Addition Compounds of Alkali Metal Hydrides. 15. Steric Effects in the Reaction of Representative Trialkylboranes with Lithium and Sodium Hydrides to Form the Corresponding Trialkylborohydrides

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Abstract: The reaction in tetrahydrofuran of lithium and sodium hydrides with representative trialkylboranes of increasing steric requirements was examined in detail with respect to rate, stoichiometry, and products. The rate of the reaction is strongly influenced by the steric requirements of the trialkylborane. Thus, the rates of reaction of lithium hydride with a series of trialkylboranes at 25 °C follows the order $Et_3B > n\text{-}Bu_3B > i\text{-}Bu_3B \gg sec\text{-}Bu_3B$. Even in refluxing tetrahydrofuran, tri-*sec*-butylborane and other hindered organoboranes react with lithium hydride sluggishly and incompletely. Sodium hydride exhibits greater reactivity than lithium hydride in these reactions. Sodium hydride reacts with essentially all of the unhindered trialkylboranes and with a number of hindered trialkylboranes even at 25 °C. Other hindered trialkylboranes such as tri-*sec*-butylborane, tricyclohexylborane, and tri-*exo*-2-norbornylborane react with sodium hydride in refluxing tetrahydrofuran rapidly and quantitatively. Here again the rate of the reaction decreases drastically with increasing size of the alkyl substituent on boron: $Et_3B > n\text{-}Bu_3B > \text{tricyclopentylborane} \geqslant i\text{-}Bu_3B > \text{tricyclohexylborane} \geqslant \text{tri-}exo\text{-2-norbornylborane} \geqslant sec\text{-}Bu_3B$. Highly hindered organoboranes such as trisiamylborane and tris(*trans*-2-methylcyclopentyl)borane are essentially inert toward both lithium hydride and sodium hydride at 65 °C. The reaction of alkali metal hydrides with trialkylboranes proceeds in 1:1 stoichiometry; the products of the reaction are alkali metal trialkylborohydrides characterized by hydride analysis, IR, and ^{11}B NMR. The present reaction serves as a convenient means for studying the steric requirements of various trialkylboranes. In addition, it also provides a simple route to a number of lithium and sodium trialkylborohydrides.

In recent years a number of alkali metal trialkylborohydrides have emerged as highly attractive reducing agents in organic synthesis, capable of achieving stereo- and regioselective transformations unequaled by any other reagents currently available. Numerous applications of these new reducing agents in organic synthetic transformations have already been reported.[2]

Lithium trimethylborohydride and sodium triethylborohydride were the members of this new class of compounds first synthesized during war research (1942–1943).[3] Since then, a few more reports on the synthesis of trialkylborohydrides from alkali metal hydrides and trialkylboranes have appeared in the literature.[4] Unfortunately, the majority of these studies were carried out utilizing relatively drastic reaction conditions resulting in rather poor yields of the trialkylborohydrides. Further, no systematic study of the effect of varying the steric requirements of the alkyl groups on boron on reaction rates has been described.

From our preliminary exploration of different alkyl-substituted borohydrides, it was clearly evident that the reactivity of these derivatives and the stereochemical course of the reactions involving them were strongly influenced by the nature of the alkyl substituent on boron. Conceivably, a simple approach for the synthesis of these derivatives would be the reaction between alkali metal hydrides and the trialkylboranes in a suitable reaction medium. Hydroboration of olefins has made available a number of trialkylboranes of varying steric requirements.[5,6] Accordingly, we undertook a systematic examination of the rates of reaction of lithium and sodium hydrides with trialkylboranes of increasing steric requirements under standard conditions.

It was evident from previous work that the reaction between trialkylboranes and alkali metal hydrides proceeds far better in ether solvents[7,8] than in hydrocarbon solvents or neat.[4] Accordingly, we decided to utilize an ether solvent for these rate studies. Since tetrahydrofuran (THF) is often the solvent of choice for hydroboration, we adopted this solvent for our studies of the effect of steric requirements in the trialkylborane on the rate of reaction with the alkali metal hydride.

Results and Discussion

Ten representative trialkylboranes of varying steric requirements were selected for this study. Their rates of reaction with lithium and sodium hydrides in tetrahydrofuran were examined. The physical and chemical characteristics of the resulting trialkylborohydride solutions were investigated.

General Procedure for the Rates of Reaction of Representative Trialkylboranes with Lithium Hydride and Sodium Hydride in Tetrahydrofuran. The general procedure adopted was to place an excess (~50%) of the given metal hydride (over that required by the stoichiometry) in the reaction flask, suspended in sufficient tetrahydrofuran so as to maintain the final concentration of the reaction mixture at 1.0 M in trialkylborane. In several cases, the lower solubility of the trialkylborane component led us to run the reaction at 0.5 M in R_3B. In the case of sodium hydride, which is commercially available as a 50% suspension in mineral oil, the oil coating was removed by washing with THF. In some cases, the required amount of distilled trialkylborane was added as the pure liquid to the alkali metal hydride suspended in THF. In other cases, where the trialkylborane was synthesized by hydroboration, a standard solution of the trialkylborane in THF was added directly to the solid alkali metal hydride. In all cases the reaction mixtures were vigorously stirred at similar rates. Depending upon the reactivity of the borane, the reactions were carried out at room temperature, 25 ± 1 °C, maintained by immersion in a water bath, or at reflux, 66 ± 1 °C.

Our earlier studies in this area had indicated that different hydride samples may exhibit different reactivities.[7] In order to minimize the effect of this factor, the same sample of each metal hydride was utilized throughout the study. We were, of course, interested primarily in the very large effects of the structure of the organoborane on the relative rate of reaction and the data clearly establish that feature.

Known aliquots from the reaction mixture were removed at various intervals of time and reacted with a known amount of *n*-octyl iodide.[9] Hydrolysis of this mixture and GLC examination for *n*-octane formed (utilizing an internal standard)

Table I. Reaction of Lithium Hydride and Sodium Hydride with Representative Trialkylboranes in Tetrahydrofuran[a]

Trialkylborane	Metal hydride	Temp, °C	Trialkylborohydride found, %[b]							
			0.25 h	0.5 h	1.0 h	2.0 h	3.0 h	6.0 h	12.0 h	24.0 h
Triethylborane	LiH	25		55	73	78	85	90	92	98
	LiH	65	97	98	98		98			
	LiD	65			100					
	NaH	25	100	100						
Tri-*n*-butylborane	LiH	25						50	74	80	90
	LiH	65	36	65	92		95	97		
	NaH	25	99	98	100					
Triisobutylborane	LiH	25						25	79	91
	LiH	65	20		74		88	98	99	
	NaH	25	87	89	93	96			100	
Tri-*sec*-butylborane	LiH	25					0			0
	LiH	65		0	0	2			7	10
	NaH	25			2	5				
	NaH	65	82	90	94	97	100	100		
Tricyclopentylborane	LiH	65					5		17	26
	NaH	25	99	100						
	NaH	65	100	100						
Tricyclohexylborane	LiH[c]	65					2		5	8
	NaH[c]	65	100	100						
Tri-*exo*-2-norbornylborane	LiH	65					3			6
	NaH[c]	65	91	97	97	97				
Perhydro-9b-boraphenalene	LiH	65		100	100					
	NaH	25	100	100	100					
Tris(*trans*-2-methylcyclopentyl)borane	LiH	65							0	0
	NaH	65							0	0
Trisiamylborane	LiH	65							0	0
	NaH	65							0	0

[a] Unless otherwise indicated, solutions were 1 M in R_3B and approximately 50% excess of alkali metal hydride was utilized. [b] Monitored by GLC by measuring the *n*-octane formed after quenching with *n*-octyl iodide, or in some cases by hydrolysis of the clear reaction mixture after filtration. [c] 0.5 M in R_3B.
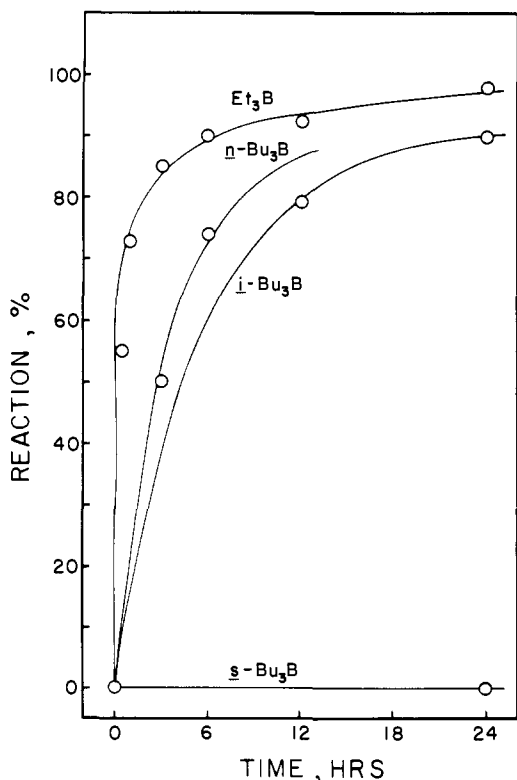

Figure 1. Reaction of representative trialkylboranes with lithium hydride in tetrahydrofuran at 25 °C.
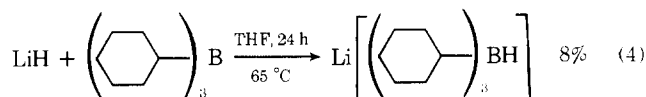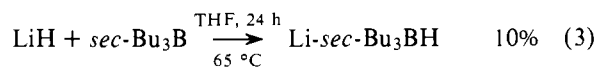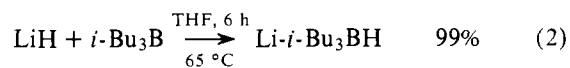
indicated the extent of the reaction. The results are summarized in Table I.

Effect of the Structure of the Trialkylborane (Steric Effects).
The results summarized in Table I reveal a number of interesting features of this reaction. One such feature is the remarkable influence of steric effects on reaction rates. The rates of reaction of organoboranes with a given alkali metal hydride are strongly dependent on the structure of the trialkylborane. Increasing the size of the alkyl group on boron decreases the reaction rate. Thus, in a typical series, the rates of reaction with lithium hydride follow the order $Et_3B > n\text{-}Bu_3B > i\text{-}Bu_3B \gg sec\text{-}Bu_3B$. Triethyl-, tri-*n*-butyl-, and triisobutylboranes react with lithium hydride at room temperature:

$$LiH + Et_3B \xrightarrow[24\ h]{THF,\ 25\ °C} LiEt_3BH \qquad 100\% \qquad (1)$$
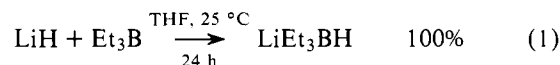
Tri-*sec*-butylborane is inert to lithium hydride under these conditions (Figure 1). Consequently, the reaction of hindered organoboranes with lithium hydride was examined in refluxing THF (Figure 2). Even under reflux, hindered organoboranes react with lithium hydride only sluggishly and incompletely in 24 h (eq 2–4). Under these conditions, highly hindered organoboranes—trisiamylborane and tris(*trans*-2-methylcyclopentyl)borane—exhibit almost no reactivity toward lithium hydride.[10]
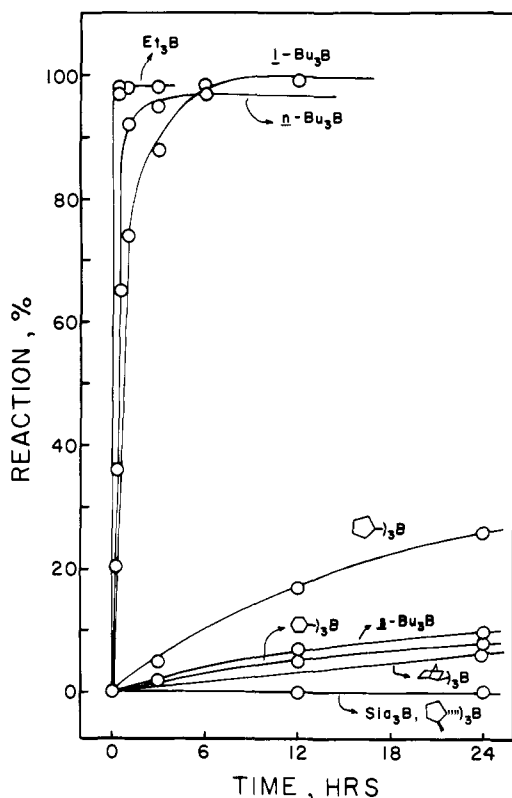
$$LiH + i\text{-}Bu_3B \xrightarrow[65\ °C]{THF,\ 6\ h} Li\text{-}i\text{-}Bu_3BH \qquad 99\% \qquad (2)$$

$$LiH + sec\text{-}Bu_3B \xrightarrow[65\ °C]{THF,\ 24\ h} Li\text{-}sec\text{-}Bu_3BH \qquad 10\% \qquad (3)$$

$$LiH + \left(\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-\right)_{\!3}\!B \xrightarrow[65\ °C]{THF,\ 24\ h} Li\left[\left(\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-\right)_{\!3}\!BH\right] \qquad 8\% \qquad (4)$$
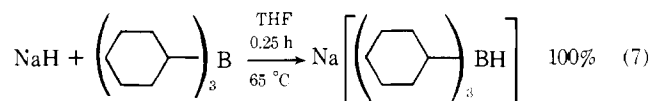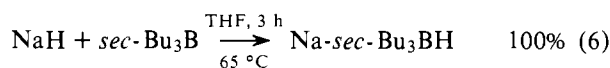
Figure 2. Reaction of representative trialkylboranes with lithium hydride in refluxing tetrahydrofuran (65 °C).

Figure 3. Reaction of tri-*n*-butylborane with lithium hydride and sodium hydride in tetrahydrofuran at 25 °C.
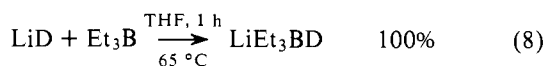
The reaction of trialkylboranes with sodium hydride is far more facile than the corresponding reactions involving lithium hydride. Thus, triethyl-, tri-*n*-butyl-, triisobutyl-, and tricyclopentylborane all react rapidly and quantitatively with sodium hydride even at 25 °C, yielding the corresponding trialkylborohydrides:

$$\text{NaH} + n\text{-Bu}_3\text{B} \xrightarrow[25\ °\text{C}]{\text{THF, 0.25 h}} \text{Na-}n\text{-Bu}_3\text{BH} \qquad 99\% \qquad (5)$$
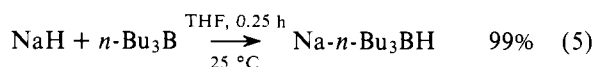
Even hindered trialkylboranes, such as tri-*sec*-butylborane, tricyclohexylborane, and tri-*exo*-2-norbornylborane, react quantitatively with sodium hydride in refluxing THF (Figure 3) (eq 6 and 7). However, even sodium hydride did not react to any appreciable extent with the highly hindered organoboranes, trisiamylborane and tris(*trans*-2-methylcyclopentyl)-borane, in refluxing THF after more than 24 h.[10]

$$\text{NaH} + sec\text{-Bu}_3\text{B} \xrightarrow[65\ °\text{C}]{\text{THF, 3 h}} \text{Na-}sec\text{-Bu}_3\text{BH} \qquad 100\% \qquad (6)$$

$$\text{NaH} + \left(\hspace{-4pt}\left\langle\bigcirc\right\rangle\hspace{-4pt}\right)_{\!3}\!\!\text{B} \xrightarrow[65\ °\text{C}]{\begin{subarray}{c}\text{THF}\\0.25\ h\end{subarray}} \text{Na}\left[\left(\hspace{-4pt}\left\langle\bigcirc\right\rangle\hspace{-4pt}\right)_{\!3}\!\!\text{BH}\right] \quad 100\% \quad (7)$$

Finally, lithium deuteride reacts with triethylborane in refluxing THF to give lithium triethylborodeuteride in quantitative yield:

$$\text{LiD} + \text{Et}_3\text{B} \xrightarrow[65\ °\text{C}]{\text{THF, 1 h}} \text{LiEt}_3\text{BD} \qquad 100\% \qquad (8)$$

It is a highly useful reagent for the stereospecific introduction of deuterium in organic molecules.[9,11]

Based on these studies, it can be concluded that the reactivity of lithium and sodium hydrides with trialkylboranes follows the order $\text{Et}_3\text{B} >$ perhydro-9b-boraphenalene[2b] $\geq n\text{-Bu}_3\text{B} >$ tricyclopentylborane $\geq i\text{-Bu}_3\text{B} >$ tricyclohexylborane $\geq$ tri-
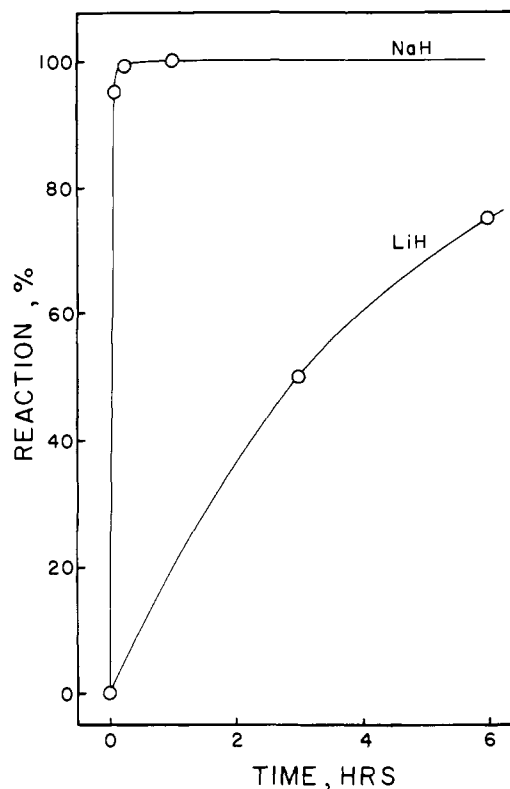
exo-2-norbornylborane $\geq sec\text{-Bu}_3\text{B} \gg$ tris(*trans*-2-methyl-cyclopentyl)borane $\simeq$ trisiamylborane.

Effect of the Metal Hydride. For the particular hydride samples employed in this study, sodium hydride proved to be far more reactive than lithium hydride toward trialkylboranes. This higher reactivity can be attributed to the lower crystal lattice energy of the former which would facilitate the reaction with the trialkylborane. This interpretation was earlier advanced by Brown to account for the markedly superior reactivity of potassium hydride relative to the lithium and sodium analogues.[12a] Thus, while the reaction of lithium hydride with tri-*n*-butylborane at 25 °C requires over 24 h, the corresponding reaction with sodium hydride is essentially complete in less than 15 min (Figure 4). Similarly, the reaction of tricyclohexylborane with lithium hydride in refluxing THF proceeds only to the extent of 8% in 24 h, the corresponding reaction with sodium hydride is complete in 0.25 h at 65 °C, while the reaction with potassium hydride is essentially complete within 0.5 h at 25 °C.[12c]

Stoichiometry of the Reaction. In the presence of excess alkali metal hydride, it was observed that the trialkylboranes which react undergo a simple acid–base reaction in a 1:1 ratio:

$$\text{R}_3\text{B} + \text{MH}_{\text{solid}} \rightarrow \text{MR}_3\text{BH}_{\text{soln}} \qquad (9)$$
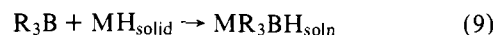
On this basis, the ratio of M:B:H in solution should be 1:1:1. Indeed, analysis of representative solutions of alkali metal trialkylborohydrides for alkali metal, boron, and hydride revealed such a 1:1:1 ratio (Table II).

Alkali metal was determined by hydrolyzing a known aliquot of the solution with water and titrating the base formed against standard acid. Boron was determined by GLC analyses, either of the trialkylborane or of the alcohols produced by oxidation of the trialkylborane to the corresponding alcohol. Hydride was determined by measuring the hydrogen evolved in hydrolysis of the solution or by reaction of an aliquot with

Table II. Analysis of Alkali Metal Trialkylborohydride Solutions in Tetrahydrofuran

MH (mmol)	R$_3$B (mmol)	Total volume,^{a} mL	Time, h	Temp, °C	M$^+$ concn,^{b} M	R$_3$B concn,^{c} M	H$^-$ concn,^{d} M	Ratio M	B	H	MR$_3$BH concn calcd^e
LiH (25)	Et$_3$B (20)	38	24	25	0.58	0.58	0.55	1.05	1.05	1.0	0.54
LiH (62)	Et$_3$B (40)	70	24	25	0.62	0.68	0.64	1.01	1.09	1.03	0.57
LiH (62)	Et$_3$B (40)	40	8	50	1.05	1.08	1.05	1.05	1.02	1.00	1.00
LiH (400)	Et$_3$B (250)	250	24	25	1.01	1.00	1.01	1.00	1.00	1.00	1.00
NaH (~40)	(c-C$_6$H$_{11}$)$_3$B (20)	40	4	25	0.52	0.54	0.50	1.00	1.04	0.96	0.50

^{a} Final volume of the reaction mixture. ^{b} Determined by titration against standard acid. ^{c} Determined either by direct GLC analysis of volatile R$_3$B or by GLC analysis of alcohol produced after oxidation. ^{d} By hydrolysis or by quenching with *n*-octyl iodide ^{e} Calculated from the amount of R$_3$B and the total volume of the reaction mixture.
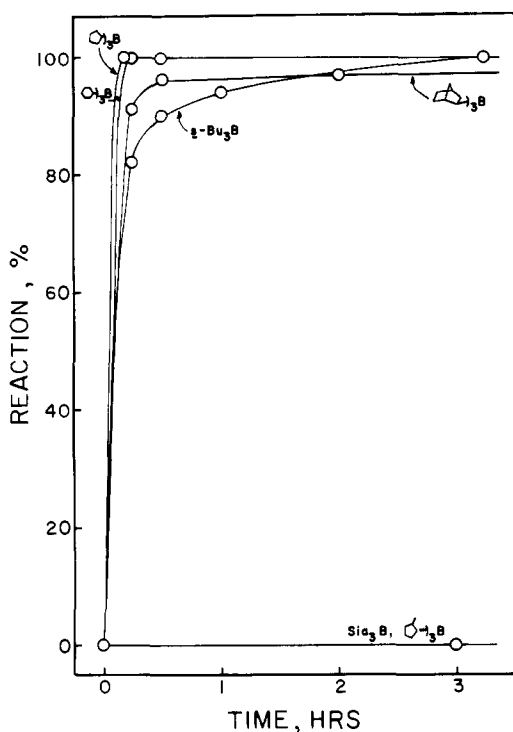

Figure 4. Reaction of hindered organoboranes with sodium hydride in refluxing tetrahydrofuran (65 °C).

Table III. Infrared Spectra of Alkali Metal Trialkylborohydrides in Tetrahydrofuran

Trialkylborohydride	ν_{B-H}, cm^{-1}
Lithium triethylborohydride	2060
Lithium tri-*n*-butylborohydride	2028
Lithium triisobutylborohydride	2061
Lithium perhydro-9b-boraphenalyl hydride	2028
Sodium triethylborohydride	1960
Sodium tri-*n*-butylborohydride	2000
Sodium triisobutylborohydride	2000
Sodium tri-*sec*-butylborohydride	2025
Sodium tricyclopentylborohydride	2010
Sodium tricyclohexylborohydride	2020
Sodium tri-*exo*-2-norbornylborohydride	2020
Sodium perhydro-9b-boraphenalyl hydride	2030

an excess of *n*-octyl iodide, followed by GLC analysis for *n*-octane. Moreover, the observed concentration of the borohydride solution agreed well with the concentration calculated on the basis of the amount of trialkylborane and the total volume of the reaction mixture. These results clearly establish beyond any doubt the stoichiometry of the reaction between trialkylboranes and alkali metal hydrides to be 1:1 (eq 9).

Infrared Spectra. Alkali metal trialkylborohydrides exhibit a strong and broad absorption in the infrared region due to the B–H stretch in the borohydride anion. This intense absorption is characteristic of this new class of compounds. Solutions of all trialkylborohydrides exhibit this characteristic absorption around 2000 cm^{-1}, the exact frequency being dependent on various factors such as the solvent, the nature of the alkyl group, and the cation.[4] The results are summarized in Table III.

^{11}B NMR Spectra. Trialkylboranes exhibit a very broad singlet around δ + 80 (BF$_3$·Et$_2$O). Solutions of lithium triethylborohydride prepared in quantitative yield (by hydride analysis) by stirring lithium hydride and triethylborane at 25 °C for 24 h exhibit a sharp singlet. Similarly, solutions of lithium tri-*n*-butylborohydride and lithium triisobutylborohydride prepared in quantitative yields in refluxing THF exhibit only singlets. These phenomena are similar to the fast exchanges observed by Brown in the KEt$_3$BH–Et$_3$B and K-

n-Bu$_3$BH–*n*-Bu$_3$B systems.[13] The observation of singlets rather than the expected doublets is attributed to the presence of a minute quantity of free triethylborane which rapidly exchanges with lithium trialkylborohydride in the NMR time scale resulting in the coalescence of the doublet.

Thus, the solution of lithium triethylborohydride prepared in refluxing THF exhibits a clean doublet at δ −12.3 (J = 55 Hz). Similarly, the addition of a minute amount of *tert*-butyllithium to the THF solution of lithium triisobutylborohydride, a procedure that converts free trialkylboranes into borohydrides,[14] converts the single peak into a clean doublet at δ −17.7 (J = 67 Hz).[8]

Unlike lithium trialkylborohydrides, all of the sodium trialkylborohydrides exhibit clean doublets. The results are summarized in Table IV.

Stability of Trialkylborohydride Solutions. Protected from moisture and air, THF solutions of trialkylborohydrides are highly stable. The stability of these solutions was monitored by following the changes in hydride concentration with time. One particular sample of lithium triethylborohydride maintained 100% hydride concentration even after 1 year.

When these solutions are exposed to the atmosphere, they lose hydride activity rapidly. Exposure to dry air destroys the hydride activity rather slowly.

These reagents react rapidly with water, aqueous hydrochloric acid, methanesulfonic acid, and simple alcohols such as methanol, evolving hydrogen quantitatively. Consequently, this can be utilized as a convenient method for the determination of active hydride.

Conclusion

The rates of reaction of trialkylboranes with lithium and sodium hydrides are sensitive to the steric requirements of the alkyl groups attached to boron. An increase in the size of the alkyl groups results in a sharp decrease in the reaction rate. Furthermore, for the particular samples of material used, sodium hydride was observed to be much more reactive than

Table IV. ^{11}B NMR Spectra of Alkali Metal Trialkylborohydrides in Tetrahydrofuran

Trialkylborohydride	Chemical shift,[a] δ (multiplicity)	J_{B-H}, Hz
Lithium triethylborohydride	−12.3 (d)	55
Lithium tri-*n*-butylborohydride	−13.3 (s)	
Lithium triisobutylborohydride[b]	−15.0 (s)	
Lithium perhydro-9b-borophenalyl hydride	−10.8 (s)	
Sodium triethylborohydride	−12.7 (d)	65
Sodium tri-*n*-butylborohydride	−14.7 (d)[c]	50
Sodium triisobutylborohydride	−17.7 (d)	65
Sodium tri-*sec*-butylborohydride	−6.32 (d)	65
Sodium tricyclopentylborohydride	−10.1 (d)	53
Sodium tricyclohexylborohydride	−6.47 (d)	63
Sodium tri-*exo*-2-norbornylborohydride	−8.4 (d)	63
Sodium perhydro-9b-boraphenalyl hydride[d]	−10.6 (d)	65
	−11.7 (d)	63

[a] All chemical shifts are relative to $BF_3 \cdot OEt_2$ with the chemical shifts upfield from $BF_3 \cdot OEt_2$ assigned as negative. [b] Addition of a few drops of *tert*-butyllithium to this solution resulted in a doublet at δ −17.7 ($J = 67$ Hz). [c] The decoupled spectrum also showed a resonance at δ −12.0 due to the presence of about 6% Na(*sec*-Bu)(*n*-Bu)$_2$BH. [d] Probably isomeric pair; area of δ −10.6/area of δ −11.7 is approximately 1/1.

lithium hydride. In addition to furnishing the order of reactivity for lithium and sodium hydrides toward various trialkylboranes, the present study provides a simple method for preparing under mild conditions in essentially quantitative yield a wide variety of lithium and sodium trialkylborohydrides of greatly varying steric requirements. Many of the sodium derivatives were previously unknown. These new compounds should find wide applicability as powerful and selective reducing agents as well as utility in several other fascinating reactions.

Experimental Section

All glassware was dried at for least 4 h at 140 °C, assembled hot, and cooled under a stream of prepurified nitrogen (Airco). All reactions were carried out under a dry nitrogen atmosphere.[15]

Materials. Tetrahydrofuran, organoboranes, and metal hydrides were stored under nitrogen. Most liquids were kept in Teflon stopcock protected ampules. Tetrahydrofuran was distilled from excess lithium aluminum hydride. Triethylborane (Callery) was used as received; the isomeric tributylboranes were distilled before use. All other trialkylboranes were prepared by the hydroboration of corresponding olefins with $BH_3 \cdot THF$.[6] Most olefins and alkanes employed in this study were from the Phillips Petroleum Co. Lithium hydride and sodium hydride (50% in oil) from the Ventron Corp. were used as received. The same sample of each hydride was utilized throughout the study.

Spectra. Spectra were obtained under inert atmosphere using apparatus and techniques described elsewhere.[15] Infrared spectra were obtained with either Perkin-Elmer 137 or 700 spectrometers using sealed liquid cells and the two-syringe technique.[15] ^{11}B NMR spectra were recorded on a Varian XL-100-15 spectrometer (32.1 MHz) fitted with a Nicolet 1080 data acquisition system. The spectra were recorded in either the CW mode or the FT mode using ^{2}H internal or ^{19}F external locks; all chemical shifts are relative to $BF_3 \cdot OEt_2$ (δ 0) with the chemical shifts downfield from $BF_3 \cdot OEt_2$ assigned as positive.

GLC Analyses. GLC analyses were carried out with either a Varian Model 1200 FID chromatograph or a Hewlett-Packard 5752B chromatograph with TC detector.

Rates of Reaction of Alkali Metal Hydrides with Organoboranes in Tetrahydrofuran. A. Reaction of Lithium Hydride with Triethylborane at 25 °C. An oven-dried 50-mL flask, equipped with a Teflon stopcock, a silicone rubber stopple, and a magnetic stirring bar, connected to a mercury bubbler, was cooled to room temperature under a stream of dry nitrogen. The flask was immersed in a water bath (ca 25 °C). In the flask were placed 0.12 g (15 mmol) of finely divided

lithium hydride and 8.6 mL of dry THF. Then 1.42 mL (10 mmol) of triethylborane was added and the resulting mixture stirred well. At appropriate intervals of time, 0.5 mL (0.5 mmol) of the reaction mixture was withdrawn using a syringe and injected into a 5-mL flask equipped with a magnetic stirring bar and maintained under a static pressure of nitrogen at 25 °C. THF (1 mL) followed by 0.5 mmol of *n*-octyl iodide and 0.5 mmol of *n*-nonane were introduced. After stirring for 10 min, 1 mL of water was added and the THF layer was dried with anhydrous potassium carbonate. The dry THF layer was subjected to GLC analysis in a 5% SE-30 column, 6 ft × 0.125 in., coated on AW-DMCS Chromosorb W. The amount of *n*-octane produced is a measure of the amount of the trialkylborohydride formed. The reaction was checked at 0.25 (73%), 0.5 (78%), 6 (90%), 12 (92%), and 24 h (98%).

B. Reaction of Lithium Hydride with Triisobutylborane at 65 °C. An oven-dried, 100-mL flask, equipped with Teflon stopcock, silicone rubber stopple, magnetic stirring bar, and reflux condenser connected to a mercury bubbler, was cooled to room temperature. In the flask were placed 0.48 g (60 mmol) of finely divided lithium hydride and 30.2 mL of tetrahydrofuran. The mixture was brought to gentle reflux under nitrogen, 9.8 mL (40 mmol) of triisobutylborane was injected into the reaction flask, and the mixture was stirred vigorously. The reaction mixture is 1.0 M in triisobutylborane.

After 15 min, 0.5 mL of the reaction mixture was reacted with *n*-octyl iodide as in the previous experiment. Analysis of the dry THF layer indicated the presence of 20% *n*-octane, corresponding to the presence of 20% triisobutylborohydride.

Similarly, the reaction was checked at 1 (74%), 3 (88%), 6 (98%), and 12 h (99%). The reaction mixture was filtered to separate the excess lithium hydride giving a crystal-clear solution of lithium triisobutylborohydride in THF, 1.05 M in hydride: ^{11}B NMR δ −15 (s); IR 2061 cm^{-1} (B–H).

Addition of a few drops of *tert*-butyllithium in pentane to this solution was followed by reexamination of the ^{11}B NMR: δ −17.7 (d, $J = 68$ Hz).

C. Reaction of Lithium Hydride with Tri-*sec*-butylborane at 65 °C. The apparatus was as in the previous experiment. In the flask were placed 0.48 g (60 mmol) of lithium hydride and 30.3 mL of THF. The mixture was brought to a constant reflux under nitrogen and 9.7 mL (40 mmol) of tri-*sec*-butylborane was injected into the flask. The mixture was stirred vigorously and the reaction was monitored by the *n*-octyl iodide reduction technique. The rate of reaction was quite slow. In 24 h reaction had proceeded only to the extent of 10%. Excess lithium hydride was removed by filtration and the clear solution exhibited hydride activity corresponding to 15% of borohydride formation. Infrared examination of the clear solution showed a weak B–H absorption at 2070 cm^{-1}.

A small portion of this solution (2 mL) was injected into a reaction flask containing aqueous HCl and then oxidized with $NaOH-H_2O_2$ at 50 °C for 1 h. The aqueous layer was saturated with anhydrous potassium carbonate. GLC examination of the dry ethereal layer in a 5% Carbowax 20M column, 6 ft × 0.125 in., indicated the presence of 100% 2-butanol and the complete absence of 1-butanol. This rules out the possibility of any isomerization of tri-*sec*-butylborane that might have taken place during the reaction.

D. Reaction of Lithium Deuteride with Triethylborane at 65 °C. A typical reaction setup was assembled. Lithium deuteride (1.44 g, 160 mmol) was placed in the reaction flask (200 mL). Then 68.6 mL of THF was injected. After the reaction mixture was brought to constant reflux, 11.4 mL (80 mmol) of triethylborane was carefully introduced into the reaction flask and vigorously stirred. Analysis of an aliquot of the reaction mixture after 1 h by quenching with a known quantity of *n*-octyl iodide revealed the presence of 100% lithium triethylborodeuteride. After an additional 1 h of stirring, the mixture was cooled and filtered resulting in a crystal-clear solution of lithium triethylborodeuteride in THF, stable under nitrogen indefinitely. The concentration was found to be 1 M (100% yield) by hydrolysis.

E. Reaction of Sodium Hydride with Tri-*n*-butylborane at 25 °C. A dry 50-mL reaction flask with magnetic stirring bar and septum inlet was capped with a large rubber septum and purged with nitrogen using a nitrogen-filled glovebag; 1.51 g (31 mmol) of the sodium hydride dispersion in mineral oil was placed in the flask. The large septum was replaced by a reflux condenser fitted with a connecting tube connected to a mercury bubbler. The dispersion was washed with three 10-mL portions of THF. The sodium hydride was dried with a stream of nitrogen while being stirred. The flask was immersed in a water bath

Table V. Stability of Alkali Metal Trialkylborohydride Solutions in Tetrahydrofuran at 25 °C[a]

| Experimental conditions | Reagent | Time | | | | | | | | | | | |
		0.0	0.25 h	0.5 h	1.0 h	3.0 h	6.0 h	12.0 h	24.0 h	7 days	15 days	1 month	1 year
Dry nitrogen	LiEt$_3$BH	1.03 (100)			1.03 (100)			1.03 (100)	1.03 (100)	1.03 (100)		1.03 (100)	1.03 (100)
	NaEt$_3$BH	0.96 (100)									1.02[b] (104)		
Dry air	LiEt$_3$BH	1.03 (100)			0.94 (91)	0.86 (84)	0.82 (80)	0.7[c] (68)	0.55 (53)				
	NaEt$_3$BH	0.9 (100)		0.84 (94)	0.8 (90)	0.66 (74)	0.52 (58)	0.24 (27)	0.0 (0)				
Air and moisture	LiEt$_3$BH	1.03 (100)	0.88 (86)	0.82 (80)	0.57 (55)	0.0 (0)							
	NaEt$_3$BH	0.9 (100)	0.80 (89)	0.74 (82)	0.62 (70)	0.28 (32)	0.0 (0)						

[a] Figures in parentheses are percentages of hydride concentration compared with initial (0 h) concentration. [b] Presumably due to slight loss of THF. [c] Solution becomes slightly turbid.
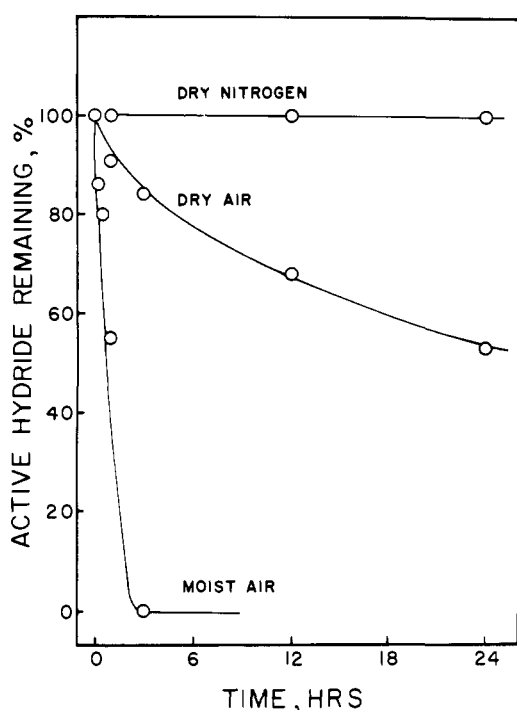

Figure 5. Loss of hydride activity in lithium triethylborohydride solution in tetrahydrofuran at 25 °C.

and 15.1 mL of THF was added. This was followed by the addition of 4.9 mL (20 mmol) of tri-*n*-butylborane. A vigorous reaction began immediately. After 15 min, analysis of the reaction mixture by the *n*-octyl iodide reduction technique indicated the presence of tri-*n*-butylborohydride in quantitative yield: ^{11}B NMR δ −14.7 (d, $J = 50$ Hz); IR 2000 cm^{-1} (B–H).

G. Attempted Reaction of Trisiamylborane and Tris(*trans*-2-methylcyclopentyl)borane with Sodium Hydride at 65 °C. The apparatus and procedure were identical with those of the previous experiments. Trisiamylborane showed at most 13% reaction after 43 h at reflux: ^{11}B NMR δ +86 (s), −14.9 (t, $J = 70$ Hz). Tris(*trans*-2-methylcyclopentyl)borane showed at most 17% reaction after 38 h: ^{11}B NMR δ +86 (s), −11.9 (t, $J = 60$ Hz). The only apparent reaction in either case is dehydroboration followed by reaction of the dialkylborane with sodium hydride to form the sodium dialkylborohydride.

Preparative Scale Synthesis of Alkali Metal Trialkylborohydrides in Tetrahydrofuran. The following procedure employed for the synthesis of lithium triethylborohydride is representative. An oven-dried, 500-mL flask equipped with a side arm fitted with a Teflon stopcock and a silicone rubber stopple, a magnetic stirring bar, and a reflux

condenser connected to a mercury bubbler was cooled to room temperature under a stream of dry nitrogen. In the flask were placed 3.2 g (400 mmol) of finely divided lithium hydride and 215 mL of dry THF. The flask was immersed in an ice bath (0 °C). Then 35.2 mL of triethylborane (250 mmol) was introduced and the resulting mixture was stirred under nitrogen. After 1–2 h, the ice bath was replaced by a water bath (ca. 25 °C). Analysis of the reaction mixture by the *n*-octyl iodide reduction technique at the end of 24 h revealed the presence of 100% lithium triethylborohydride. The resulting solution was filtered under nitrogen through a sintered-glass disk.[15] The solution was stored in a 500-mL flask with a Teflon stopcock. The solution was standardized by withdrawing a known aliquot with a hypodermic syringe, hydrolyzing with a THF-glycerine–water mixture (1:1:1), and measuring the hydrogen evolved. The concentration was found to be 1.0 M in LiEt$_3$BH.(100% yield) which is also the expected concentration based on the stoichiometry of the reaction: IR 2060 cm^{-1} (B–H).

In another experiment, 1 mol of lithium triethylborohydride was synthesized without difficulty.

Similarly, a number of other alkali metal trialkylborohydrides were synthesized on a preparative scale in quantitative yields.

Stoichiometry. A. Ratio of Li$^+$:B:H$^-$ in Lithium Triethylborohydride. In a typical experiment, a 2-mL aliquot of the crystal-clear solution of lithium triethylborohydride, approximately 1.0 M, was hydrolyzed in a THF–water–glycerine mixture (1:1:1) and the hydrogen evolved (54 mL) was measured. This indicated the hydride concentration to be 1.05 M.

To a mixture of 2 mL of THF, 0.8 mL (1.6 mmol) of 2 M aqueous hydrochloric acid, and *n*-nonane (internal standard, 1 mmol) 1 mL of the borohydride solution was added and the resulting mixture stirred well for 0.5 h. The mixture was analyzed by GLC as described previously. From the amount of triethylborane, the concentration of boron was calculated to be 1.08 M.

Lithium triethylborohydride solution (1 mL) was quenched with water and titrated with 0.116 N hydrochloric acid to a phenolphthalein end point. It required 9 mL of the standard acid, indicating the concentration of the lithium ion to be 1.05 M. The ratio of Li$^+$:B:H$^-$ is thus 1.00:1.02:1.00.

B. Ratio of Na$^+$:B:H$^-$ in Sodium Tricyclohexylborohydride. Determination of active hydride was by addition of 1.0 mL of an approximately 0.5 M solution in THF to a solution of *n*-nonane and *n*-octyl iodide in THF as described previously. GLC analysis revealed 0.50 mmol of *n*-octane corresponding to 0.50 M in active hydride.

Sodium was determined by injection of 1 mL of the hydride solution into 3 mL of water, adding sufficient THF to dissolve the precipitated tricyclohexylborane formed, and titration with standard hydrochloric acid (0.2394 M); 2.18 mL of the acid was required, indicating the concentration to be 0.52 M.

Boron was determined by oxidation of 3 mL of the hydride solution using 1 mL of 3 M sodium hydroxide and 1.5 mL of 30% hydrogen peroxide. GLC analysis using *n*-tetradecane as an internal standard revealed 4.85 mmol of cyclohexanol. This corresponds to a boron concentration of 0.54 M in the solution.

The ratio of Na^+:B:H^- is thus 1.00:1.04:0.96 indicating 1:1:1 stoichiometry. The results are summarized in Table II.

Stability of Alkali Metal Trialkylborohydrides. A. Dry Nitrogen. Solutions of lithium triethylborohydride and sodium triethylborohydride were analyzed for the hydride concentration periodically either by hydrolysis or by the *n*-octyl iodide reduction technique. The results clearly indicate that under dry nitrogen these reagents are indefinitely stable.

B. Effect of Dry Air. A 100-mL flask with a side arm was fitted with a condenser protected by a drying tube (filled with Drierite®) and flushed with dry air. Lithium triethylborohydride, 20 mL (~20 mmol) of a standard solution in THF, was introduced and allowed to stand exposed to dry air with constant stirring. At appropriate intervals, aliquots were removed and analyzed for residual hydride. Thus, in 1 h only, 6% hydride loss was observed and in 24 h 45% hydride had been destroyed.

A similar experiment was conducted with a solution of sodium triethylborohydride.

C. Effect of Air and Moisture. Lithium triethylborohydride solution (15 mL) was syringed into a 50-mL Erlenmeyer flask. The flask was covered with a lid which had an opening 0.4 in. in diameter. Periodically, aliquots were removed and analyzed for the residual hydride. The solution lost the hydride activity completely in 3 h, revealing that the THF solution of this reagent is more sensitive to moisture than dry air alone. A similar study was conducted with sodium triethylborohydride.

The results are summarized in Table V and Figure 5.

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An Ultraviolet Photoelectron Spectroscopic-Molecular Orbital Study of Some Cyclopolyphosphines

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Abstract: He(1) photoelectron spectra of the cyclotriphosphine, $(C_2F_5P)_3$ (**1**), the cyclotetraphosphines $(CF_3P)_4$ (**2**), $(C_2F_5P)_4$ (**3**), $(t\text{-}C_4H_9P)_4$ (**4**), and $(C_6H_{11}P)_4$ (**5**), and the cyclopentaphosphines $(CF_3P)_5$ (**6**), $(CH_3P)_5$ (**7**), $(C_2H_5P)_5$ (**8**), and $(n\text{-}C_3H_7P)_5$ (**9**) have been measured. The technique of ultraviolet photoelectron spectroscopy (PES) has been shown to be capable of differentiating cyclopentaphosphines from other cyclopolyphosphines in the vapor phase. The trends in the observed ionization energies (IEs) of the phosphorus lone pair electrons are discussed from the standpoints of nearest neighbor and cross-ring lone pair interactions, substituent electronegativity effects, and P(3d) orbital participation. The PES assignments are based principally on MNDO molecular orbital (MO) calculations on **2** and the model compounds $(PH)_3$, $(PH)_4$, $(CH_3P)_4$, and $(PH)_5$. MO calculations of the STO-6G type have also been performed on $(PH)_4$.

Ring size assessment has turned out to be one of the more contentious problems in the chemistry of the cyclopolyphosphines.[3-5] X-ray crystallography has played an important role in the delineation of ring sizes and conformations in the solid state; however, to date only a small number of molecules have been investigated by this technique.[6-11] More recently, the advent of Fourier transform ^{31}P NMR spectroscopy has permitted the measurement of ring sizes in solution.[4] However, the study of ring sizes in the vapor state has been much more limited. In principle mass spectrometry could be employed for this purpose. However, in practice the technique has proved unreliable because of the weakness of the parent peak, the occurrence of collision species, and the sensitivity of the results to ionizing voltage and inlet temperature.[12] In the present article it will be demonstrated that in certain cases UV photoelectron spectroscopy can be used to assess the ring sizes of cyclopolyphosphines in the vapor phase.[13] The technique might be applicable to a wide variety of homocatenates which feature lone pair electrons.

An additional facet of interest in the cyclopolyphosphines relates to the nature of the bonding. Following the discovery that cyclopolyphosphines exhibit intense ultraviolet spectra a model was suggested in which circumannular delocalization of phosphorus lone pair electrons is achieved by 3d orbital participation.[14] It has been found that PES data have a bearing both on this postulate and also on the question of cross-ring interactions. As an interpretational aid we have performed MNDO (modified neglect of diatomic overlap) molecular