lithium chloride was allowed to settle. The clear liquid phase and washings (2 × 15 mL of ethyl ether) were transferred to a distillation flask. Volatiles were removed in vacuo. Distillation furnished pure diphenylisopropoxyborane: yield 8.56 g (38.3 mmol, 87%); bp 88–90 °C (0.1 mmHg); proton NMR ($CDCl_3$) δ 7.57 (m, 2 H), 7.37 (m, 3 H), 4.57 (septet, J = 18 Hz, 1 H), 1.25 (d, J = 18 Hz, 6 H); boron NMR (neat) +44.8 ppm (s).

2-Furyldiisopropoxyborane. The reaction was run as described above with 2-furyllithium,[21] prepared from furan (200 mmol, 15 mL), *n*-butyllithium (200 mmol, 77 mL), and triisopropoxyborane (17.5 g, 93 mmol).[22] The "ate" complex was treated with acetyl chloride (7.85 g, 100 mL). Isolation yielded 2-furyldiisopropoxyborane: yield 13.5 g (69 mmol, 74%); bp 76–78 °C (15 mmHg); $n^{20}{}_D$ 1.4306; proton NMR ($CDCl_3$) δ 7.60 (m, 1 H), 6.97 (m, 1 H), 6.40 (m, 1 H), 4.83 (septet, J = 18 Hz, 2 H), 1.33 (d, J = 18 Hz, 12 H); boron (neat) +23.3 ppm (s).

Phenylisopropylisopropoxyborane. The reaction was conducted as described under the general procedure using isopropyllithium (22.8 mmol, 40 mL) and triisopropoxyborane (4.64 g, 22.5 mmol). Workup with acetyl chloride (1.96 g, 25 mmol) and isolation yielded 3.60 g (18.9 mmol, 84%): bp 106–108 °C (15 mmHg); proton NMR ($CDCl_3$) δ 7.27 (m, 5 H), 4.47 (septet, J = 18 Hz, 1 H), 1.22 (d, J = 18 Hz, 6 H), 1.02 (b d, J = 15 Hz, 6 H); boron NMR (neat) +48.6 ppm (s).

Dimethylisopropoxyborane. The reaction was conducted as described under the general procedure using methyldiisopropoxyborane (15.3 g, 106 mmol) and methyllithium (66.3 mL, 106 mmol). The reaction was quenched with benzoyl chloride (14.9 g, 106 mmol) to yield, after careful distillation, 8.7 g (87 mmol, 82%): bp 52–54 °C (7.58 mmHg); proton NMR ($CDCl_3$) δ 4.40 (septet, J = 18 Hz, 1 H), 1.19 (d, J = 18 Hz, 6 H), 0.37 (b s, 6 H); boron NMR (neat) +52.1 ppm (s).

Phenyldiisopropoxyborane. The reaction was run as described under the general procedure using phenyllithium (17 mL, 30.6 mmol) and triisopropoxyborane (5.6 g, 30 mmol). The reaction was quenched with acetyl chloride (2.1 mL, 30 mmol) to yield after distillation 5.2 g (25.2 mmol, 84%).

Acknowledgment. We thank the Lady Davis Fellowship from the Hebrew University in Jerusalem, Israel, for the grant of a fellowship which made this study possible.

Registry No. MeB(O-*i*-Pr)$_2$, 86595-27-9; *i*-PrB(O-*i*-Pr)$_2$, 103885-29-6; BuB(O-*i*-Pr)$_2$, 86595-32-6; *s*-BuB(O-*i*-Pr)$_2$, 86595-33-7; *t*-BuB(O-*i*-Pr)$_2$, 86595-34-8; PhB(O-*i*-Pr)$_2$, 1692-26-8; *t*-BuMeB-(O-*i*-Pr), 97782-73-5; Me$_2$B(O-*i*-Pr), 95407-90-2; Ph$_2$B(O-*i*-Pr), 69737-51-5; RB(O-*i*-Pr)$_2$ (R = 2-Furyl), 103885-30-9; *i*-PrPhB(O-*i*-Pr), 97782-97-3; LiMeB(O-*i*-Pr)$_3$, 103885-14-9; Li-*i*-PrB(O-*i*-Pr)$_3$, 103885-15-0; LiBuB(O-*i*-Pr)$_3$, 103885-16-1; Li-*s*-BuB(O-*i*-∞Pr)$_3$, 103885-17-2; Li-*t*-BuB(O-*i*-Pr)$_3$, 103885-18-3; LiPhB(O-*i*-Pr)$_3$, 103885-19-4; LiMe$_2$B(O-*i*-Pr)$_2$, 103885-20-7; Li-*t*-BuMeB(O-≤*i*-Pr)$_2$, 103885-21-8; LiRB(O-*i*-Pr)$_3$ (R = 2-furyl), 103885-22-9; Li-*i*-PrPhB(O-*i*-Pr)$_2$, 103885-23-0; LiPh$_2$B(O-*i*-Pr)$_2$, 103885-24-1; LiPhMeB(O-*i*-Pr)$_2$, 103885-25-2; Li(*t*-Bu)$_2$(B(O-*i*-Pr)$_2$, 103885-26-3; LiRB(O-*i*-Pr)$_3$ (R = cyclohexyl), 103885-27-4; Li-*t*-BuPhB(O-*i*-Pr)$_2$, 103885-28-5; BnO-*i*-Pr)$_3$, 5419-55-6; *LiMe*, 917-54-4; Li-*i*-Ph, 1888-75-1; LiBu, 109-72-8; Li-*s*-Bu, 598-30-1; Li-*t*-Bu, 594-19-4; LiPh, 591-51-5; 2-furyllithium, 2786-02-9; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4.

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[21] Ramanathan, V.; Levine, R. *J. Org. Chem.* **1962**, *27*, 1216.

[22] Possibly because of its low solubility, it was necessary to reflux 2-furyllithium with triisopropoxyborane 8 h to obtain good yields of the lithium borate. More soluble organolithium compounds reacted rapidly at −78 °C (compare ref 13).

Organoboranes. 49. An Examination of Convenient Procedures for the Generation of Borane and Monoalkyl- and Dialkylboranes from Lithium Borohydride and Monoalkyl- and Dialkylborohydrides

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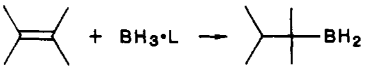
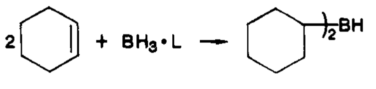
The simple preparation of monoalkyl- and dialkylboranes previously developed by the addition of methyl iodide to lithium monoalkyl- and dialkylborohydrides in tetrahydrofuran solution has been expanded to alternative procedures involving other solvents, such as diethyl ether (EE) and *n*-pentane, and other reagents, such as phenol, acetic acid, methanesulfonic acid, ethereal hydrogen chloride, trimethylsilyl chloride, and trimethylsilyl methanesulfonate. The practicality of generating monoalkyl- and dialkylboranes from the corresponding borohydrides has been demonstrated in representative solvents utilizing appropriate reagents. The reaction of lithium borohydride with the above reagents was also studied. The reaction of lithium borohydride with 1 equiv of acetic acid produces a mixture of lithium tetraacetoxyborohydride and unreacted lithium borohydride instead of the expected lithium monoacetoxyborohydride. Because of discrepancies with the reported results for sodium borohydride, the study was extended to this reagent.

Hydroboration of olefins with $BH_3{\cdot}THF$ or $BH_3{\cdot}Me_3S$ generally proceeds rapidly past the monoalkylborane stage to the dialkyl- and trialkylborane stages.[2] Consequently it is generally not possible to synthesize monoalkyl- or dialkylboranes by the direct reaction of most olefins with borane. Only in the case of certain hindered and highly hindered olefins is is possible to control the hydroboration so as to achieve the synthesis of pure monoalkyl and dialkylboranes (eq 1 and 2).[2] Additionally, these monoalkyl- and dialkylboranes possess limited stability upon storage, so they must be freshly prepared before use.



(1)



(2)

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[1] (a) Postdoctoral research associate on Grant GM 10937-23 of the National Institutes of Health. (b) Lady Davis Fellow from the Hebrew University, Israel.

[2] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis* via Boranes; Wiley-Interscience: New York, 1975.

We undertook to circumvent these difficulties by developing procedures for preparing a wide variety of lithium monoalkyl- ($LiRBH_3$) and dialkylborohydrides (LiR_2BH_2) under mild conditions, valuable intermediates for storing monoalkyl- and dialkylboranes in a stable form for extended periods of time, with a simple method for generating pure monoalkyl- and dialkylboranes from these borohydrides (eq 3 and 4).[3,4] We extended this reaction to

$$\mathrm{LiRBH_3 + MeI \xrightarrow{THF,\ 0\ ^\circ C} RBH_2 + LiI + CH_4} \tag{3}$$

$$\mathrm{LiR_2BH_2 + MeI \xrightarrow{THF,\ 0\ ^\circ C} R_2BH + LiI + CH_4} \tag{4}$$

the preparation of optically active lithium monoalkyl- and dialkylborohydrides.[5] Recently, this reaction was exploited for the synthesis of optically active 2,5-dimethylborolane, an asymmetric hydroborating agent.[6] In the course of our studies we noted that the reaction of methyl iodide with lithium alkylborohydrides is impractically slow in many solvents other than tetrahydrofuran. More seriously, the byproduct lithium iodide is highly soluble in ether solvents and is difficult to remove from the reaction mixture. Its presence in the reaction mixture can interfere with the oxidation and other desirable reactions of organoboranes. It appeared desirable, therefore, to explore alternative convenient procedures, utilizing other solvents and reagents, for the generation of monoalkyl- and dialkylboranes from the corresponding lithium alkylborohydrides.

Results and Discussion

For this study we selected lithium *n*-hexyl- and di-*n*-hexylborohydride as representative mono- and dialkylborohydrides, respectively. For easy comparison, we included lithium borohydride also in this study. The solvents utilized were diethyl ether (EE), tetrahydrofuran (THF), and *n*-pentane. Later, when it became of interest to extend our observations to sodium borohydride, we utilized diglyme (DG) to solubilize the derivative. Finally, we utilized phenol, acetic acid, methanesulfonic acid, ethereal hydrogen chloride, trimethylsilyl chloride, trimethylsilyl methanesulfonate, and methyl iodide to study their scope and limitation for the conversion of the borohydrides into the active borane derivatives.

A standard procedure was usually followed: 5 mL of a 1.0 M solution of the borohydride was treated with 5 mL of a 1.0 M solution of the reagent in the same solvent at 25 °C. Gas evolution was measured by using a gas burette.[2] After the gas evolution, a sample was analyzed both by ^{11}B NMR spectroscopy and by hydride analysis.[2] The reaction mixture was then examined again by ^{11}B NMR spectroscopy after 24 h at 25 °C.

Lithium and Sodium Borohydride. Lithium borohydride is readily soluble in EE and THF, but insoluble in *n*-pentane. Consequently, the reactions of $LiBH_4$ were studied only in EE and THF. Phenol readily reacts with a THF solution of $LiBH_4$, generating an equivalent of hydrogen at 25 °C. The ^{11}B NMR spectrum of the clear solution shows the products to be a mixture of equal amounts of $LiBH(OPh)_3$ (+3.9 ppm) and $LiB(OPh)_4$ (+2.0 ppm) along with the unreacted $LiBH_4$ (−41.5 ppm). Apparently the reaction proceeds in the manner indicated by eq 5. Reaction of $LiBH_4$ with 2 and 3 equiv of phenol

$$\mathrm{7LiBH_4 + 7PhOH \xrightarrow[0.25h]{THF,\ 25\ ^\circ C} 5LiBH_4 + LiBH(OPh)_3 + LiB(OPh)_4 + 7H_2} \tag{5}$$

similarly produces essentially a 1:1 mixture of $LiBH(OPh)_3$ and $LiB(OPh)_4$ along with unreacted $LiBH_4$ (eq 6 and 7).

$$\mathrm{7LiBH_4 + 14PhOH \xrightarrow[0.25\ h]{THF,\ 25\ ^\circ C} 3LiBH_4 + 2LiBH(OPh)_3 + 2LiB(OPh)_4 + 14H_2} \tag{6}$$

$$\mathrm{7LiBH_4 + 21PhOH \xrightarrow[0.25\ h]{THF,\ 25\ ^\circ C} LiBH_4 + 3LiBH(OPh)_3 + 3LiB(OPh)_4 + 21H_2} \tag{7}$$

Addition of the fourth equivalent of phenol generates 1 equiv of hydrogen over a period of 24 h at 25 °C, affording $LiB(OPh)_4$ cleanly. Sodium borohydride in THF has been reported to react with 3 equiv of phenol to give $NaBH(OPh)_3$, a selective reducing agent for aldehydes.[7]

Reaction of $LiBH_4$ in EE with 1 equiv of phenol readily liberates an equivalent of hydrogen with the concurrent formation of a precipitate. The clean supernatant solution was analyzed, and the results indicate that the reaction proceeds essentially according to eq 5.

Lithium borohydride in THF solution reacts readily with 1 equiv of acetic acid at 25 °C to liberate an equivalent of hydrogen. The ^{11}B NMR spectrum of the clean solution shows the presence of unreacted $LiBH_4$ and a broad peak at −0.5 ppm attributable to $LiB(OAc)_4$ and/or $LiBH(OAc)_3$. This result is unexpected since $NaBH_3OAc$ has been reported frequently to be formed from sodium borohydride and an equivalent of acetic acid.[8-10] Moreover, it had been reported from our laboratories, long before the days of ^{11}B NMR, that the reaction of $NaBH_4$ with an equivalent of propionic acid, or the reaction of diborane with sodium propionate, probably affords $NaBH_3O_2CC_2H_5$.[11] The results obtained from the reaction of $LiBH_4$ and acetic acid prompted us to extend this study to the reaction of $NaBH_4$ with an equivalent of acetic acid, characterizing the products by ^{11}B NMR spectroscopy.

One equivalent of acetic acid readily reacts with $NaBH_4$ in DG at 25 °C, generating an equivalent of hydrogen. The reaction mixture remains clear. The ^{11}B NMR spectrum of the reaction mixture is essentially identical with that obtained for $LiBH_4$ and an equivalent of acetic acid in THF. These results indicate that either the reaction of alkali-metal borohydrides with an equivalent of acetic acid does not produce monoacetoxyborohydride, as is often postulated in the literature,[8-11] or that monoacetoxyborohydrides, if first produced are very labile in solution and undergo rapid disproportionation to give a mixture of borohydride and tetraacetoxyborate. Similarly, addition of $BH_3{\cdot}THF$ to a suspension of an equivalent amount of NaOAc in DG at 25 °C produces a clear solution of $NaBH_4$ and $NaB(OAc)_4$ (eq 8).

$$\mathrm{4BH_3{\cdot}THF + 4NaOAc \xrightarrow[0.25\ h]{DG,\ 25\ ^\circ C} 3NaBH_4 + NaB(OAc)_4} \tag{8}$$

Lithium borohydride in EE, with 1 equiv of acetic acid at 25 °C, reacts differently. Apparently, more than 1 equiv

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(11) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1960**, *82*, 681.

(~1.7 equiv) of hydrogen is evolved, with concurrent precipitation of a solid. ^{11}B NMR spectrum of the supernatant solution shows the presence of unreacted $\mathrm{LiBH_4}$ along with trace amounts of $\mathrm{B(OR)_3}$ and a trivalent boron compound containing a B–H bond. The excess hydrogen was traced to the formation of insoluble diborane, which escaped from the reaction mixture and is hydrolyzed in the gas buret, affording the excess hydrogen. Alternatively, the escaping diborane could be captured by dimethyl sulfide ($\mathrm{Me_2S}$) at –78 °C, in a trap inserted into the line. The $\mathrm{BH_3{\cdot}SMe_2}$ formed was identified by ^{11}B NMR analysis and the yield determined by hydrolysis. Alternatively, the diborane generated from $\mathrm{LiBH_4}$ and an equivalent of acetic acid could be trapped in situ by using a 1:1 EE–$\mathrm{Me_2S}$ as the solvent (eq 9).

$$\mathrm{LiBH_4 + HOAc \xrightarrow[25^\circ C,\ 0.25\ h]{EE\text{–}Me_2S\ (1:1)} BH_3{\cdot}SMe_2 + LiOAc + H_2} \tag{9}$$

Hydrogen chloride dissolved in EE affords a convenient means for converting borohydrides into active borane derivatives. Such solutions are stable for long periods of time, they are readily standardized by titration, and the reaction with $\mathrm{LiBH_4}$ in THF is complete almost immediately following the addition, providing an essentially quantitative yield of $\mathrm{BH_3{\cdot}THF}$ (eq 10). We also observed

$$\mathrm{LiBH_4 + HCl \xrightarrow[<0.25\ h]{THF,\ 25\ ^\circ C} BH_3{\cdot}THF + LiCl + H_2} \tag{10}$$

that methanesulfonic acid reacts readily with $\mathrm{LiBH_4}$ in THF to give $\mathrm{BH_3{\cdot}THF}$ quantitatively (eq 11). In this case the salt produced, $\mathrm{LiO_3SMe}$, is insoluble in THF and precipitates, avoiding the presence of LiCl in the THF solution.

$$\mathrm{LiBH_4 + MeSO_3X \xrightarrow[<0.25\ h]{THF,\ 25\ ^\circ C} BH_3{\cdot}THF + LiO_3SMe + HX} \tag{11}$$

$$\mathrm{X = H,\ SiMe_3}$$

Reaction of trimethylsilyl methanesulfonate with $\mathrm{LiBH_4}$ in THF is rapid providing an essentially quantitative yield of $\mathrm{BH_3{\cdot}THF}$ (eq 11). Bis(trimethylsilyl) sulfate also liberates $\mathrm{BH_3{\cdot}THF}$ from $\mathrm{LiBH_4}$. However, the byproduct $\mathrm{Li_2SO_4}$ forms a gelatinous precipitate rendering difficult the recovery of the borane solution.

Both trimethylsilyl chloride and methyl iodide, when used in approximately 50% excess, convert $\mathrm{LiBH_4}$ in THF to $\mathrm{BH_3{\cdot}THF}$ through the intermediate $\mathrm{LiB_2H_7}$ (eq 12).[12]

$$\mathrm{LiBH_4 + Me_3SiCl \xrightarrow[<0.5\ h]{THF,\ 25\ ^\circ C} BH_3{\cdot}THF + LiCl + Me_3SiH} \tag{12}$$

The first half of the reaction, involving $\mathrm{LiBH_4}$, is faster than the second half, involving $\mathrm{LiB_2H_7}$. Reaction of methanesulfonic acid, trimethylsilyl chloride, ethereal hydrogen chloride, and methyl iodide with $\mathrm{LiBH_4}$ in EE is accompanied by considerable loss of diborane from the ether solution. The reactions provide convenient means for generating pure gaseous diborane.

Lithium Monoalkylborohydride. Since phenol has limited solubility in *n*-pentane, its reaction with lithium *n*-hexylborohydride was studied only in THF and EE. In the reaction of $\mathrm{LiRBH_3}$, at 25 °C, with 1 equiv of phenol, there was a brisk evolution of 1 equiv of hydrogen. The ^{11}B NMR spectrum of the reaction mixture showed none of the desired monoalkylborane. Instead, the reaction mixture contained diphenoxymonoalkylboronate (+29.9 ppm), lithium triphenoxymonoalkylborate (+8.2 ppm), and lithium monoalkylborohydride (–29.0 ppm). One possible explanation is that the observed products were obtained from a series of reactions in which a stronger Lewis acid displaces a weaker Lewis acid from Lewis acid–base complexes (eq 13–15).[13]

$$\mathrm{LiRBH_3 + PhOH \xrightarrow[25\ ^\circ C,\ 0.25\ h]{EE\ or\ THF} RBH_2 + LiOPh + H_2 \rightarrow LiRBH_2OPh} \tag{13}$$

$$\mathrm{LiRBH_2OPh + RBH_2 \rightarrow LiRBH_3 + RBH(OPh)} \tag{14}$$

$$\mathrm{LiOPh + RBH(OPh) \rightarrow LiRBH(OPh)_2 \xrightarrow{etc.} LiRB(OPh)_3} \tag{15}$$

Reaction of 1 equiv of acetic acid with $\mathrm{LiRBH_3}$, in the three solvents studied, is quite fast at 25 °C, evolving 1 equiv of hydrogen. In THF, the reaction proceeds in a similar fashion to eq 13–15, and we observed $\mathrm{LiRBH_3}$, $\mathrm{RB(OAc)_2}$, and $\mathrm{LiRB(OAc)_3}$ in the ^{11}B NMR spectrum of the reaction mixture. However, in EE or in *n*-pentane, lithium acetate precipitates from the solution and formation of the desired monoalkylborane (+24.0 ppm) could be observed (eq 16). Presumably it is the insolubility of

$$n\text{-}\mathrm{C_6H_{13}BH_3Li + HOAc \xrightarrow[25\ ^\circ C,\ 0.25\ h]{EE\ or\ \mathit{n}\text{-}pentane}} n\text{-}\mathrm{C_6H_{13}BH_2 + LiOAc + H_2} \tag{16}$$

LiOAc in these two solvents that diverts the reaction to this desired pathway. If the reaction mixture is allowed to stand at 25 °C for >24 h, the lithium monoalkylborohydride is slowly regenerated. Alternatively, addition of THF to the EE or *n*-pentane reaction mixture solubilizes the LiOAc and the $\mathrm{LiRBH_3}$ is readily regenerated.

Reaction of methyl iodide with $\mathrm{LiRBH_3}$ is quite fast in THF, while EE or *n*-pentane solution requires reaction times longer than 24 h. This long reaction time can be shortened by using an excess of methyl iodide and 10% of THF. The monoalkylborane is cleanly formed. However, the presence of lithium iodide in solution can interfere with the oxidation and cyanidation reactions of the resulting organoborane derivatives.

Lithium monoalkylborohydride reacts readily with 20% excess of neat trimethylsilyl chloride, in all the solvents studied, to afford the monoalkylborane with concurrent precipitation of LiCl. Redistribution of the monoalkylborane is less in EE or *n*-pentane.

Methanesulfonic acid reacts with lithium monoalkylborohydride to liberate 1 equiv of hydrogen readily. Unfortunately both the monoalkylborane liberated and the borohydride compete for the reagent, leading to a mixture of products. However, trimethylsilyl methanesulfonate reacts readily with $\mathrm{LiRBH_3}$ to give the monoalkylborane and lithium methanesulfonate which precipitates from the solution.

Similarly, ethereal hydrogen chloride reacts very fast with $\mathrm{LiRBH_3}$, in all three solvents utilized, and generates the monoalkylborane cleanly, together with the formation of an equivalent of hydrogen and LiCl (eq 17). The lithium chloride precipitates from ether or *n*-pentane.

$$\mathrm{LiRBH_3 + HCl \xrightarrow[25\ ^\circ C,\ 0.25\ h]{EE\ or\ \mathit{n}\text{-}pentane\ or\ THF} RBH_2 + LiCl + H_2} \tag{17}$$

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Table I. Summary of the Data for the Liberation of Borane, Monoalkylborane, and Dialkylborane from the Corresponding Lithium Borohydrides[a]

	$LiBH_4$		$LiRBH_3$			LiR_2BH_2		
	EE	THF	pentane	EE	THF	pentane	EE	THF
phenol			b			b		
acetic acid	+[c]		+[d]	+[d]		+[d]	+[d]	
methyl iodide	+[e]	+	+	+	+	+	+	+
trimethylsilyl chloride	+[e]	+	+	+	+	+	+	+
methanesulfonic acid	+[e]	+						
trimethylsilyl methanesulfonate[f]	+[e]	+	+	+	+	+	+	+
hydrogen chloride/EE	+[e]	+	+	+	+	+	+	+

[a] The symbol + indicates that the reaction is satisfactory for the generation of boranes. EE = diethyl ether. [b] Reaction was not examinated due to the limited solubility. [c] Borane product was isolated as the dimethyl sulfide complex. [d] Product undergoes a slow redistribution reaction to form other products. [e] Considerable amounts of diborane are lost due to its limited solubility in EE. [f] Has the advantage of providing solution of boranes free of dissolved metal salts.

Table II. Generation of Alkylboranes from the Corresponding Alkylborohydrides

lithium alkylborohydrides[a]	reagent	solv	alkylboranes	^{11}B NMR,[b] ppm	IR ν_{BH}, cm^{-1}
mono-*n*-hexylborohydride	Me_3SiO_3SMe	EE[c]	mono-*n*-hexylborane	+22.8	2501, 1577
mono-*tert*-butylborohydride	Me_3SiCl	EE	*tert*-butylborane	+23.8	2605
mono-*exo*-norbornylborohydride	Me_3SiCl	EE	*exo*-norbornylborane	+21.8	2497, 1558
monophenylborohydride	Me_3SiCl	EE	phenylborane	+10.0	2512, 1537
di-*n*-hexylborohydride	HCl	EE	di-*n*-hexylborane	+30.5	2424, 1487
di-*n*-2-methyl-1-propylborohydride	HCl	EE/pentane	diisobutylborane	+28.5	
cyclohexyl-*tert*-butylborohydride	Me_3SiCl	EE	cyclohexyl-*tert*-butylborane	+82.1[d]	2437

[a] See ref 3 and 4. [b] See Experimental Section. [c] EE = diethyl ether. [d] Generally these alkylboranes exist in EE solutions as dimers; however, this dialkylborane exists as a monomer in EE solution. See also: Brown, H. C.; Negishi, E.; Katz, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 2791.

Lithium Dialkylborohydride. In THF, the reaction of lithium di-*n*-hexylborohydride with phenol proceeds in a manner similar to that observed for lithium *n*-hexylborohydride (eq 18). The reaction may be proceeding

$$2LiR_2BH_2 + PhOH \xrightarrow[0.5\ h]{THF,\ 25\ ^{\circ}C} LiR_2BH_2 + LiR_2B(OPh)_2 + 2H_2 \quad (18)$$

through the initial formation of LiR_2BHOPh, followed by a fast second reaction with phenol. Alternatively, the reaction may be proceeding through the initial formation of the dialkylborane which reacts with lithium phenoxide to regenerate the lithium dialkylborohydride with the concurrent formation of lithium diphenoxydialkylborate. We cannot at present decide between the alternative mechanisms. Reaction of phenol with LiR_2BH_2 in EE is slow at 25 °C. The ^{11}B NMR spectrum of the reaction mixture shows the presence of dialkylborane, dialkylborinate, and unreacted LiR_2BH_2. After 24 h at 25 °C, the ^{11}B NMR spectrum of the reaction mixture is significantly changed. The product now consists of R_3B, R_2BOPh, and $LiRBH_3$. Apparently, the R_2BH initially formed redistributes to give R_3B and RBH_2 and the latter then reacts with LiR_2BH_2 to form $LiRBH_3$ (eq 19).

$$LiR_2BH_2 + RBH_2 \rightarrow R_2BH + LiRBH_3 \quad (19)$$

One equivalent of acetic acid reacts rapidly with LiR_2BH_2 at 25 °C, giving an equivalent of hydrogen. In THF, the reaction proceeds according to eq 18. In EE, the desired dialkylborane is formed with the concurrent precipitation of lithium acetate. However, the ^{11}B NMR spectrum of the reaction mixture, obtained after 24 h, shows a major peak due to R_2BOR'. It is probable that R_2BH is reducing the lithium acetate and in turn is converted into a dialkylborinate.

Methanesulfonic acid reacts in a complex manner with LiR_2BH_2. Both LiR_2BH_2 and the initially formed R_2BH compete for the reagent. On the other hand, the reaction of LiR_2BH_2 with trimethylsilyl methanesulfonate is facile, yielding the corresponding R_2BH cleanly.

Reaction of methyl iodide with LiR_2BH_2 is very fast in THF and generates the desired R_2BH cleanly. In EE and *n*-pentane the reaction takes longer than 24 h for completion. The reaction time can be shortened considerably (to approximately 2 h) by using an excess of methyl iodide and 10% of THF. The dialkylborane is formed cleanly in all the cases.

Lithium dialkylborohydride reacts with 20% excess of neat trimethylsilyl chloride, in all solvents used in this study, to generate the dialkylborane.

Similarly, ethereal hydrogen chloride reacts very rapidly with LiR_2BH_2 and liberates the dialkylborane along with an equivalent of hydrogen and lithium chloride.

Generation of Alkylboranes from the Corresponding Borohydrides. In the present study, methyl iodide, trimethylsilyl chloride, trimethylsilyl methanesulfonate, and ethereal hydrogen chloride emerged as the reagents of choice to generate active borane derivatives from the corresponding borohydrides. These results are summarized in Table I. We utilized these reagents to liberate representative mono- and dialkylboranes from the corresponding mono- and dialkylborohydrides. Accordingly, we treated representative alkylborohydrides with these reagents, and the alkylboranes thus generated were characterized by ^{11}B NMR and IR spectroscopy. The results are summarized in Table II.

Conclusion

This study demonstrates that the generation of active borane derivatives from the corresponding borohydrides can be realized with a variety of reagents and solvents.

Ethereal hydrogen chloride, methanesulfonic acid, trimethylsilyl chloride, and methyl iodide react readily with lithium borohydride in THF to give $BH_3\cdot THF$ complex in essentially quantitative yields. It should be pointed out that the result obtained from the reaction of $LiBH_4$ with 1 equiv of acetic acid indicates that the reaction may be proceeding in two stages (eq 20 and 21). In coordinating

$$4LiBH_4 + 4HOAc \rightarrow 4BH_3\cdot L + 4LiOAc + 4H_2 \quad (20)$$

$$4BH_3{\cdot}L + 4LiOAc \rightarrow 3LiBH_4 + LiB(OAc)_4 \quad (21)$$

solvents, such as THF, the reaction proceeds according to eq 20 and 21. In noncoordinating solvents, such as EE, the reaction proceeds to eq 20 followed by the evolution of diborane. Generation of diborane from lithium borohydride and carboxylic acids has been observed before.[10b,14] Equation 20 explains the hydroboration properties of borohydride–carboxylic acid system. Incidently, the mixture of $LiBH_4$ and $LiB(OAc)_4$, obtained from $LiBH_4$, and an equivalent of acetic acid, also hydroborates olefins. Diborane generated in the reaction of borohydride with acetic acid can be effectively trapped in situ by using Lewis bases such as dimethyl sulfide. Similar results have been reported for the reaction of amino acids with $NaBH_4$.[15]

The reaction of either ethereal hydrogen chloride, trimethylsilyl chloride, and trimethylsilyl methanesulfonate with lithium mono- and dialkylborohydrides appears to be a convenient procedure for the generation of the corresponding alkylboranes. In cases where the presence of lithium iodide in the reaction medium would not be deletorious, the use of methyl iodide to liberate the alkylboranes offers unusual convenience. The reaction of methyl iodide with lithium mono- and dialkylborohydrides in solvents such as diethyl ether (EE) and *n*-pentane can be facilitated by the addition of 10% of THF. It should be pointed out that methyl iodide, trimethylsilyl chloride, and trimethylsilyl methanesulfonate react only with the borohydride and not with the product. Use of methanesulfonic acid as a liberating agent should be avoided if possible since it invariably gives mixtures of products.

Experimental Section

All operations were carried out under a nitrogen atmosphere with oven-dried glassware.[2] The spectra were obtained in an inert atmosphere. The infrared spectra were obtained with a Perkin-Elmer 1420 spectrometer using sealed cells and a two-syring technique. The ^{11}B NMR spectra were recorded on a Varian FT-80A spectrometer. The ^{11}B NMR chemical shifts are in parts per million relative to $BF_3{\cdot}EE$ (EE = diethyl ether) with chemical shifts downfield from $BF_3{\cdot}EE$ assigned as positive. Typical chemical shifts (ppm) are as follows: $LiBH_4$ (−41.5), $LiBH(OAc)_3$ (∼+1.1), $LiB(OAc)_4$ (∼−1.2), $LiB(OPh)_4$ (+2.0), $LiBH(OPh)_3$ (+3.6), $BH_3{\cdot}SMe_2$ (−19.8), $BH_3{\cdot}THF$ (−0.6), LiB_2H_7 (−27.0), $LiRBH_3$ (−29.0), $LiRB(OPh)_3$ (+8.2), $RB(OPh)_2$ (+30.4), $LiRB(OAc)_3$ (−3.2), $RB(OAc)_2$ (+30.7), RBH_2 (∼+24.0), LiR_2BH_2 (−18.5), R_2BOPh (+53.8), and R_2BH (+28.2).

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketal. Anhydrous diethyl ether (EE) was purchased from Mallinckrodt, Inc., and was used directly. *n*-Pentane (99%) purchased from Phillips Petroleum Co., was used without further purification. Lithium borohydride, phenol, methanesulfonic acid, methyl iodide, and trimethylsilyl chloride were purchased from Aldrich Chemical Co., and were used as such. Acetic acid was purified by distillation from small amounts of acetic anhydride. Ethereal hydrogen chloride,[16] lithium monoalkylborohydrides,[3] and lithium dialkylborohydrides[4] were prepared according to methods reported previously.

Trimethylsilyl Methanesulfonate. A 100-mL flask fitted with a rubber septum, magnetic stirring bar, and a condenser was charged with freshly distilled methanesulfonic acid (100 mmol) and trimethylsilyl chloride (100 mmol). The immiscible liquids were refluxed for 1 h to get a clear homogeneous solution. Hydrogen chloride was evolved and adsorbed by a water trap. The condenser was replaced quickly with a distillation head, and the product was isolated by distillation under reduced pressure: 13.4 g (80% yield); bp 104–106 °C (20 mmHg); ^1H NMR ($CDCl_3$, ppm) 0.43 (s, 9 H), 3.0 (s, 3 H).

General Procedure. Individual 1.0 M solutions of the borohydrides and the reagents in different solvents were prepared and used in this study. A 50-mL centrifuge vial fitted with a rubber septum and a magnetic stirring bar was charged with 5 mmol of the borohydride solution. The centrifuge vial was then connected to the gas buret using a double-ended needle. The reagent solution (5 mmol, 5 mL) was then added to the borohydride solution at 25 °C with constant stirring. Gas evolved during the reaction was measured. Following the gas evolution, an aliquot (0.5 mL) of the solution was withdrawn and analyzed by ^{11}B NMR spectroscopy and by hydride analysis. The reaction mixture was analyzed again after 24 h at 25 °C.

In cases where diborane escaped from the reaction mixture, a trap at −78 °C containing dimethyl sulfide (5 mL) was inserted between the reaction vial and the gas buret. The results are summarized in Table I.

Generation of Mono- and Dialkylboranes. A 50-mL centrifuge vial fitted with a rubber septum and a magnetic stirring bar was charged with 5 mmol of an alkylborohydride solution in an appropriate solvent. It was then reacted with an equivalent amount of a reagent solution at 25 °C for 0.5 h. The reaction mixture was then centrifuged, and the clear supernatent solution was analyzed by ^{11}B NMR and IR spectroscopy. The results are summarized in Table II.

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