium hydride was considerably slower than the corresponding reaction of methyl borate. Here also active hydride was lost from the solution and the conclusion was reached that the product was not homogeneous.

The reaction of isopropyl borate with sodium hydride was very much slower. In refluxing tetrahydrofuran the reaction required some 7–10 days for completion in contrast to the minutes required for the methyl borate reaction under identical conditions.

In this case no disporportionation reaction was observed. Because of the low solubility of sodium tetraisopropoxyborohydride in tetrahydrofuran,[8] such disproportionation should have been observed easily. Therefore, in this case the reaction must proceed smoothly to the desired trialkoxyborohydride without subsequent disproportionation.

$$\mathrm{NaH} + (i\text{-}\mathrm{PrO})_3\mathrm{B} \longrightarrow \mathrm{Na}^+[(i\text{-}\mathrm{PrO})_3\mathrm{BH}]^-$$

Finally, no reaction was observed between tri-*t*-butyl borate and sodium hydride in refluxing tetrahydrofuran.

Its stability toward disproportionation led us to select sodium triisopropoxyborohydride for study of the reducing potential of the alkoxy substituted borohydrides. However, the long reaction time required for its preparation was a serious disadvantage, particularly in view of the great precautions necessary to exclude air and moisture from the reaction mixture. We undertook, therefore, to investigate means of improving the synthesis.

No reaction was observed in tetrahydrofuran between sodium hydride and sodium tetraisopropoxyborohydride. Similarly, sodium borohydride and sodium tetraisopropoxyborohydride failed to produce the desired product after 150 hours in refluxing tetrahydrofuran. Consequently, these reactions cannot serve for the preparation of the product.

$$\mathrm{NaH} + \mathrm{Na}[(i\text{-}\mathrm{PrO})_4\mathrm{B}] \dashrightarrow \mathrm{Na}[(i\text{-}\mathrm{PrO})_3\mathrm{BH}] + i\text{-}\mathrm{PrONa}$$

$$\mathrm{NaBH_4} + 3\mathrm{Na}[(i\text{-}\mathrm{PrO})_4\mathrm{B}] \dashrightarrow 4\mathrm{Na}[(i\text{-}\mathrm{PrO})_3\mathrm{BH}]$$

It proved possible to shorten the reaction time by carrying out the reaction between sodium hydride and isopropyl borate at higher temperatures in the dimethyl ethers of diethylene glycol (diglyme) and triethylene glycol (triglyme). In these solvents the reaction can be completed in 1 hour at 130°. Because of their high boiling points, it proved to be considerably more difficult to separate the product from the solvent. Consequently, when the solid product was desired we continued to utilize the tetrahydrofuran procedure. In those cases where a solution of the reagent was adequate, the synthesis in di- and triglyme was adopted.

It was mentioned earlier that no reaction was observed between *t*-butyl borate and sodium hydride in refluxing tetrahydrofuran. However, reaction between these reagents was observed in diglyme or triglyme at 150°. Sodium and hydride increased slowly in the solution in a ratio of 1.00/1.00, corresponding to the formation of the expected sodium tri-*t*-butoxyborohydride. However, the reaction with *t*-butyl borate was relatively slow at 130°, and even at 150° it was relatively difficult to bring to completion. Moreover, the instability of *t*-butyl borate at this temperature made long reaction times impractical. Consequently, the reaction was usually stopped before all of the borate ester had reacted and the excess ester removed together with the solvent at low pressures. The product was a white solid which proved to be highly reactive and very difficult to handle. It was therefore decided to utilize the sodium triisopropoxyborohydride in our reactivity studies.

Sodium borohydride is moderately soluble in isopropyl alcohol and the solution can be heated under reflux for days without noticeable reaction.[9] Sodium triisopropoxyborohydride is also soluble in isopropyl alcohol. However, in this case reaction with the solvent occurs, slowly at 0° and relatively rapidly at 60°.

$$\mathrm{Na}[(i\text{-}\mathrm{PrO})_3\mathrm{BH}] + i\text{-}\mathrm{PrOH} \longrightarrow \mathrm{Na}[(i\text{-}\mathrm{PrO})_4\mathrm{B}] + \mathrm{H_2}$$

The reaction of sodium borohydride with acetone proceeds at a measurable rate at 0° in isopropyl alcohol ($k_2 = 0.078$ l. mole^{-1} min.$^{-1}$) and at a negligible rate in diglyme.[9] However, the reaction of sodium triisopropoxyborohydride with acetone in isopropyl alcohol at 0° was too fast to measure, the reaction being over within the first minute after the reagents were mixed. Even in tetrahydrofuran and diglyme the reaction was far too fast to measure, with half-lives of approximately 30 seconds.

The reaction of sodium borohydride with esters is very slow. Thus a reaction mixture of 35 mmoles of ethyl benzoate and 25 mmoles of sodium borohydride in 125 cc. of diglyme lost but 12% of the available active hydrogen in 6 hours at 75°. A similar reaction mixture of sodium triisopropoxyborohydride in refluxing tetrahydrofuran (65°) showed complete utilization of active hydrogen by the ester.

The rate of reaction of excess sodium triisopropoxyborohydride with ethyl benzoate in tetrahydrofuran solution at 40° was followed to test the possibility of the formation of a stable 1:1 adduct. However, the rate data showed no evidence for the formation of such an addition compound and tests for aldehyde (after hydrolysis) were negative. It

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

was concluded that the second stage in the reduction must be faster than the first so that the ester reacts only with the uptake of two equivalents of hydride to form the alcohol.

Discussion

The marked difference in the rates observed in the reaction of methyl, ethyl, isopropyl and *t*-butyl borates with sodium hydride in tetrahydrofuran is noteworthy. Presumably the borate ester must react with the hydride ion on the surface of the solid sodium hydride. With increasing steric requirements of the alkyl groups, the central boron atom must find it increasingly difficult to approach within bonding distance of the hydride ion.

In an earlier paper it was pointed out that *t*-butyl borate fails to react with sodium *t*-butoxide, presumably because of steric difficulties.[8] Although sodium isopropoxide reacts with isopropyl borate, steric strains of considerable magnitude are presumably present in the product, $Na[(i\text{-PrO})_4B]$. The failure of sodium triisopropoxyborohydride and sodium tri-*t*-butoxyborohydride to undergo the disproportionation reactions exhibited by the corresponding methyl and ethyl derivatives is attributed to an unfavorable equilibrium arising from the strain in the highly branched tetraalkoxyborohydride ions. Although we prefer this interpretation, the available data do not eliminate the possibility that the equilibrium may favor disproportionation here also, and that the failure to observe this reaction in the highly branched derivatives may arise from very slow rates in the attainment of equilibrium.

$$2Na[(i\text{-PrO})_3BH] \rightleftharpoons Na[(i\text{-PrO})_2BH_2] + Na[(i\text{-PrO})_4B]$$

It was originally pointed out that the observed kinetics for the reaction of sodium borohydride with ketones could be understood only if it were postulated that the first transfer of hydride from borohydride to the ketone was much slower than the subsequent transfers.[10] In the reaction of acetone with sodium borohydride the reaction must proceed successively through the formation of mono-, di-, tri- and tetraisopropoxyborohydride.

$$BH_4^- + (CH_3)_2CO \longrightarrow (CH_3)_2CHOBH_3^-$$

$$(CH_3)_2CHOBH_3^- + (CH_3)_2CO \longrightarrow [(CH_3)_2CHO]_2BH_2^-$$

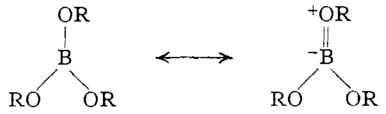
$$[(CH_3)_2CHO]_2BH_2^- + (CH_3)_2CO \longrightarrow [(CH_3)_2CHO]_3BH^-$$

$$[(CH_3)_2CHO]_3BH^- + (CH_3)_2CO \longrightarrow [(CH_3)_2CHO]_4B^-$$

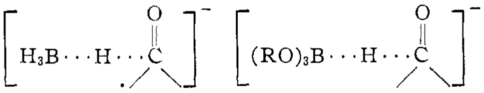
In isopropyl alcohol as solvent, these alkoxyborohydrides must be the actual intermediates involved in the reaction.

The validity of the proposal by Garrett and Lyttle is clearly established by the very fast reaction observed in the present study between sodium triisopropoxyborohydride and acetone. The reactions with isopropyl alcohol and with ethyl benzoate likewise support the conclusion that, as compared to the parent compound, the alkoxyborohydrides must possess an enhanced tendency to transfer hydride ion.

The effect of the alkoxy groups may be rationalized in terms of the strengths of related Lewis acids. Alkyl borates are very weak Lewis acids, presumably because the resonance stabilization greatly diminishes the tendency of the central boron atom to coördinate with donor molecules.



The transfer from the parent borohydride ion of a hydride particle requires its separation from the strong Lewis acid, borane, whereas the transfers from trialkoxyborohydrides require its separation from the weak Lewis acid, alkyl borate.



According to this interpretation, it should be possible to correlate the reducing tendency of a series of trisubstituted borohydride ions, X_3BH^-, with the strength of the parent Lewis acid, X_3B. We hope to investigate this point.

Experimental Part

Materials.—Tetrahydrofuran was allowed to stand for several hours over potassium hydroxide pellets and then twice distilled from lithium aluminum hydride in a nitrogen atmosphere.[11] Freshly purified solvent was used for all the experimental work. Diglyme and triglyme were purified as previously described.[9]

Sodium hydride and sodium borohydride were the commercial products (Metal Hydrides, Inc.) and were used without further purification. Both materials analyzed for 94% or better purity.

The borate esters and sodium tetraalkoxyborohydrides were prepared as described previously.[8,12]

Analyses.—Sodium was determined, after quenching the measured sample in water, as total base by titration of the solution with standard acid against methyl red. Boron was then determined by titration with base in the presence of mannitol. In the case of borohydride, trimethoxyborohydride and triethoxyborohydride the "hydride" content was determined by the method of Lyttle, Jensen and Struck.[13] In all other cases the samples were hydrolyzed and the analyses based upon the hydrogen evolved.

Reaction of Sodium Hydride with the Borate Esters.—The following procedure was developed for studying the reaction of sodium hydride with the alkyl borates. Distilling flasks of 125 or 250-cc. capacity were used. The side arm was bent up to a vertical position to serve as the inlet for nitrogen. The long neck of the distilling flask served as an air condenser during the slow reflux of the reaction mixture. Materials were added and samples removed through the top of the flask as a vigorous current of nitrogen prevented diffusion of air into the reaction flask. A slight positive pressure of nitrogen was maintained throughout the reaction.

In a typical experiment the flask was heated with a Bunsen burner as a slow steady stream of nitrogen was passed through. The flask was permitted to cool in the nitrogen atmosphere and a weighed sample of hydride was quickly introduced in a nitrogen stream through the long neck of the distilling flask along with freshly purified solvent, added from a dry pipet. The mixture was brought to slow reflux and the borate ester was added from a hypodermic syringe which was weighed before and after the addition.

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[10] E. R. Garrett and D. A. Lyttle, THIS JOURNAL, **75**, 6051 (1953).

[11] T. Higuchi, *Anal. Chem.*, **22**, 534 (1950); THIS JOURNAL, **73**, 2676 (1951).

[12] H. C. Brown, E. J. Mead and C. J. Shoaf, *ibid.*, **78**, 3613 (1956).

[13] D. A. Lyttle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

TABLE I

REACTION OF SODIUM HYDRIDE WITH ALKYL BORATES IN REFLUXING TETRAHYDROFURAN (THF)

	Alkyl borate, mmole	Sodium hydride, mmole	THF, cc.	Time, hr.	Sodium, mmoles/ml.	Hydrogen, mmoles/ml.	Boron, mmoles/ml.
Methyl	90.1	63.3	150	0	0[a]	0[a]	0.563[a]
				0.3	0.362	0.318	.571
				.9	.355	.262	.548
				1.6	.345	.239	.538
				3.0	.335	.206	.522
				6.5	.347	.192	.484
Ethyl	63.8	63.8	100	0	0[a]	0[a]	0.582[a]
				18	0.493	0.248	.545
				42	.486	.222	.529
				82	.513	.211	.546
Isopropyl	67.2	63.6	100	0	0[a]	0[a]	0.589[a]
				18	0.042	0.021	0.597
				42	.134	.080	.598
				82	.296	.188	.605
				150	.573	.410	.618
	12	127	200	18	0.113	0.103	0.515
				168	.545	.545	.545
	126	191	200	32	0.213	0.213	0.547
				56	.420	.398	.560
				83	.562	.562	.562
t-Butyl	48.9	38.5	75	0[a]	0[a]	0[a]	0.556[a]
				42	0.03	0.00	.552

[a] Estimated from the initial concentrations.

TABLE II

REACTION OF SODIUM HYDRIDE WITH ALKYL BORATE IN DIGLYME (D) AND TRIGLYME (T)

	Alkyl borate, mmole	Sodium hydride, mmole	Solvent, cc.	Temp., °C.	Time, hr.	Sodium, mmoles/ml.	Hydrogen, mmoles/ml.	Boron, mmoles/ml.
Isopropyl	49	45	150 D	73	20	0.01	0.00	0.24
					68	.18	.18	.24
	45	51	100 D	125	2	.36	.29	.34
	9.0	20	35 T	130	1.0	.23	.23	.23
t-Butyl	17.4	31	75 T	150	1.0	.26	.22	.22
	33	146	100 T	150	1.0	.33	.29	.30

The reaction with methyl borate is quite vigorous and the borate ester should be added with care!

To remove samples for analysis, the heating was temporarily interrupted and a dry pipet, flushed out with nitrogen, was introduced to remove the sample. Glass wool was wrapped over the tip of the pipet to prevent the introduction of solid particles. The samples were then analyzed as described above.

At the end of the reaction the total contents of the flask were hydrolyzed to obtain the residual hydride content. The material balance on the total hydride used in the reaction and that found in the samples and in the final hydrolysis served as a check on the validity of the experimental techniques. With these precautions it was possible to account for 90% or more of the hydride initially introduced, even with reaction times of over one week.

Experimental results are summarized in Table I.

Similar procedures were utilized for studying the reaction of sodium hydride with isopropyl and *t*-butyl borate in diglyme and triglyme at higher temperatures. Representative results are summarized in Table II.

Disproportionation of Sodium Trimethoxyborohydride.—Evidence for the non-homogeneity of sodium trimethoxyborohydride synthesized in tetrahydrofuran was obtained in the following experiment in which fractional precipitation of the product was followed.

Sodium hydride (7.5 g.) and 200 ml. of tetrahydrofuran were refluxed for 5 min. with stirring, under nitrogen. Then the heating was stopped and 30 ml. of methyl borate in 200 ml. of tetrahydrofuran was added as rapidly as possible while keeping the vigorous refluxing under control. After completion of reaction, the clear solution of the product was transferred with nitrogen pressure through a tube fitted with a sintered glass filter. The solution analyzed for 0.558 sodium, 0.612 boron, 0.539 hydride, all in mmoles per cc.

To 200 ml. of this solution there was added 100 cc. of ethyl ether in four 25-cc. portions. After each addition, the precipitated material was permitted to settle and a small sample of the supernatant liquid was taken for analysis. The results are summarized in Table III.

TABLE III

FRACTIONAL PRECIPITATION OF A SOLUTION OF "SODIUM TRIMETHOXYBOROHYDRIDE"

Ether added, ml.	Sodium, mmoles/cc.	Boron, mmoles/cc.	Hydride, mmoles/cc.	Ratio
0	0.588	0.612	0.539	1.00:1.04:0.92
25	.503	.546	.437	1.00:1.08:0.87
25	.434	.447	.214	1.00:1.03:0.45
25	.375	.388	.140	1.00:1.03:0.37
25	.300	.316	.079	1.00:1.05:0.26

The precipitate was collected and the adhering solvent removed under vacuum. It analyzed for sodium, 1:00; boron, 1.04; hydrogen, 2.5.

Isolation of Sodium Triisopropoxyborohydride.—The sidearm of a 500-cc. distilling flask was made vertical upward and used to introduce purified nitrogen. Into the flask was placed 3.01 g. (0.125 mole) of sodium hydride, 200 ml. of tetrahydrofuran and 27.2 g. (0.144 mmole) of isopropyl borate. The neck of the flask was tightly stopped and the mixture was brought to a slow reflux with a slight positive pressure of nitrogen. After 180 hours, the clear solution was passed through glass wool into a dry nitrogen filled flask. Most of the volatile liquid (165 cc.) was removed by distillation at atmospheric pressure. The remaining material was removed at low pressures (1 mm.) until the weight was constant. There was obtained 25.6 g. (0.120 mole) of sodium triisopropoxyborohydride, a yield of 90%.

Anal. Calcd. for $C_9H_{21}BNaO_3H^-$: Na, 10.85; B, 5.10; H^-, 0.472. Found: Na, 10.68; B, 5.31; H^-, 0.424.

Reactions of Sodium Triisopropoxyborohydride.—Sodium triisopropoxyborohydride was soluble in isopropyl alcohol. At 0° a slow evolution of hydrogen was observed. However, the reaction was sufficiently slow so that such solutions (0.2 *M*) could be worked with for several hours without major losses of active hydrogen. At 60° such solutions lost 50% of their active hydrogen content in 10 min. and 85% in 30 min.

A solution of sodium triisopropoxyborohydride in isopropyl alcohol (0.179 *M*) was placed in a vessel maintained at 0° and a similar solution of acetone in the same solvent (0.176 *M*) was quickly mixed. After 1 min., 4 *N* sulfuric acid was added to destroy the unreacted "hydride." The hydrogen evolved indicated at least 90% reaction. A similar experiment using 0.21 *M* solutions in tetrahydrofuran showed 76% reaction in 1 min., 86% in 3 min. and 91% reaction in 10 min.

By means of automatic burets, 5-ml. portions of standard solutions of sodium triisopropoxyborohydride and ethyl benzoate in tetrahydrofuran were placed in 50-ml. round-bottom flasks. Blanks were made by substituting 5 ml. of the solvent for the ethyl benzoate solution. Each reaction mixture contained 2.96 mmoles of "hydride" and 0.975 mmole of ethyl benzoate in 10 ml. of solvent. The reaction vessels were maintained at 40 ± 0.1°. At appropriate intervals of time, the flasks were hydrolyzed and the hydride utilization estimated from the hydrogen evolved. The results show "hydride" used to be 30% in 15 hours, 50% in 30 hours, 65% in 60 hours. Under the same conditions sodium borohydride shows no hydrogen utilization.

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