

Hydroboration. 79. Preparation and Properties of Methylborane and Dimethylborane and Their Characteristics as Hydroborating Agents. Synthesis of Tertiary Alcohols Containing Methyl Groups via Hydroboration

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Lithium methylborohydride and lithium dimethylborohydride are readily prepared from the corresponding boronic and borinic esters. Methylborane and dimethylborane are cleanly liberated from these borohydrides by protonation with hydrogen chloride in ether, thus permitting the ready liberation of these methylboranes from the stable methylborohydrides. In contrast to the earlier gas-phase studies, methylborane in solution is remarkably stable to disproportionation, forming a strong dimer complex. However, dimethylborane in solution is less stable, undergoing some disproportionation at room temperature. By liberating these boranes in appropriate solvents in the presence of the alkenes, the redistribution can be controlled and a satisfactory preparation of dialkylmethylboranes achieved. These organoboranes can be carbonylated-oxidized to form the corresponding tertiary alcohols containing one or two methyl groups, the first time these valuable derivatives have been available via hydroboration. Gas chromatographic examination of these tertiary alcohols established the absence of significant redistribution. The regioselectivity of these two new hydroborating agents was investigated with representative alkenes, and excellent selectivities with terminal and trisubstituted alkenes were achieved.

Methylborane, MeBH_2 , and dimethylborane, Me_2BH , are the simplest of the monoorganylboranes and diorganylboranes. These compounds were first prepared by H. I. Schlesinger and co-workers^{1,2} in the 1930s. The method of preparing these compounds has changed little over the years, employing the redistribution of trimethylborane with diborane,^{1,2,3} or a related method using lithium borohydride, hydrogen chloride, and trimethylborane.⁴ However, the present routes to these compounds are experimentally tedious, difficult to carry out for large-scale preparations, and give a mixture of products that must be carefully fractionated at low temperatures. Furthermore, these boranes readily disproportionate in a relatively short period of time, producing a complex mixture of boron-containing compounds.⁵ These factors have hindered the application of these simplest of the organylboranes as a means of preparing substituted methylboranes via hydroboration and their conversion to other valuable products.

Unlike these boranes, the corresponding methylborohydrides should be stable with respect to redistribution or disproportionation, readily stored under nitrogen without hydride loss, and, in principle, readily converted into the corresponding methylboranes. Lithium methylborohydride was prepared some time ago from trimethylborane and lithium aluminum hydride.⁶ We have recently reported several routes to the preparation of monomethylboron compounds: methylboronic acid, trimethylboroxin,⁷ and methyl-diisopropoxyborane,⁸ as well as the dimethylboron compounds, dimethylisopropoxyborane and dimethyl(3-acetoxy-1-propoxy)borane.⁹ These boron compounds can be prepared readily in high yields and purities. The reaction of the methylboronic esters with

Table I. Spectral Data of Methylborohydrides

	¹¹ B NMR chem shift	J _{BH} , Hz	IR ν _{BH} , cm ⁻¹
LiMeBH ₃	-30.8 (q)	73	2167
LiMe ₂ BH ₂	-22.9 (t)	68	2097

an equivalent of lithium aluminum hydride gives lithium methylborohydride in high isolated yields without detectable redistribution.¹⁰ Similarly, the reaction of dimethylboronic esters with lithium monoethoxyaluminum hydride,¹¹ LiEtOAlH_3 , yields dimethylborohydride.

As part of our continuing effort to develop convenient synthetic routes to organoboranes that cannot be obtained by direct hydroboration, we have developed new, efficient routes to these simplest of the alkylboranes, i.e., monomethylborane and dimethylborane, and have tested their utility as hydroborating agents.

Results and Discussion

Preparation and Properties. Only recently has it become possible to prepare cleanly such lithium mono- and dialkylborohydrides.¹⁰ Lithium methylborohydride was prepared by treatment of methylboronic ester¹² or acid with lithium aluminum hydride. A new compound, lithium dimethylborohydride, was prepared and isolated from the reaction of dimethylisopropoxyborane¹² with lithium ethoxyaluminum hydride, LiEtOAlH_3 . Alternatively, the compound could be conveniently prepared by a new procedure, the reaction of lithium dimethyl-diisopropoxyborate with the same reagent, LiEtOAlH_3 . Both of these borohydrides were isolated in 80-95% yield with a chemical purity in excess of 98%. In contrast to the corresponding boranes, these borohydrides can be stored at room temperature, either as solids, or in solutions for an extended period of time without observable disproportionation or loss of hydride activity.

The lithium methylborohydride are soluble in excess of 2.0 M in nonreactive nonprotonic solvents: pentane, ether,

(1) Schlesinger, H. I.; Walker, A. O. *J. Am. Chem. Soc.* **1935**, *57*, 621.
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(4) Long, L. H.; Wallbridge, M. G. H. *J. Chem. Soc.* **1965**, 3513.

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(6) Wartik, T.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1953**, *75*, 835.

(7) Brown, H. C.; Cole, T. E. *Organometallics* **1985**, *4*, 816.

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(9) Brown, H. C.; Cole, T. E.; Srebnik, M. *Organometallics* **1985**, *4*, 1788.

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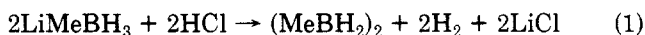
(11) Singaram, B.; Cole, T. E.; Brown, H. C. *Organometallics* **1984**, *3*, 1520.

(12) Brown, H. C.; Srebnik, M.; Cole, T. E. *Organometallics* **1986**, *5*, 2300.

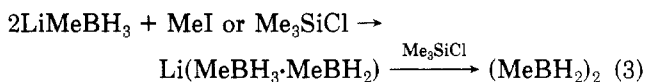
and THF. The spectral data for these borohydrides are summarized in Table I.

Generation. The ability to liberate the corresponding borane from the borohydride as needed was demonstrated only recently.¹¹ Because of the potential importance of this development, a detailed study was made and a number of possible reagents were tested for this conversion.¹³ Four potentially useful reagents are anhydrous hydrogen chloride in diethyl ether, trimethylsilyl chloride, methyl iodide, and trimethylsilyl methanesulfonate.

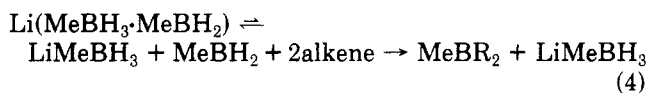
Hydrogen chloride reacts very rapidly with both the methylborohydride and dimethylborohydride in the three solvents examined: pentane, ether, and THF, forming the corresponding methylborane (eq 1) or dimethylborane (eq 2), an equivalent of hydrogen, and lithium chloride.



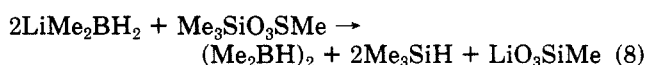
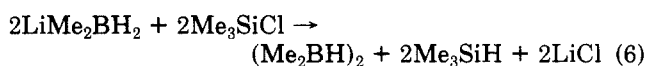
The rate of reaction of methyl iodide and trimethylsilyl chloride with these borohydrides is strongly dependent on the solvent (eq 3). The reaction is much faster in THF



than in ether and is relatively slow in pentane. The multiplicity of the lithium methylborohydride collapses shortly after addition of either reagent and a new species is observed in the ¹¹B NMR at approximately $\delta -27.5$. This material was shown to be the borane-borohydride addition complex, $\text{Li}(\text{MeBH}_3 \cdot \text{MeBH}_2)$, which can also be generated from the reaction of lithium methylborohydride and methylborane (eq 3). Trimethylsilyl chloride slowly reacts with this addition complex, forming the methylborane dimer within 2 h at room temperature. In contrast, methyl iodide does not react with this addition complex within 24 h. However, this complex can hydroborate alkenes, forming the trialkylborane and liberating the lithium methylborohydride, which is readily converted into the methylborane with methyl iodide or trimethylsilyl chloride (eq 4). This suggests that the addition complex is in



equilibrium with the methylborane and lithium methylborohydride, although these species are not observable in the ¹¹B NMR. In contrast, dimethylborane does not form an addition complex with lithium dimethylborohydride. The lithium dimethylborohydride is readily converted into the dimethylborane with hydrogen chloride (eq 5), trimethylsilyl chloride (eq 6), methyl iodide (eq 7), and trimethylsilyl methane sulfonate (eq 8), in all solvents examined. The latter reagent has the advantage that lithium



methanesulfonate is essentially insoluble, both in ethyl ether and in THF, permitting the formation of solutions of the reagents free of dissolved salt.

Table II. Spectral Data of Methylboranes

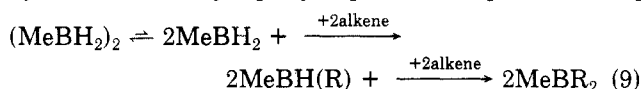
	¹¹ B NMR chem shift	J _{BH} , Hz
MeBH ₂	+21.9 (q)	129, 45
MeBH ₂ ·pyridine	+5.8 (t)	97.0
Me ₂ BH	+24.9 (t)	43
Me ₂ BH·pyridine	-1.9 (d)	90.3

The formed boranes are observed as dimers in the ¹¹B NMR at $\delta +21.9$ and $+25.0$, respectively. By treatment with pyridine, these boranes are readily converted into the pyridine addition complexes. The spectral data for these compounds are summarized in Table II. THF forms an addition complex to only a small degree with methylborane. Addition of a large excess of dimethyl sulfide (12 equiv) cleanly forms the sulfide addition complex of methylborane, as observed at $\delta -10.3$.

Properties of Methyl- and Dimethylborane Solutions. Methylborane in solution is a surprisingly stable sterically nonhindered monoalkylborane. There is no appreciable amount of disproportionation products observed in the ¹¹B NMR within 2–3 h at room temperature. Noncoordinating solvents increase the stability of the borane slightly. In contrast, dimethylborane, like other sterically nonhindered dialkylboranes, undergoes a faster disproportionation, forming methylated boranes. The solvent dramatically affects the stability of the dimethylborane. Redistribution of the methyl groups is faster in THF solutions than in ether or pentane solutions.

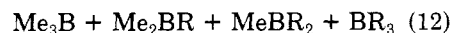
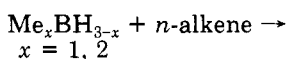
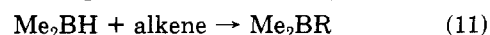
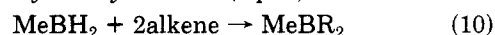
Redistribution during Hydroboration. The fast rate of redistribution of dimethylborane suggested that a similarly fast redistribution for the first hydroboration product from methylborane, RMeBH , might also be a factor. Such redistribution had not been a problem in our earlier work involving hydroborations with more hindered derivatives such as disiamylborane and thexylborane. Accordingly, it was important to find conditions that would avoid such redistribution in the synthesis of RMe_2B and R_2MeB .

Methylborane hydroborates quickly with the first equivalent of an alkene, forming an alkylmethylborane at a rate essentially independent of the structure of the alkene. The rate of the second hydroboration is slower than the first and is dependent on the steric requirements of the olefin. This suggests that the rate of the first hydroboration is limited by the dissociation of the methylborane dimer, forming free methylborane, which then undergoes hydroboration very rapidly (eq 9). The equilibrium (eq



9) favors the methylborane dimer, as observed in the ¹¹B NMR, and only a small amount of $\text{MeBH}_2 \cdot \text{THF}$ is seen at $\sim\delta +15$. The rate of hydroboration of dimethylborane in ether is dependent on the structure of the alkene and is generally slower than the second hydroboration of methylborane.

Although the hydroboration products from methylborane or dimethylborane show a single peak in the ¹¹B NMR at approximately +84 ppm, indicating the clean formation of a trialkylborane, the spectrum does not establish whether this is the desired dialkylmethylborane (eq 10), the alkyl dimethylborane (eq 11), or the various redistributed alkylmethylboranes (eq 12).



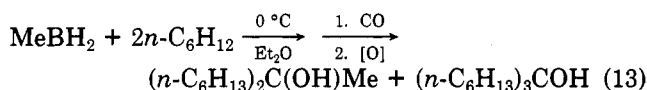
(13) Cole, T. E.; Bakshi, R. K.; Singaram, B.; Srebnik, M.; Brown, H. C., manuscript submitted.

Table III. Tertiary Alcohols Prepared from the Hydroboration of Methylborane and Dimethylborane with Representative Alkenes

borane	alkene	alcohol	yield, ^a %
MeBH ₂	1-hexene	7-methyl-7-tridecanol	96 ^b
MeBH ₂	2-methyl-1-heptene	(±)-6,8,10-trimethyl-8-pentadecanol	70
MeBH ₂	cyclopentene	1,1-dicyclopentylethanol	52
MeBH ₂	<i>trans</i> -3-hexene	(±)-4,6-diethyl-5-methyl-5-nonanol	70
MeBH ₂	1-methylcyclopentene	(±)-1,1-bis(<i>trans</i> -2-methylcyclopentyl)ethanol	67
MeBH ₂	cyclohexene	1,1-dicyclohexylethanol	56
Me ₂ BH	1-hexene	2-methyl-2-octanol	91 ^b
Me ₂ BH	2-methyl-1-heptene	(±)-2,4-dimethyl-2-nonanol	70
Me ₂ BH	cyclopentene	1-cyclopentyl-1-methylethanol	90 ^b
Me ₂ BH	<i>trans</i> -3-hexene	(±)-3-ethyl-2-methyl-2-hexanol	69
Me ₂ BH	cyclohexene	1-cyclohexyl-1-methylethanol	88 ^b
Me ₂ BH	1-methylcyclohexene	(±)-1-(<i>trans</i> -2-methylcyclohexyl)-1-methylethanol	73

^a Isolated distilled yields. Physical and spectral properties are in agreement with expected values. ^b GC yields using an internal standard.

In order to examine the purity of the triorganylboranes produced, it was necessary to convert these labile boron intermediates into stable carbon compounds that reflect the structure of the trialkylborane.¹⁴ It has been demonstrated that all three organic groups migrate from boron to the carbon via carbonylation,¹⁵ cyanidation,¹⁶ and reaction with α,α -dichloromethyl methyl ether,¹⁷ forming the corresponding tertiary alcohol after oxidation.¹⁸ Examination of the isomeric tertiary alcohols produced reflects the purity of the intermediate trialkylborane. The reaction of methylborane with 2.3 equiv of 1-hexene in ether at 0 °C gave a product that exhibited a single peak in the ¹¹B NMR spectrum. Conversion to the tertiary alcohol by carbonylation-oxidation and analysis by gas chromatography gave approximately equal amounts of 7-methyl-7-tridecanol and 7-hexyl-7-tridecanol (eq 13).



Clearly, the boron NMR spectra are not indicative of the purity of the trialkylborane. The purity of the 7-methyl-7-tridecanol produced could only be improved following a number of changes in the reaction conditions: hydroborating at a lower temperature, -25 °C, with a large excess of 1-hexene (10 equiv). However, there still remained a small amount of the undesired 7-hexyl-7-tridecanol, as well as the expected, but not analyzed, products from the redistribution.¹⁹

Carbonylation of the pure dihexylmethylborane, prepared from methyl lithium and dihexylmethoxyborane, cleanly gave the desired alcohol, indicating that redistribution occurred during the hydroboration, not during the carbonylation. Changing the solvent from ether to THF dramatically improved the selectivity of the reaction, with 7-methyl-7-tridecanol as the sole product produced. Hydroboration of cyclohexene with methylborane in ether

likewise reveals a redistribution of cyclohexyl and methyl groups, as evidenced by the presence of 1,1,1-tricyclohexylmethanol. This problem likewise vanishes by carrying out the hydroboration in THF. Consequently, THF is the solvent of choice for hydroboration with methylborane.

In contrast to methylborane, the hydroboration of various alkenes with dimethylborane in THF gives complex ¹¹B NMR spectra and formation of redistributed tertiary alcohols following carbonylation-oxidation. On the other hand, in diethyl ether, these hydroborations are complete within 1 h at 0 °C, exhibiting a single peak in the ¹¹B NMR spectra, whereas, in THF, 30% of an unreacted dialkylborane remained. Carbonylation-oxidation of the organoborane formed in ether gave a 91% yield of essentially pure 2-methyl-2-octanol. However, the THF reaction gave a much lower yield of this product, approximately 30%, as well as 30% of the redistributed product, 7-methyl-7-tridecanol. Therefore, to prepare the desired alkylidimethylboranes from dimethylborane, it is important to hydroborate in ethyl ether. On the other hand, the dialkylmethylboranes are best produced by hydroboration with methylborane in THF.

This remarkable difference in the preferred hydroborating solvent for the two reagents may in part be due to the lower stability of dimethylborane in THF, as pointed out earlier. Changes in the liberating agent from hydrogen chloride to other liberating agents either had no effect or actually diminished the selectivity of the hydroboration-carbonylation-oxidation process. The precise reasons for this pronounced effect of solvent are unclear and are the subject of current investigation.

Synthesis of Tertiary Alcohols Containing Methyl Groups. The hydroboration of methylborane in THF with 2.3 equiv of alkene or dimethylborane in ether with 1.15 equiv of alkene gives a single peak on the ¹¹B NMR spectrum at ca. δ +84, indicating trialkylborane(s) formation. The purity of these trialkylboranes was established by their carbonylation-oxidation to yield the tertiary alcohols of the same structure as the organoborane. These results are summarized in Table III. A variety of olefins, 1-alkenes, 2-methyl-1-alkenes, and trisubstituted and cyclic alkenes, can be cleanly hydroborated to the dialkylmethylboranes and alkylidimethylboranes and converted into the corresponding tertiary alcohols in high yields.

It is of interest that these methyl groups undergo transfer from boron to carbon with relative difficulty. Indeed, in applying the cyanidation or the DCME reaction, we frequently observed incomplete transfer of the methyl groups. Complete transfer was readily achieved in the carbonylation reaction. Consequently, this development makes available via hydroboration a wide variety of tertiary alcohols containing one or two methyl groups.

(14) Low molecular weight boranes can be analyzed by gas chromatography; however, the larger molecular weight boranes may undergo a thermal redistribution at temperatures necessary to volatilize them.

(15) Brown, H. C. *Acc. Chem. Res.* **1969**, *2*, 65.

(16) Pelter, A.; Hutchings, M. G.; Smith, K. *J. Chem. Soc. D* **1971**, 1048.

(17) Brown, H. C.; Carlson, B. A. *J. Org. Chem.* **1973**, *38*, 2422.

(18) Testing revealed carbonylation-oxidation to be the most satisfactory reaction for the conversion of these methylalkylboranes into the corresponding tertiary alcohols. The cyanidation reaction requires the prior removal of the lithium chloride, either by precipitation using a hydrocarbon solvent, or by extraction with water, followed by drying. The DCME reaction works satisfactorily with the dialkylmethylboranes but also gives small amounts of the ketone (5-20%). However, in the reaction of alkylidimethylboranes, only two of the groups migrate cleanly, yielding the methyl ketones. Evidently, the methyl groups are relatively resistant to transfer from boronate carbon.

(19) Other carbinols that should be present are *tert*-butyl alcohol and dimethylhexylcarbinol.

Table IV. Product Distribution from the Hydroboration-Oxidation of Representative Alkenes with Methylborane and Dimethylborane at 0 °C

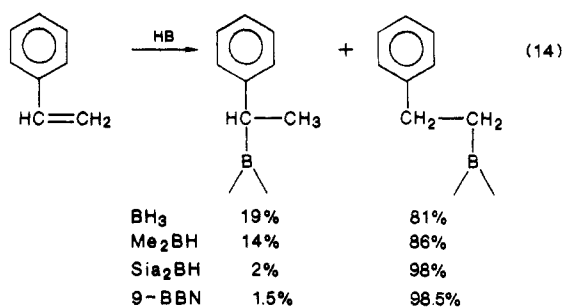
alkene	alcohol	product distribution, ^a %	
		MeBH ₂	Me ₂ BH
1-hexene	1-hexanol	99.5	99.5
	2-hexanol	0.5	0.5
styrene	1-phenylethanol	85	86
	2-phenylethanol	15	14
<i>cis</i> -2-hexene	2-hexanol	54	61
	3-hexanol	46	39
<i>trans</i> -2-hexene	2-hexanol	63	57
	3-hexanol	37	43
<i>cis</i> -4-methyl-2-pentene	4-methyl-2-pentanol	79	88
	4-methyl-3-pentanol	21	12
<i>trans</i> -4-methyl-2-pentene	4-methyl-2-pentanol	76	90
	4-methyl-3-pentanol	24	10
2-methyl-2-butene	2-methyl-3-butanol	>99.2	>99.9
	2-methyl-2-butanol	<0.8	<0.1
1-methylcyclopentene	<i>trans</i> -2-methylcyclopentanol	>99.5	>99.9
	1-methylcyclopentanol	<0.5	<0.1

^a See Experimental Section for details.

Regioselectivity of Hydroboration. It was of interest to examine the regioselectivity achieved in the hydroboration of representative alkenes by mono- and dimethylborane. Previously, data were available only for mono- and dialkylboranes of much greater steric requirements, thexylborane²⁰ (ThxBH₂), diisiamylborane²¹ (Si₂BH), and 9-borabicyclo[3.3.1]nonane²² (9-BBN).

We observed no significant difference in the regioselectivities realized in either THF or ethyl ether. Accordingly, we adopted ethyl ether for the hydroboration and 0 °C for the temperature. Following completion of the hydroboration, the reaction mixture was oxidized by alkaline hydrogen peroxide and the alcohols produced were analyzed by GC. The results are summarized in Table IV.

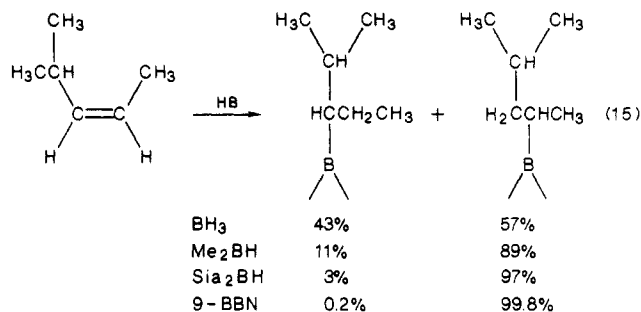
In the hydroboration of styrene, dimethylborane reacts to place 14% of the boron at the α -position (eq 14).



Consequently, the directive effects are similar to those realized with borane hydroboration²³ and are very different from those achieved by diisiamylborane²¹ or 9-BBN.²²

Similarly, in hydroborating *cis*-4-methyl-2-pentene, dimethylborane reacts to place 11% of the boron at the more crowded position of the double bond (eq 15).

In both cases the difference in directive effect is simply accounted for in terms of the much lower steric requirements of the dimethylborane reagent, more nearly com-



parable to those of borane²³ itself, rather than to the much larger steric requirements of diisiamylborane²¹ and 9-BBN.²²

Hydroboration with methylborane represents the net result of two successive stages. Thus it is probable that the 85:15 distribution for styrene is the average of a larger ratio for the first stage and a smaller value for the second. Similarly, the 79:21 distribution for *cis*-4-methyl-2-pentene must be the average of an even lower ratio for the first stage and a larger ratio for the second. Thus, the distribution achieved by methylborane in these two cases must be approaching the low regioselectivity exhibited by diborane itself (eq 14 and 15).

In one case there is an unexpected result. Methylborane gives a 1/2-distribution of boron in the hydroboration of 1-hexene of 99.5:0.5. This means that the distribution in the first stage must be at least 99.0:1.0. This is comparable to the distributions realized in hydroboration with chloroborane and bromoborane but very different from the average distribution realized with thexylborane,²⁰ 94:6, as well as with borane itself,²³ 94:6. It will be of interest in the future to establish the precise distribution realized in the first hydroboration stage for 1-hexene with borane, methylborane, and thexylborane. We are now attaining the technical ability for determining these quantities precisely.

Conclusion

Lithium methylborohydride and lithium dimethylborohydride can be thought of as stabilized forms of methylborane and dimethylborane. These borohydrides are readily prepared in quantity from the methylboronic and dimethylborinic esters. The methylboranes, which previously have been unavailable for hydroborations, are readily liberated from the borohydrides with hydrogen chloride in ether, as well as other reagents. The regioselectivity achieved in hydroboration of a selection of alkenes with methylborane and dimethylborane showed excellent selectivity for 1-alkenes and trisubstituted alkenes. The hydroboration of alkenes with methylborane in THF gives the pure dialkylmethylboranes, while hydroboration with dimethylborane in ether gives the pure alkyl dimethylboranes. Trialkylboranes are converted to the corresponding tertiary alcohols in high yield by carbonylation-oxidation. This reaction also serves to establish the purities of the trialkylboranes formed, R₂MeB and RMe₂B.

Experimental Section

General Comments. All glassware was dried at 140 °C for at least 3 h, assembled hot, and cooled under a stream of nitrogen. Anhydrous diethyl ether (Mallinkrodt) was stored over 4-Å molecular sieves under nitrogen and was used without further purification. The tetrahydrofuran was distilled from sodium ketal and stored under nitrogen prior to use. The alkenes were obtained from commercial sources (Aldrich or Wiley Organics) and were distilled from lithium aluminum hydride or used as received. Techniques for handling air-sensitive compounds have been previously described.²⁴

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(21) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 1241.

(22) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765.

(23) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4708.

The lithium methylborohydride was prepared from methylboronic acid⁷ in a 200-mmol scale reaction based on the previous reported procedure.¹⁰ The anhydrous hydrogen chloride in ether solution (ca. 3 M) was prepared by using a Brown²⁴ apparatus from hydrochloric acid and sulfuric acid.²⁵ The solutions were standardized by hydrolyzing an aliquot in water and titrating with a standard solution of sodium hydroxide to a phenolphthalein endpoint.

¹¹B NMR spectra were obtained on a Varian FT-80A spectrometer (25.517 MHz) relative to boron trifluoride etherate. Infrared spectra were recorded on a Perkin-Elmer 1420 ratio recording infrared spectrometer. Mass spectra were obtained on a Finnigan Model 4000 gas chromatograph mass spectrometer.

Preparation of Lithium Dimethylborohydride. A 500-mL, round-bottomed flask fitted with a side arm capped with a rubber septum and containing a magnetic stirring bar was charged with 100 mmol of methyl-diisopropoxyborane (14.4 g) in 100 mL of diethyl ether. The solution was cooled to -78 °C on a dry ice/acetone bath. Methylolithium (100 mmol, 71.4 mL in ether) was slowly added via a double-ended needle. After the addition was complete the reaction solution was stirred for 2 h at -78 °C. The clear solution was warmed to room temperature and then slowly added via a double-ended needle to a suspension of LiOEtAlH₃ prepared from ethyl acetate (50 mmol) and LiAlH₄ (100 mmol) at 0 °C. This mixture was stirred for an additional 15 min at 0 °C and then allowed to warm to room temperature. The reaction mixture was transferred via a needle to a 250-mL centrifuge bottle. The clear supernate was transferred via a double-ended needle to a 250-mL, round-bottomed flask. The resultant precipitate was washed with ether (2 × 25 mL), centrifuging after each wash, and combined with the previous fractions. The volatile materials were removed under reduced pressure (0.1 mmHg), leaving a thick viscous residue that was triturated with pentane (100 mL). The residual aluminum salts were allowed to settle and the clear solution was transferred to another 250-mL flask. The volatiles were removed under reduced pressure. This solid material was then dissolved in an appropriate solvent, pentane, ether, or tetrahydrofuran to make 100-mL solution. The concentration was estimated by hydrolysis.

General Procedure for the Determination of the Rate of Hydroboration. In a 50-mL flask fitted with a rubber-capped septum, magnetic stirring bar, and gas inlet adaptor was added 4.0 mmol of either lithium methylborohydride or lithium dimethylborohydride. The reaction flask was cooled to 0 °C in an ice bath and 1.30 mL of a 3.08 M hydrogen chloride in ether solution (4.0 mmol) was carefully added as the hydrogen generated was vented. The alkene, 15% molar excess, 4.6 mmol or 9.2 mmol, was quickly added. Samples were withdrawn via a double-ended needle and the sample was methanolized at 0 °C. The samples were then analyzed by ¹¹B NMR for the extent of reaction and the formation of intermediates.

General Procedure for the Hydroboration of Representative Alkenes with Methylborane and Carbonylation-Oxidation to the Corresponding Tertiary Alcohols. In a 100-mL flask with a septum-covered side arm, magnetic stirring bar, and gas inlet adaptor was added 15 mmol of lithium methylborohydride in THF. The reaction flask was cooled to 0 °C and 15 mmol, 4.9 mL, of a 3.08 M ethereal solution of hydrogen chloride was slowly added, with venting of the resultant hydrogen. A 15% molar excess of the representative alkene, 34.5 mmol, was added and the reaction stirred at -25 °C, 0 °C or room temperature for an appropriate period of time. Upon warming to room temperature, the lithium chloride formed precipitated from solution. The ¹¹B NMR at this point gave a single peak at ca. δ +83. The lithium chloride was allowed to settle and the clear supernatant was decanted via a double-ended needle into the nitrogen-flushed Parr "mini" reactor. The remaining solid lithium chloride was washed with THF, 2 × 3 mL, and added to the pressure reactor, along with 22.5 mmol, 1.25 mL, of ethylene glycol. The Parr reactor was sealed and pressurized to 1000 psi (6890 kPa) with carbon monoxide and heated to 150 °C for 24 h. After cooling and carefully venting the reactor, the contents were transferred to a

100-mL flask fitted with a septum-capped side arm, magnetic stirring bar, and reflux condenser. The ¹¹B NMR showed a single peak at δ +34, indicating clean formation of the boronic ester. Oxidation used a cosolvent of 6.0 mL of ethanol and 5.5 mL of 6 M sodium hydroxide, followed by the careful dropwise addition of 5.5 mL of 30% hydrogen peroxide. The reaction mixture was heated to 50–60 °C for at least 2 h to insure complete oxidation. Potassium carbonate was added to the aqueous fraction to near saturation and the organic layer separated. The aqueous portion was extracted with pentane, 3 × 20 mL. The combined organic fractions were washed with a near saturated solution of potassium carbonate, 2 × mL, and then dried over anhydrous magnesium sulfate. The volatile materials were removed under reduced pressure (13 mmHg), obtaining the crude product. This was then analyzed by gas chromatography to determine purity or percentage yield in conjunction with an internal standard, dodecane. The isolated material was then vacuum distilled and analyzed by IR and mass spectrometry. These results are summarized in Table III.

General Procedure for the Hydroboration of Representative Alkenes with Dimethylborane and Carbonylation-Oxidation to the Corresponding Tertiary Alcohols. In a 100-mL flask with a septum-covered side arm, magnetic stirring bar, and gas inlet adaptor was added 15 mmol (12.4 mL) of lithium dimethylborohydride in ether. The reaction flask was cooled to 0 °C. A 15% molar excess of the representative alkene, 17.25 mmol, was added followed by 15 mmol (4.4 mL, 3.40 M) of an ethereal solution of hydrogen chloride, the hydrogen was vented, and there was an immediate precipitate of lithium chloride. The reaction was stirred for an appropriate period of time for completion of reaction. The ¹¹B NMR spectrum gave a single peak at ca. + 86 ppm. The lithium chloride was allowed to settle and the clear supernate was decanted via a double-ended needle into the nitrogen-flushed pressure reactor. The remaining solid lithium chloride was washed with THF, 2 × 3 mL, and added to the pressure reactor along with 22.5 mmol, 1.25 mL, of ethylene glycol. The reactor was sealed and pressurized to 1000 psi (6890 kPa) with carbon monoxide and heated to 150 °C for 24 h. After cooling and carefully venting the reactor, the contents were transferred to a 100-mL flask fitted with a septum-capped side arm, magnetic stirring bar, and reflux condenser. The ¹¹B NMR spectrum showed a single peak at + 34 ppm, indicating clean formation of the boronic ester. Oxidation of the borane was done at 0 °C, using 6.0 mL of ethanol as a cosolvent, and 15 mL, 45 mmol, of sodium hydroxide followed by the careful dropwise addition of 5.1 mL of 30% hydrogen peroxide. The reaction mixture was heated to 50–60 °C for at least 2 h to insure complete oxidation. The aqueous fraction was saturated with sodium chloride and the organic layer separated. The aqueous portion was extracted with ether, 2 × 50 mL. The combined organic fractions were washed with brine and then dried over anhydrous magnesium sulfate. The volatile materials were removed under reduced pressure (13 mmHg) obtaining the crude product. This was then analyzed by gas chromatography to determine purity or percentage yield in conjunction with an internal standard. The isolated material was then bulb-to-bulb vacuum distilled and analyzed by IR and mass spectrometry. These results are summarized in Table III.

7-Methyl-7-tridecanol. The reaction was carried out as described above, liberating the methylborane from lithium methylborohydride (17.0 mL, 15.0 mmol) with anhydrous hydrogen chloride (4.8 mL, 15.0 mmol) at 0 °C. The hydroboration with 1-hexene (7.5 mL, 60 mmol) was complete at -25 °C in 4 h in the presence of dodecane as an internal standard for the gas chromatographic analysis. After carbonylation, oxidation, and extraction the organic phase was dried and the yield determined relative to the internal standard (96%).

2-Methyl-2-octanol. This reaction was conducted as described above using lithium dimethylborohydride (1.65 mL, 2.0 mmol), 1-hexene (0.27 mL, 2.3 mmol), undecane as an internal standard, and hydrogen chloride (0.58 mL, 2.0 mmol). The hydroboration was complete within 1 h. The carbonylation was done in a small pressure reactor; then oxidation and extraction gave a 91% yield of 2-methyl-2-octanol.

(±)-6,8,10-Trimethyl-8-pentadecanol. The methylborane was generated from lithium methylborohydride (17.0 mL, 15.0 mmol) and hydrogen chloride in ether (4.8 mL, 15.0 mmol) using the

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

(25) Brown, H. C.; Rei, M.-H. *J. Org. Chem.* 1966, 31, 1090.

above procedure. 2-Methyl-1-heptene (5.4 mL, 34.5 mmol) was added at 0 °C, and the reaction was complete within 1 h. The crude yield of alcohol was 3.3 g (82%) after carbonylation, oxidation, and extraction. Distillation gave 2.4 g (8.9 mmol, 60%): bp 98–100 °C (0.045 mmHg); n_D^{20} 1.4490; mass spectrum (chemical ionization, isobutane), m/z (relative intensity) 253 (M + H - H₂O, 100); IR ν_{OH} 3459 cm⁻¹.

(±)-2,4-Dimethyl-2-nonanol. The dimethylborane was liberated from lithium dimethylborohydride (12.4 mL, 15.0 mmol) and hydrogen chloride in ether (4.4 mL, 15.0 mmol) in the presence of 2-methyl-1-heptene (2.7 mL, 17.0 mmol) by using the above procedure. The hydroboration was complete within 1 h at 0 °C. After carbonylation, oxidation, and extraction from the aqueous solution, the alcohol was bulb-to-bulb distilled, yielding 1.8 g (10.5 mmol, 70%): bp 150–170 °C (15 mmHg); n_D^{20} 1.4366; mass spectrum, (chemical ionization, isobutane), m/z (relative intensity) 155 (M + H - H₂O, 100); IR ν_{OH} 3381, $\nu_{gem-dimethyl}$ 1377, 1160 cm⁻¹.

1,1-Dicyclopentylethanol. The preparation of this compound follows the above procedure using lithium methylborohydride (17.0 mL, 15.0 mmol) and hydrogen chloride in ether (4.8 mL, 15.0 mmol). The hydroboration was complete in 2 h at 0 °C using cyclopentene (3.1 mL, 34.5 mmol). Isolation of the crude product after carbonylation, oxidation and extraction gave 2.42 g (88%). Distillation yielded 1.42 g (7.8 mmol, 52%): bp 68–70 °C (0.15 mmHg); n_D^{20} 1.4897; mass spectrum (chemical ionization, isobutane), m/z (relative intensity) 165 (M + H - H₂O, 100); IR ν_{OH} 3477 cm⁻¹.

1-Cyclopentyl-1-methylethanol. The dimethylborane was liberated from lithium dimethylborohydride (1.65 mL, 2.0 mmol) and hydrogen chloride in ether (0.27 mL, 2.0 mmol) in the presence of undecane as an internal standard and cyclopentene (0.19 mL, 2.2 mmol). The hydroboration was complete within 1 h at 0 °C. Oxidation and extraction following the carbonylation in the small pressure reactor gave a gas chromatographic yield of 90%.

4,6-Diethyl-5-methyl-5-nonanol. This reaction was carried out by using the above-described procedure generating the methylborane from lithium methylborohydride (17.0 mL, 15.0 mmol) and anhydrous hydrogen chloride in ether (4.8 mL, 15.0 mL). *trans*-3-Hexene (4.3 mL, 34.5 mmol) was hydroborated in 6 h at 0 °C, yielding the triorganylborane as observed in the ¹¹B NMR spectrum (+81 ppm). Isolation of the crude product following the carbonylation, oxidation, and extraction gave 2.83 g (88%). Distillation of this material yielded 2.24 g (10.5 mmol, 70%): bp 60–62 °C (0.05 mmHg); n_D^{20} 1.4505; mass spectrum (chemical ionization, isobutane), m/z (relative intensity) 197 (M + H - H₂O, 100); IR ν_{OH} 3490 cm⁻¹.

3-Ethyl-2-methyl-2-hexanol. This compound was prepared by using the above procedure and lithium dimethylborohydride (12.4 mL, 15.0 mmol), hydrogen chloride in ether (4.4 mL, 15.0 mmol), and *trans*-3-hexene (2.1 mL, 17.0 mmol). The reaction was complete within 1 h at 0 °C. After carbonylation, oxidation, and extraction the alcohol was isolated by a bulb-to-bulb distillation at 150 °C (15 mmHg), yielding 1.50 g (10.35 mmol, 69%): n_D^{20} 1.4346; mass spectrum (chemical ionization, isobutane), m/z (relative intensity) 127 (M + H - H₂O, 100); IR ν_{OH} 3400, $\nu_{gem-dimethyl}$ 1378, 1155 cm⁻¹.

1,1-Bis(*trans*-2-methylcyclopentyl)ethanol. This reaction was conducted as described above using lithium methylborohydride (17.0 mL, 15.0 mmol) and hydrogen chloride in ether (4.8 mL, 15.0 mmol), hydroborating with methylcyclopentene (3.65 mL, 34.5 mmol) first at 0 °C and then allowing the solution to warm to room temperature overnight. Carbonylation, oxidation, and then extraction yielded 2.77 g (88%) of crude material. Distillation yielded 2.13 g (10.1 mmol, 67%) of pure alcohol: bp 77–79 °C (0.05 mmHg); n_D^{20} 1.4505; mass spectrum (chemical ionization, isobutane), m/z (relative intensity) 193 (M + H - H₂O, 100); IR ν_{OH} 3490 cm⁻¹.

1,1-Dicyclohexylethanol. Using the procedure described above, the methylborane was liberated from lithium methylborohydride in THF (17.0 mL, 15.0 mmol) and hydrogen chloride in ether (4.8 mL, 15.0 mmol). Hydroboration with cyclohexene (3.5 mL, 34.5 mmol) was first done at 0 °C for 0.5 h and then the solution was warmed to room temperature for 6 h. The crude alcohol, 2.60 g (82%), was isolated following the carbonylation, oxidation, and extraction. Distillation yielded 1.79 g (8.5 mmol,

56%): bp 108–110 °C (0.05 mmHg); n_D^{20} 1.4505; mass spectrum (chemical ionization, isobutane), m/z (relative intensity) 193 (M + H - H₂O, 100); IR ν_{OH} 3478 cm⁻¹.

1-Cyclohexyl-1-methylethanol. Dimethylborane was liberated from lithium dimethylborohydride (1.65 mL, 2.0 mmol), hydrogen chloride in ether (0.58 mL, 2.0 mmol), in the presence of cyclohexene (0.22 mL, 2.2 mmol), and the dodecane as an internal standard. The hydroboration was complete within 24 h at 0 °C. The reaction mixture was carbonylated in the small pressure reactor and then oxidized and extracted from the aqueous solution. The gas chromatographic yield of the 1-cyclohexyl-1-methylethanol was 88%.

(±)-1-(*trans*-2-Methylcyclohexyl)-1-methylethanol. Using the above-described procedure, dimethylborane was liberated from lithium dimethylborohydride (12.4 mL, 15.0 mmol) and hydrogen chloride in ether (4.4 mL, 15.0 mmol) in the presence of methylcyclohexene (1.72 mL, 17.0 mmol) at 0 °C. The hydroboration was complete within 24 h. Following the carbonylation, oxidation, and extraction from the aqueous solution, the material was bulb-to-bulb distilled, 150–170 °C (15 mmHg), which solidified on cooling. This solid material was recrystallized from cold pentane, obtaining 1.7 g (10.9 mmol, 73%) of product alcohol: mp 51–52 °C; mass spectrum (chemical ionization, isobutane), m/z (relative intensity) 139 (M + H - H₂O, 100); IR ν_{OH} 3316, $\nu_{gem-dimethyl}$ 1375, 1160 cm⁻¹.

General Procedure for the Determination of Regioselectivity in the Hydroboration of Representative Alkenes by Methylborane and Dimethylborane. In a 50-mL flask fitted with a rubber-capped side arm, magnetic stirring bar, and gas inlet adaptor was added 3.0 mmol of an ethereal solution of either the lithium methylborohydride or lithium dimethylborohydride. The reaction flask was cooled to 0 °C in an ice bath, and a known amount of internal standard and 3.3 or 6.6 mmol of the alkene were added, followed with 3.5 mmol, 0.38 g, of trimethylsilyl chloride. The cooling bath was removed and the reaction stirred for 2 h at room temperature. At this time, the extent of reaction was analyzed by ¹¹B NMR, which showed a single peak at ca. δ +85, indicating formation of the trialkylborane. The organoborane was oxidized at room temperature with 1.5 mL of 3 M solution of sodium hydroxide and the slow dropwise addition of 1.5 mL of a 30% hydrogen peroxide. Potassium carbonate was added to the aqueous phase to near saturation and the ether layer was separated and dried with anhydrous magnesium sulfate. This was analyzed for alcohols by gas chromatography to establish both the regioisomers and the yields. These results are summarized in Table IV.

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Registry No. LiMeBH₂, 52950-75-1; LiMe₂BH₂, 84280-31-9; MeLi, 917-54-4; LiEtOAlH₂, 26522-31-6; MeBH₂, 12538-96-4; Me₂BH, 7216-97-9; MeBH₂-C₅H₅N, 105064-83-3; Me₂BH-C₅H₅N, 105064-84-4; methyl-diisopropoxyborane, 86595-27-9; 1-hexene, 592-41-6; 2-methyl-1-heptene, 15870-10-7; cyclopentene, 142-29-0; *trans*-3-hexene, 13269-52-8; 1-methylcyclopentene, 693-89-0; cyclohexene, 110-83-8; 7-methyl-7-tridecanol, 19016-75-2; (±)-6,8,10-trimethyl-8-pentadecanol, 105064-85-5; 1,1-dicyclopentylethanol, 60836-09-1; (±)-4,6-diethyl-5-methyl-5-nonanol, 105064-86-6; (±)-1,1-bis(*trans*-2-methylcyclopentyl)ethanol, 105064-87-7; 1,1-dicyclohexylethanol, 53317-13-8; 2-methyl-2-octanol, 628-44-4; (±)-2,4-dimethyl-2-nonanol, 105064-88-8; 1-cyclopentyl-1-methylethanol, 1462-06-2; (±)-3-ethyl-2-methyl-2-hexanol, 105064-89-9; 1-cyclohexyl-1-methylethanol, 16664-07-6; (±)-1-(*trans*-2-methylcyclohexyl)-1-methylethanol, 66740-32-7; styrene, 100-42-5; *cis*-2-hexene, 7688-21-3; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0; 2-methyl-2-butene, 513-35-9; 1-hexanol, 111-27-3; 1-phenylethanol, 98-85-1; 2-phenylethanol, 60-12-8; 2-hexanol, 626-93-7; 3-hexanol, 623-37-0; 4-methyl-2-pentanol, 108-11-2; 4-methyl-3-pentanol, 565-67-3; 2-methyl-3-butanol, 598-75-4; *trans*-2-methylcyclopentanol, 25144-04-1.