2,2,4-Trimethyl-4-(*p*-methoxyphenyl)cyclohexanol (15). To freshly distilled geraniolene monoepoxide (0.85 g, 6 mmol) in 15 mL of sodium-dried anisole was added slowly 0.4 g (1.5 mmol) of $SnCl_4$ at 0 °C. The resulting mixture was stirred at room temperature for 3 h. The organic layer was diluted with 25 mL of ether, then washed with 10% HCl, 5% $NaHCO_3$, and H_2O, and dried ($MgSO_4$). The in vacuo evaporated organic layer (0.12 g) was analyzed by VPC (Carbowax column, 192 °C) and found to give the same compounds as reported by Goldsmith for the previous reaction in benzene[12a] and also a late peak at 30.5 min (which was 67% of the product distribution, or 5% yield) identified as **15** as follows. The compound was isolated by preparative VPC: IR (AgCl disks) 825 (m, para-disubstituted benzene), 1015 (s, br, OH), 1250 (s, anisole ether), 1510 (s), 3100–3600 (br s, OH) cm^{-1}; NMR (CCl_4) δ 6.9 (AB, 4 H, *p*-anisyl, J_{AB} = 9 Hz), 3.7 (s, 3 H), 3.2 (m, 1 H, CH–O), 0.8–2.3 (m, br, remaining 16 H); mass spectrum, m/z (relative intensity) 51 (100), 77 (20), 91 (22), 121 (42), 133 (22), 147 (20), 148 (44), 161 (35), 162 (21), 215 (43), 230 (4), 233 (12), and 248 (6).

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Addition Compounds of Alkali Metal Hydrides. 20. Reaction of Representative Mono- and Dialkylboranes with Saline Hydrides To Form the Corresponding Alkylborohydrides

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The reaction of lithium, sodium, and potassium hydrides with representative mono- and dialkylboranes in tetrahydrofuran was examined in detail with respect to rate, stoichiometry, and products. With the exception of 9-borabicyclo[3.3.1]nonane and thexylborane, all other organoboranes examined react with lithium hydride sluggishly and incompletely. On the other hand, sodium hydride exhibits a much greater reactivity than lithium hydride in these reactions. The rate of the reaction is strongly influenced by the steric requirements of the alkylboranes. Thus, the rates of reaction of sodium hydride with a series of dialkylboranes at 25 °C follow the order 9-borabicyclo[3.3.1]nonane > dicyclohexylborane > disiamylborane > diisopinocampheylborane. The reactivity of potassium hydride in this reaction greatly exceeds that of sodium hydride. It reacts almost instantaneously and quantitatively. The reaction with mono- and dialkylboranes involves a 1:1 stoichiometry, producing the corresponding alkali metal mono- and dialkylborohydrides, characterized by hydride analysis, IR, and ^{11}B NMR spectral characteristics. These derivatives are very stable and can be stored under nitrogen at 25 °C without any hydride loss, redistribution, or isomerization of the alkyl groups. Methyl iodide readily and quantitatively removes metal hydride from these adducts, regenerating the free mono- and dialkylboranes. The present study also provides a simple method for preparing a wide variety of hitherto unknown lithium, sodium, and potassium mono- and dialkylborohydrides under mild conditions, as well as a procedure for storing mono- and dialkylboranes for extended periods of time.

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 other reagents currently available. Numerous applications of these new reducing agents have already been reported.[2]

This paper deals exclusively with the alkali metal alkylborohydrides. Consequently, a short history of these derivatives is in order. Trialkylborohydrides were first prepared by Schlesinger, Brown, and co-workers in the period of 1942 to 1945.[3] A detailed study of these reactions was later carried out using vacuum-line techniques.[4] Köster and co-workers have reported the synthesis of a number of trialkylborohydrides using rather harsh reaction conditions in the absence of ethereal solvents.[5] However, the results reveal that the reaction between trialkylboranes and alkali metal hydrides proceeds far better in tetrahydrofuran (THF)[2a] or ethyl ether (EE) than in hydrocarbon solvents or under neat conditions.[5]

Recently a systematic study of the rates of reaction of lithium and sodium hydrides with trialkylboranes of increasing steric requirements has been described.[6] Most unhindered organoboranes react completely with lithium hydride in a few hours under reflux. The corresponding deuterium derivatives can be conveniently prepared from lithium deuteride. However, the reaction of hindered

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(1) (a) Postdoctoral research associate on Grant No. GM-10937 from the National Institutes of Health. (b) Postdoctoral research associate on Grant No. DAAG 29-79-C-0027 from the U.S. Army Research Office.

(2) (a) Krishnamurthy, S. *Aldrichimica Acta* **1974**, *7*, 55. (b) Brown, H. C.; Dickason, W. C. *J. Am. Chem. Soc.* **1970**, *92*, 709. (c) Krishnamurthy, S.; Brown, H. C. *Ibid.* **1976**, *98*, 3383. (d) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1976**, *41*, 3064. (e) Krishnamurthy, S.; Vogel, F.; Brown, H. C. *Ibid.* **1977**, *42*, 2534.

(3) Brown, H. C.; Schlesinger, H. I.; Sheft, I.; Ritter, D. M. *J. Am. Chem. Soc.* **1953**, *75*, 192.

(4) Khuri, A. Ph.D. Thesis, Purdue University, 1960.

(5) Binger, P.; Benedikt, G.; Rotermund, G. W.; Köster, R. *Justus Liebigs Ann. Chem.* **1968**, *717*, 21.

(6) Brown, H. C.; Krishnamurthy, S.; Hubbard, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3343.

0022-3263/81/1946-2712$01.25/0

Table I. Reaction of Saline Hydrides with Representative Mono- and Dialkylboranes in THF[a]

mono- or dialkylborane	metal hydride	temp, °C	mono- or dialkylborohydride, %,[b] at time, h							
			0.25	0.5	1.0	2.0	3.0	6.0	12.0	24.0
9-borabicyclo[3.3.1]nonane	LiH	25	0	0	0	0	0	0	30	81
	LiH	65	0	4	30	38	54	97	97	
	NaH	25	0	0	0	56	100	100		
	KH	25	100	100						
dicyclohexylborane	LiH	25	0	0	0	0	0	0	0	20
	LiH	65	0	24	42	58	65	70		
	NaH	25	0	0	0	4	29	98	98	
	KH	25	100	100						
disiamylborane	LiH	25	0	0	0	0	0	0	12	49
	LiH	65	0	8	73	98	98			
	NaH	25	0	14	27	47	63	89	100	100
	KH	25	100	100						
diisopinocampheylborane	LiH	25	0	0	14	25	34	49	68	89
	LiH	65	0	12	26	61	95	100		
	NaH	25	0	0	0	12	28	70	99	
	KH	0	0	65	100	100				
thexylborane	LiH	25	0	0	0	0	0	0	0	0
	LiH	65	0	0	22	78	98	98		
	NaH	25	0	0	0	20	40	100	100	
	KH	25	100	100						
monoisopinocampheylborane	NaH	25	0	5	10	18	27	55	99	99
	KH	25	80	100	100					

[a] Solutions were 0.5 M in organoborane and approximately 50% excess of alkali metal hydride was utilized. [b] Monitored by hydrolysis of the centrifuged reaction mixture and by ^{11}B NMR spectroscopy.

trialkylboranes with lithium hydride is incomplete under these conditions. Fortunately, potassium hydride[7] and, to a lesser extent, sodium hydride[6] are much more reactive than lithium hydride.[6]

Suprisingly, very little is known about the synthesis and chemistry of dialkylborohydrides which could be derived from the reaction between alkali metal hydrides and dialkylboranes.[8] On the other hand, the alkali metal monoalkylborohydrides are not described in the literature. Therefore, we undertook a systematic examination of the reaction of lithium, sodium, and potassium hydrides with repesentative di- and monoalkylboranes as a possible route to the corresponding di- and monoalkylborohydrides.

Results and Discussion

The following dialkyl- and monoalkylboranes of varying steric requirements were selected for this study: 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane [$(Chx)_2BH$], disiamylborane [bis(3-methyl-2-butyl)borane, Sia_2BH], diisopinocampheylborane [IPC_2BH], thexyl borane ($ThxBH_2$), and monoisopinocampheylborane ($IPCBH_2$). The rates of reaction of these borane derivatives with lithium, sodium, and potassium hydrides were examined. The physical and chemical characteristics of the resulting alkylborohydride solutions were investigated.

Reaction of Representative Di- and Monoalkylboranes with Saline Hydrides in Tetrahydrofuran. The reactions were generally carried out with a 50% excess of metal hydride suspended in a 0.5 M solution of an alkylborane in THF. In the case of potassium hydride, which is commercially available as a 22–25% suspension in mineral oil, the oil coating was removed by washing with *n*-pentane. In most of the cases, when an alkylborane was soluble in THF, a standard solution of the alkylborane was added to the solid metal hydride. In other cases where the alkylborane was insoluble in THF, a suspension of metal hydride in THF was added to the alkylborane. In all cases the reaction mixtures were vigorously stirred at similar rates. The reactions were carried out either at room temperature or under reflux conditions, depending on the reactivity of the borane.

When $IPCBH_2$ was prepared in the usual manner[9] from bis(monoisopinocampheylborane)-*N*,*N*,*N*′,*N*′-tetramethylethylenediamine ($TMED{\cdot}2IPCBH_2$) and $Et_2O{\cdot}BF_3$, the excess $Et_2O{\cdot}BF_3$ present in solution interfered with the reaction between $IPCBH_2$ and the metal hydride. This difficulty was circumvented by using $Me_2S{\cdot}BH_3$ (BMS) to liberate $IPCBH_2$ from its TMED adduct (eq 1). Excess BMS was removed by stirring the reaction mixture over NaH or KH (eq 2 and 3). Pure $IPCBH_2$ was then separated by centrifugation and treated with fresh MH to get the corresponding monoalkylborohydrides.

$$TMED{\cdot}2IPCBH_2 + 2Me_2S{\cdot}BH_3 \xrightarrow[1\ h,\ 25\ ^\circ C]{THF} 2IPCBH_2 + TMED{\cdot}2BH_3\downarrow \quad (1)$$

$$Me_2S{\cdot}BH_3 + KH \xrightarrow[10\ min,\ 25\ ^\circ C]{THF} KBH_4\downarrow + Me_2S \quad (2)$$

$$Me_2S{\cdot}BH_3 + NaH \xrightarrow[30\ min,\ 25\ ^\circ C]{THF} NaBH_4\downarrow + Me_2S \quad (3)$$

Earlier studies in this field had revealed that different hydride samples may exhibit different reativities.[10] In order to minimize the effect of this factor, the same sample of each metal hydride was utilized throughout the study.

The reaction course was monitored by measuring the hydrogen evolved on hydrolysis of a known aliquot of the solution (centrifuged to remove suspended metal hydride). The reaction was also followed by withdrawing known aliquots of the reaction mixture at various intervals of time and determining its ^{11}B NMR spectrum. The results are summarized in Table I.

Effects of the Structure of the Alkylborane (Steric Effects). The data summarized in Table I disclosed a number of interesting characteristics of this reaction. One

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(7) (a) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913; (b) *J. Am. Chem. Soc.* **1973**, *95*, 4100. (c) Brown, C. A.; Krishnamurthy, S., *J. Organomet. Chem.* **1978**, *156*, 111.

(8) Hubbard, J. L.; Kramer, G. W. *J. Organomet. Chem.* **1978**, *156*, 89.

(9) Brown, H. C.; Schwier, J. R.; Singaram, B. *J. Org. Chem.* **1978**, *43*, 4375.

(10) Brown, H. C.; Khuri, A.; Kim, S. C. *Inorg. Chem.* **1977**, *16*, 2229.

Table II. Reaction of Dialkylboranes with Lithium Hydride at 65 °C[a]

			product, mmol[c]			
R	ROH,[b] mmol	[H], M	dehydroborated olefin	R_3B	$Li^+[RBH_3]^-$	$Li^+[R_2BH_2]^-$
cyclohexyl	17	0.8	2.0	3.33	4.0	2.0
3-methyl-2-butyl	15	1.05	4.5	1.5	6.0	2.5
isopinocampheyl	14	1.21	6.0		6.0	4.0

[a] Solutions were 0.5 M in R_2BH and reactions were carried out on a 10-mmol scale. [b] Obtained after oxidation of the reaction mixture. [c] Based on GLC analyses of the oxidation product, hydride estimation, and ^{11}B NMR data.

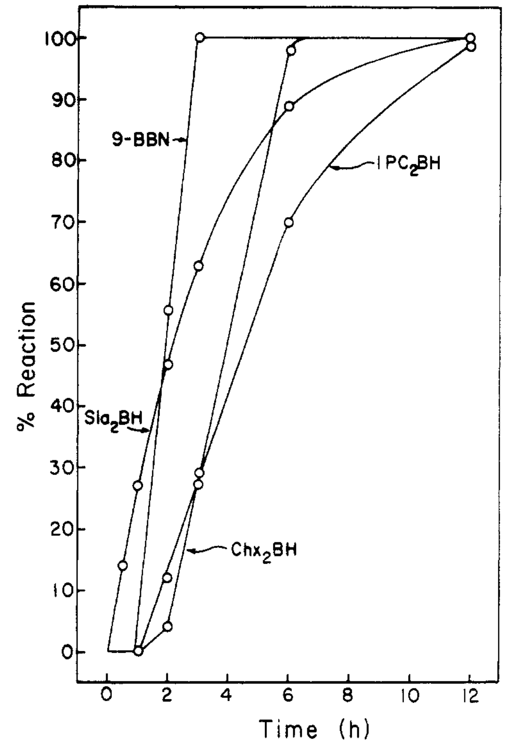
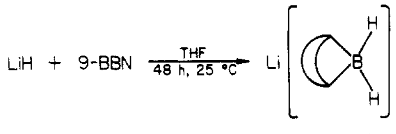


Figure 1. Reaction of sodium hydride with dialkylboranes in THF at 25 °C.

such feature is the remarkable influence of steric effects on reaction rates. The rate of reaction of organoboranes with a given metal hydride is strongly dependent upon the structure of the alkylborane. Increasing the size of the alkyl group on boron markedly decreases the reaction rate. The rates of reaction with metal hydride followed the order 9-BBN > Chx_2BH > Sia_2BH > IPC_2BH (Figure 1).

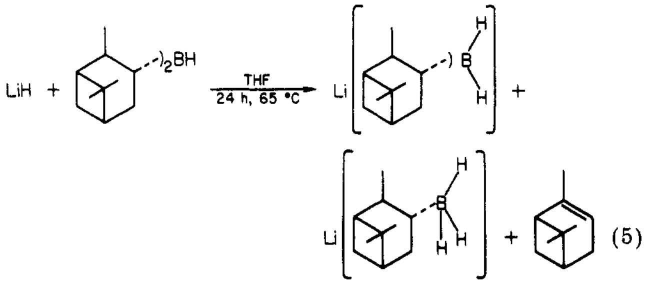
Lithium hydride reacts completely with 9-BBN and $ThxBH_2$ at room temperature after 48 h (eq 4). Di-



(4)

100% yield

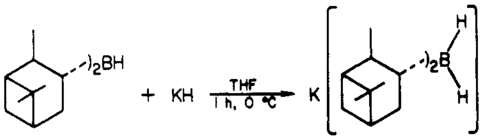
cyclohexylborane, disiamylborane, and diisopinocampheylborane are almost inert to lithium hydride under these conditions. In all cases there was an induction period of 6–8 h before lithium hydride started reacting. Consequently, the reaction of mono- and dialkylboranes with lithium hydride was examined in THF under reflux where lithium hydride reacted rapidly with 9-BBN and $ThBH_2$ and the reaction was complete in 3 h. However, this procedure is not suitable for the preparation of the lithium dialkylborohydrides derived from Chx_2BH, Sia_2BH, and IPC_2BH. Unlike 9-BBN, these organoboranes are thermally unstable. They undergo rapid redistribution and/or elimination of alkyl groups at higher temperatures. As a result, a mixture of products was invariably obtained (Table II) (eq 5).



(5)

The reactions of these organoboranes with sodium hydride are far more facile than the corresponding reactions with lithium hydride. The rates of these reactions vary with the structure of the alkyl group on boron (Figure 1). However, even relatively hindered dialkylboranes, such as IPC_2BH, react quantitatively with sodium hydride at 25 °C.

Finally, potassium hydride reacts almost instantly and quantitatively with all of the alkylboranes examined in this study. Indeed, reactions were so rapid and vigorous that care was needed in controlling the reactions by effectively cooling the flask in a bath (~20 °C). Even such cooling was not adequate for the reaction between IPC_2BH and potassium hydride, which proceeded vigorously, resulting in up to 20% dehydroboration. However, this side reaction could be minimized by mixing the reactants at 0 °C and maintaining that temperature for 1 h (eq 6).



(6)

>95%

Effect of the Metal Hydride. For the particular hydride samples employed in this study, potassium hydride proved to be far more reactive than sodium hydride, which in turn was more reactive than lithium hydride. This result is in agreement with those obtained for the related reaction between metal hydrides and trialkylboranes.[7] The higher reactivity of potassium hydride has been attributed to its lower crystal-lattice energy which facilitates the reaction with alkylboranes.[7a] As shown by the data for the reaction of these three hydrides with 9-BBN at 25 °C, potassium hydride is exceptionally reactive: lithium hydride, 30% in 12 h; sodium hydride, 100% in 3 h; potassium hydride, 100% in <10 min (Figure 2).

Stoichiometry of the Reaction. In the presence of excess alkali metal hydride, both mono- and dialkylboranes exhibit a simple acid–base reaction in a 1:1 ratio (eq 7 and 8). On the basis of this, the ratio of M:B:H in solution

$$R_2BH + MH_{solid} \rightarrow MR_2BH_{2\,soln} \tag{7}$$

$$RBH_2 + MH_{solid} \rightarrow MRBH_{3\,soln} \tag{8}$$

Table III. Analysis of Alkali Metal Mono- and Dialkylborohydride Solutions in THF

MH[a]	RBH_2/ R_2BH[b,c]	time, h	temp, °C	$[M^+]$,[d] M	$[RBH_2]$/ $[R_2BH]$,[e] M	$[H^-]$,[f] M	ratio M	ratio B	ratio H
LiH	9-BBN	6	65	0.46	0.50	0.96	1	1.09	2.07
NaH	9-BBN	3	25	0.46	0.50	0.95	1	1.09	2.06
KH	9-BBN	<0.1	25	0.48	0.50	0.98	1	1.04	2.04
LiH	$ThBH_2$	3	65	0.48	0.50	1.49	1	1.04	3.10
NaH	$ThBH_2$	6	25	0.50	0.50	1.47	1	1	2.94
KH	$ThBH_2$	<0.1	25	0.50	0.50	1.50	1	1	3.00

[a] In each experiment 15 mmol of alkali metal hydride was taken. [b] 10 mmol of alkylborane was added. [c] Final volume was 20 mL. [d] Determined by titration against standard acid. [e] Determined by GLC analysis of alcohol produced after oxidation. [f] By hydrolysis.

Table IV. Infrared and ^{11}B NMR Spectral Data of Alkali Metal Alkylborohydrides in THF

mono- and dialkylborohydrides	ν_{B-H}, cm^{-1}	chemical shift,[a] δ (multiplicity)	J_{B-H}, Hz
lithium 9-boratabicyclo[3.3.1]nonane	2150	−17.4 (t)	72.1
lithium disiamylborohydride	2100	−14.8 (t)	69.0
lithium thexylborohydride	2200	−24.47 (q)	71.0
sodium 9-boratabicyclo[3.3.1]nonane	2125	−18.37 (t)	72.0
sodium disiamylborohydride	2100	−14.95 (t)	71.0
sodium dicyclohexylborohydride		−11.82 (t)	71.8
sodium thexylborohydride	2225	−25.69 (q)	72.0
potassium 9-boratabicyclo[3.3.1]nonane	2145	−16.27 (t)	69.0
potassium disiamylborohydride	2125	−13.06 (t)	71.0
potassium diisopinocampheylborohydride		−4.84 (t)	69.0
potassium thexylborohydride	2200	−21.74 (q)	71.0
potassium monoisopinocampheylborohydride		−21.20 (q)	71.0

[a] With reference to $BF_3 \cdot OEt_2$; negative sign indicates chemical shift upfield from the reference.

should be 1:1:2 for the dialkylborane derivative, and 1:1:3 for the monoalkylborane derivative.

Alkali metal was determined by hydrolyzing a known aliquot of the reaction solution with water and titrating the base formed with a standard acid. Boron was estimated by GC analyses of the alcohol obtained from oxidation of the alkylboranes to the corresponding alcohol. Hydride was determined by measuring the hydrogen evolved from hydrolysis of the solution. Analysis of representative solutions of alkali metal alkylborohydrides for metal, boron, and hydride revealed these M:B:H ratios (Table III). Moreover, the observed concentration of the borohydride solution agreed well with the concentration calculation based on the amount of alkylborane and the total volume of reaction mixture. These data unambiguously establish the stoichiometry of these reactions to be 1:1.

Infrared Spectra. Alkali metal alkylborohydrides display a strong and broad absorption in the infrared region due to the B–H stretch in the borohydride anion. This absorption is typical of this new class of compounds. For example, trialkylborohydrides[6] exhibit characteristic absorption around 2000 cm^{-1}. The exact frequency depends on various factors such as the solvent and the nature of the alkyl group and the cation.[5] Dialkylborohydrides exhibit B–H absorption around 2100 cm^{-1}, while the monoalkylborohydrides absorb at 2200 cm^{-1} and sodium borohydride at 2300 cm^{-1}. The regular change in the B–H stretching frequency, as we go from trialkylborohydride to unsubstituted borohydride, is interesting and may be related to the inductive effect of the alkyl substituents. The results are summarized in Table IV.

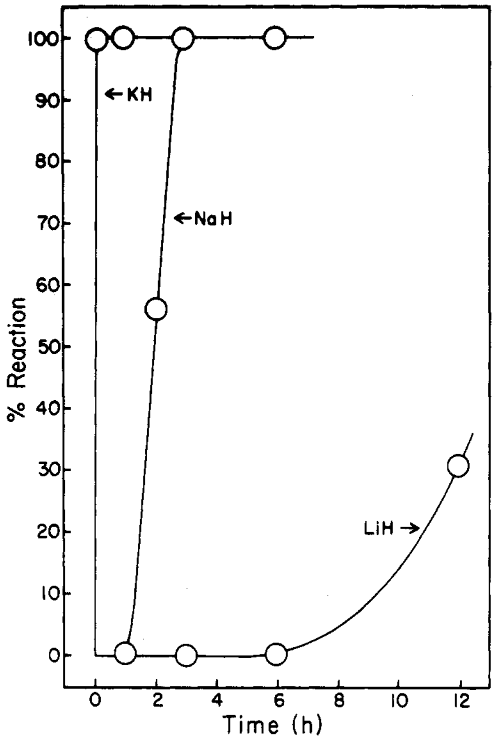


Figure 2. Reaction of 9-borabicyclo[3.3.1]nonane (9-BBN) with various alkali metal hydrides in THF at 25 °C.

^{11}B NMR Spectra. The reaction between the alkylborane and alkali metal hydride was monitored also by ^{11}B NMR spectroscopy. Mono- and dialkylboranes exhibit signals between δ +20 to +35, whereas the corresponding borohydrides exhibit signals between δ −5 to −22. Consequently, the reactions could be easily followed by the disappearance of the mono- or dialkylborane signal with complete formation of the borohydride signal. In the 9-BBN and the $ThxBH_2$ systems, even in the presence of unreacted alkylboranes, the borohydrides exhibit sharp triplets and quartests, respectively. On the contrary, the borohydrides of Chx_2BH, Sia_2BH, and IPC_2BH exhibit broad singlets in the presence of unreacted dialkylboranes. When all of the dialkylboranes have been utilized, the broad signals resolve into sharp triplets. This phenomenon is similar to the fast exchange reported earlier for KEt_3BH–Et_3B and K-n-Bu_3BH-n-Bu_3B systems.[11] When an alkali metal borohydride is mixed with the corresponding alkylborane, the tendency to exchange is greatest in the potassium derivative and least in the lithium derivative.

Stability of Alkylborohydride Solutions. Solutions of mono- and dialkylborohydrides in THF are very stable at room temperature when protected from moisture and air. The stabilities of these solutions were followed both by analyses for hydride estimation and by their ^{11}B NMR spectra. These borohydride solutions were stored for at least 3 months at 25 °C without any detectable loss of hydride or evidence for redistribution or isomerization. These solutions rapidly lose hydride activity when exposed to the atmosphere. Dry air destroys the hydride activity relatively slowly.

Stabilization of Certain Mono- and Dialkylboranes as Alkylborohydrides. A problem in borane chemistry has been the relative instability of the borane reagents.[12] For example, $\mathrm{Chx_2BH}$, $\mathrm{Sia_2BH}$, $\mathrm{IPC_2BH}$, and $\mathrm{ThxBH_2}$ all possess limited stability upon storage. These organoboranes can be stabilized at 0 °C as their ethylenediamine adducts.[13] When stored at 25 °C, these adducts evolve hydrogen to form the corresponding aminoboranes.

The alkali metal borohydrides are very stable, even at 25 °C. Consequently, it is now possible to store these organoboranes as their alkali metal borohydrides for extended periods of time and then to convert these borohydrides conveniently to the free organoboranes when needed by a simple reaction with methyl iodide (eq 9 and 10).

$$\mathrm{MR_2BH_2} + \mathrm{MeI} \xrightarrow[0.5\text{ h},\ 25\ ^\circ\text{C}]{\text{THF}} \mathrm{R_2BH} + \mathrm{MI}\downarrow + \mathrm{CH_4}\uparrow \qquad (9)$$

$$\mathrm{MRBH_3} + \mathrm{MeI} \xrightarrow[0.5\text{ h},\ 25\ ^\circ\text{C}]{\text{THF}} \mathrm{RBH_2} + \mathrm{MI}\downarrow + \mathrm{CH_4}\uparrow \qquad (10)$$

$$\mathrm{M} = \mathrm{Li, Na, K}$$

Conclusion

The rates of reaction of mono- and dialkylboranes with alkali metal hydrides are sensitive to the steric requirements of the alkyl groups attached to boron. In general, potassium hydride is much more reactive than sodium hydride, which in turn is more reactive than lithium hydride. The present study also provides a simple method for preparing a wide variety of lithium, sodium, and potassium mono- and dialkylborohydrides hitherto unknown under mild conditions in essentially quantitative yields. Furthermore, certain mono- and dialkylboranes could be stabilized as their alkali metal hydride adducts and could be regenerated from these derivatives, when needed, by simply reacting with methyl iodide.

Experimental Section

The reaction flasks and other glass equipment were dried in an oven and assembled in a stream of dry nitrogen gas. Special experimental techniques used in handling air-sensitive material are described in detail elsewhere.[14]

Materials. Tetrahydrofuran, organoboranes, and metal hydrides were stored under nitrogen. Most liquids were kept in Teflon stopcock protected ampules. THF was distilled from excess lithium aluminum hydride. 9-Borabicyclo[3.3.1]nonane (Aldrich) was recrystallized from monoglyme. All other organoboranes were prepared by the hydroboration of corresponding olefins with borane methyl sulfide (BMS).[15] Lithium hydride and sodium hydride (50% in oil) were used as received from Ventron Corp. Potassium hydride (24% in oil) was washed with *n*-pentane before use. In order to minimize differences in the reactivity of different samples of alkali metal hydrides, the same sample of each hydride was utilized for the different experiments involving that hydride.

Spectra. Infrared spectra were recorded with Perkin-Elmer 700 spectrometer, using sealed liquid cells and the two-syringe technique.[14] ^{11}B NMR spectra were recorded by using a Varian FT-80A instrument and the chemical shifts are in δ relative to $\mathrm{Et_2O{\cdot}BF_3}$.

GLC Analyses. GLC analyses were carried out with a Hewlett-Packard 5750 chromatograph with a TC detector.

Reaction of Alkali Metal Hydrides with Organoboranes in Tetrahydrofuran. A. Reaction of Lithium Hydride with 9-BBN at 25 °C. In a 50-mL centrifuge vial was placed 0.12 g (15 mmol) of finely divided lithium hydride and 20 mL of a 0.5 M solution of 9-BBN in THF was added to it with constant stirring. At appropriate intervals of time, lithium hydride was centrifuged down and 0.5 mL (0.25 mmol) of the clear supernatant solution was withdrawn for hydride estimation. The aliquots were hydrolyzed by using a THF–water–glycerine mixture (1:1:1) and the hydrogen evolved was measured. Another aliquot (0.5 mL) was analyzed via ^{11}B NMR for unreacted 9-BBN. The reaction was checked at 3 (0%), 6 (0%), 9 (30%), 24 (75%), and 48 h (98%): ^{11}B NMR δ –17.4 (t, J = 72.1 Hz); IR 2150 cm^{-1} (B–H).

B. Reaction of Lithium Hydride with Thexylborane at 65 °C. An oven-dried, 100-mL flask, equipped with a sidearm, magnetic stirring bar, and reflux condenser connected to a mercury bubbler, was cooled to room temperature. In the flask was placed 0.12 g (15 mmol) of finely divided lithium hydride and 20 mL of a 0.5 M solution of $\mathrm{ThBH_2}$ in THF.[15] The mixture was brought to gentle reflux under nitrogen. At different intervals of time, aliquots were withdrawn and centrifuged and the clear solution was used for hydride estimation and for determination of ^{11}B NMR spectrum. The reaction was checked at 1 (20.2%), 1.5 (50%), 2 (87%), and 3 h (100%). The reaction mixture was transferred to a centrifuge vial and the lithium hydride was centrifuged down. The clear supernatant solution, which was transferred into a flask by using a double-ended needle, was found to be pure lithium thexylborohydride in THF, 1.5 M in hydride: ^{11}B NMR δ –24.47 (q, J = 69 Hz); IR 2200 cm^{-1} (B–H).

C. Reaction of Sodium Hydride with Disiamylborane at 25 °C. Into a 50-mL centrifuge vial was placed 0.73 g (15 mmol) of sodium hydride, using a nitrogen-filled glovebag. To this was added 20 mL of a 0.5 M solution of $\mathrm{Sia_2BH}$[15] in THF and the reaction mixture was stirred at 25 °C. Aliquots were withdrawn at appropriate intervals of time and used for active hydride estimation and ^{11}B NMR spectral analysis (Table I): ^{11}B NMR δ –14.95 (t, J = 71.6 Hz); IR 2100 cm^{-1} (B–H).

D. Reaction of Dicyclohexylborane with Sodium Hydride at 25 °C. A suspension of dicyclohexylborane (10 mmol) in THF (20 mL) was prepared[15] in a centrifuge vial, 0.73 g (15 mmol) of sodium hydride was added in a nitrogen-filled glovebag, and the slurry was stirred well at 25 °C. Periodically, aliquots were withdrawn in the manner described above and the progress of the reaction was monitored by hydride estimation and ^{11}B NMR technique. The results in Table I indicate that reaction was complete in 6 h, producing sodium dicyclohexylborohydride in quantitative yield; ^{11}B NMR δ –11.82 (t, J = 71.8 Hz).

E. Reaction of Diisopinocampheylborane with Potassium Hydride at 0 °C. The experimental setup was the same as in the previous experiment. A slurry of diisopinocampheylborane (10 mmol) in THF (10 mL) was prepared in the usual manner[15] and the reaction mixture was kept at 0 °C. Potassium hydride, 2.5 g (~15 mmol), was placed in another centrifuge vial and it was freed from the oil coating by washing with *n*-pentane. It was then suspended in THF (10 mL) and was added to $\mathrm{IPC_2BH}$ at 0 °C, using a double-ended needle. Temperature was maintained

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[11] Brown, C. A. *J. Organomet. Chem.* **1978**, *156*, C17.

[12] Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972.

[13] Brown, H. C.; Singaram, B. *Inorg. Chem.* **1979**, *18*, 53.

[14] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Insterscience: New York, 1975; Chapter 9.

[15] Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.* **1977**, *42*, 1392.

at 0 °C for 1 h and analysis showed that potassium diisopinocampheylborohydride had formed in quantitative yield; ^{11}B NMR δ -4.84 (t, J = 69 Hz).

F. Reaction of Monoisopinocampheylborane with Potassium Hydride. The *N,N,N',N'*-tetramethylethylenediamine (TMED) adduct of $IPCBH_2$ (10 mmol) was prepared as described previously[9] and was dissolved in THF so as to give a 1 M solution. To this, BMS (~10 M), 1 mL, was added with constant stirring. After 1 h, the solid TMED·$2BH_3$ was centrifuged and the supernatant liquid was transferred to a vial containing potassium hydride (oil free, 10 mmol) and stirred for 10 min at 25 °C to remove any traces of BMS in the reaction mixture. Pure $IPCBH_2$ solution in THF was then removed from potassium hydride by centrifugation and its concentration was adjusted to 0.5 M by dilution with THF. This solution was used for the reaction with potassium hydride (15 mmol) and the reaction was complete in 0.5 H; ^{11}B NMR δ -21.2 (q, J = 72 Hz).

Stoichiometry. A. Ratio of Li^+:B:H^- in Lithium 9-Boratabicyclo[3.3.1]nonane. In a typical experiment, a 1.0-mL aliquot of the clear solution of lithium 9-boratarabicyclo[3.3.1]nonane, ~0.5 M, was hydrolyzed in a THF–water–glycerine mixture (1:1:1) and the hydrogen evolved (24.7 mL) was measured. This indicated the hydride concentration to be 0.96 M. In another experiment, 10 mL (~5 mmol) of Li-9-BBNH was quenched with methanol and oxidized with NaOH–H_2O_2. The oxidation product was analyzed by GLC as described previously. From the amount of cyclooctanediol, the concentration of boron was calculated to be 0.5 M.

The above borohydride solution (3 mL) was quenched with water and titrated with 0.4985 N hydrochloric acid to a phenolphthalein endpoint. It required 2.77 mL of the standard acid, indicating the concentration of the lithium ion to be 0.46 M. The ratio of Li^+:B:H^- is thus 1.00:1.09:2.08.

B. Ratio of Na^+:B:H^- in Sodium Thexylborohydride. Upon hydrolysis, a 1.0-mL aliquot of a solution of sodium thexylborohydride gave 37.9 mL of hydrogen, indicating the hydride concentration to be 1.47 M. Oxidation of 10 mL (5 mmol) of this solution produced 5.0 mmol of thexyl alcohol, indicating a 0.5 M concentration of boron. Sodium thexylborohydride solution (3 mL) was quenched with water and titrated with 0.4985 N hydrochloric acid to a phenolphthalein endpoint. It required 3.05 mL of the acid, revealing the concentration of the sodium ion to be 0.5 M. Hence, the ratio of Na^+:B:H^- is 1.00:1.00:2.94.

C. Ratio of K^+:B:H^- in Potassium Thexylborohydride. The hydrolysis of 1.0 mL of an approximately 0.5 M solution liberated 38.7 mL of hydrogen, corresponding to a hydride concentration of 1.5 M. The oxidation of 10 mL of the hydride solution using alkaline hydrogen peroxide, followed by GLC analysis, using *n*-dodecane as an internal standard, revealed 5.0 mmol of thexyl alcohol. This indicates the boron concentration to be 0.5 M. Potassium was estimated by hydrolyzing 3 mL of the hydride solution, followed by titration with standard acid (0.4985 N); 3.05 mL of the acid was required, indicating a concentration of 0.5 M in potassium.

Stability of Alkali Metal Alkylborohydrides. Solutions of alkali metal mono- and dialkylborohydrides were stored at 25 °C under dry nitrogen and analyzed for the active hydride concentration periodically. The stability of these solutions was also monitored by determining their ^{11}B NMR spectra periodically. The results clearly indicated that, under dry nitrogen, these are stable at least for 90 days without any detectable hydride loss, isomerization, or redistribution.

Regeneration of Mono- and Dialkylboranes from Their Alkali Metal Borohydrides. The following procedure for the liberation of free 9-BBN from K-9-BBNH in THF is representative. To a solution of 5 mmol of K-9-BBNH in 10 mL of THF was added 7.5 mmol (50% excess) of CH_3I with stirring at 25 °C. A heavy white solid precipitated immediately with evolution of methane (5 mmol) gas. Stirring was continued for 15 min and then the solid centrifuged down. The supernatant solution was decanted and ^{11}B NMR revealed the presence of pure 9-BBN dimer in equilibrium with its monomer–THF complex; ^{11}B NMR δ +27.8 (s), +13.9 (d, J = 61 Hz).

Registry No. Lithium 9-boratobicyclo[3.3.1]nonane, 76448-08-3; sodium 9-boratobicyclo[3.3.1]nonane, 76448-07-2; potassium 9-boratobicyclo[3.3.1]nonane, 76448-06-1; lithium dicyclohexylborohydride, 67813-27-8; sodium dicyclohexylborohydride, 76430-43-8; potassium dicyclohexylborohydride, 76430-44-9; lithium disiamylborohydride, 67813-43-8; sodium disiamylborohydride, 76430-45-0; potassium disiamylborohydride, 76430-46-1; lithium diisopinocamphenylborohydride, 76430-47-2; sodium diisopinocamphenylborohydride, 76496-36-1; potassium diisopinocamphenylborohydride, 76496-37-2; lithium thexylborohydride, 76430-48-3; sodium thexylborohydride, 76430-49-4; potassium thexylborohydride, 76430-50-7; sodium monoisopinocamphenylborohydride, 76430-51-8; potassium monoisopinocamphenylborohydride, 76496-38-3; cyclohexanol, 108-93-0; 3-methyl-2-butanol, 598-75-4; isopinocamphenol, 27779-29-9; cyclohexene, 110-83-8; 2-methyl-2-butene, 513-35-9; 2-pinene, 80-56-8; tricyclohexylboron, 1088-01-3; tris(3-methyl-2-butyl)boron, 32327-52-9; lithium cyclohexylborohydride, 76430-52-9; lithium (3-methyl-2-butyl)borohydride, 76430-53-0; 9-BBN, 280-64-8; $(CChx)_2BH$, 1568-65-6; Sia_2BH, 1069-54-1; IPC_2BH, 24041-59-6; $ThxBH_2$, 3688-24-2; $IPCBH_2$, 28875-08-3; LiH, 7580-67-8; NaH, 7646-69-7; KH, 7693-26-7.

Reaction of Enol Silyl Ethers with Silver Carboxylate–Iodine. Synthesis of α-Acyloxy Carbonyl Compounds

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The sequential treatment of enol silyl ethers with silver carboxylate–iodine (2:1) and then fluoride affords high yields of the corresponding α-acyloxy carbonyl compounds. Thus a wide range of variation is now possible for the acyloxy portion of the molecule. The oxidation is most successful when used with five- and six-membered-ring enol silyl ethers. When applied to larger ring sizes, the formation of α-iodo carbonyl compounds occurs as an important side reaction. The oxidation is regiospecific with respect to double bond placement in the enol silyl ethers.

The oxidation of enol silyl ethers **1** with *m*-chloroperbenzoic acid (MCPBA)[1,2] or lead(IV) carboxylates[3] affords ready access to a variety of useful α-oxygenated carbonyl systems **2** and **3**. Continuing interest in the use of these