Hydroboration. 84. Controlled and Sequential Hydroboration of Simple Representative Alkenes with Monoorganylboranes in Tetrahydrofuran. A Convenient Synthesis of Mixed Borinic Esters, $R^1R^2BOR^3$, and Mixed Trialkylboranes, $R^1R^2R^3B$. An Examination of Positional Selectivity in the First and Second States of Hydroboration

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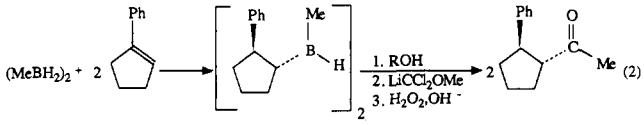
Received March 14, 1989

Six representative monoorganylboranes, including methylborane ($MeBH_2$), isopropylborane (i-$PrBH_2$), *sec*-butylborane (s-$BuBH_2$), *n*-butylborane (n-$BuBH_2$), *tert*-butylborane (t-$BuBH_2$), and monoisopinocampheylborane ($IpcBH_2$), have been prepared from their respective borohydrides, $LiRBH_3$, by treatment with ethereal hydrogen chloride. These boranes exist primarily as dimers in tetrahydrofuran (THF) with varying amounts of monomer·THF adduct, depending on the steric bulk of the organo groups. Solutions of these monoorganylboranes are stable for at least 3–5 h in THF. t-$BuBH_2$ is exceptional. Solutions of t-$BuBH_2$ in THF are stable for at least 1 week at 0 °C with no noticeable redistribution, isomerization, or loss of hydride activity. An improved procedure for the preparation of *tert*-butylboronic acid in high yield and purity by the reaction of *tert*-butylmagnesium chloride with 1 equiv of trimethoxyborane has been developed. These monoorganylboranes react with 1 equiv of an internal alkene to give mixed diorganylboranes, R^1R^2BH. t-$BuBH_2$ and $MeBH_2$ can cleanly monohydroborate 2-methyl-1-pentene, while only $MeBH_2$ can monohydroborate 1-hexene. These mixed diorganylboranes either can be converted into synthetically useful borinic esters, $R^1R^2BOR^3$, or can be treated with a different alkene to yield totally mixed triorganylboranes, $R^1R^2R^3B$. The latter, upon carbonylation–oxidation, furnish mixed tertiary alcohols, $R^1R^2R^3COH$. The positional selectivity of these monoorganylboranes in the first and second stages of hydroboration with four representative alkenes—1-hexene, *trans*-2-hexene, *trans*-4-methyl-2-pentene, and styrene—has been investigated. Being more sterically demanding, the regioselectivity in the second hydroboration step is more profoundly influenced by the newly formed diorganylboranes. Thus, n-$BuBH_2$ in the second hydroboration of styrene achieves a C2/C1 ratio of 96:4. Both t-$BuBH_2$ and $IpcBH_2$ in the second hydroboration of *trans*-4-methyl-2-pentene place boron exclusively on the less hindered carbon. The hydroboration of 4-hexene in both stages of hydroboration proceeds with very high regioselectivity for all monoorganylboranes examined.

Recently we reported the synthesis of methylborane, $MeBH_2$.[2] During the course of studying the chemistry of this compound, we discovered that $MeBH_2$ in tetrahydrofuran (THF) hydroborates simple alkenes in a 1:1 molar ratio to give methylmonoorganylboranes (eq 1).[3]

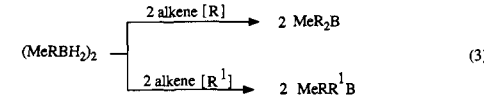
$$(MeBH_2)_2 + 2(\text{alkene}) \xrightarrow{\text{THF}} (MeRBH)_2 \qquad (1)$$

These methylmonoorganylboranes are highly useful organoborane intermediates. They can be converted via their borinates into methyl ketones, which retain the high regio- and stereoselectivity typical of the hydroboration reaction.[4] For instance, the reaction of methylborane with 1 equiv of 4-phenylcyclopentene yields methyl(*trans*-2-phenylcyclopentyl)borane, which is readily converted via the DCME reaction[5] to *trans*-2-phenylcyclopentyl methyl ketone[3] in 89% yield (eq 2).



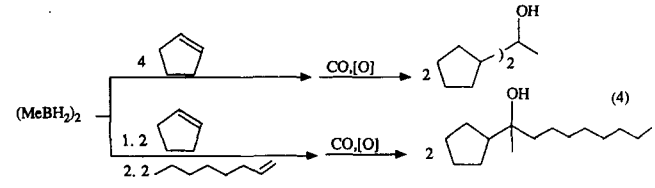
(2)

On the other hand, these newly formed methylmonoorganylboranes can hydroborate another equivalent of the same alkene to give methyldiorganylboranes, MeR_2B, or hydroborate a different alkene to give mixed methyldiorganylboranes, MeR^1R^2B (eq 3). These triorganylboranes can then be converted into tertiary alcohols by a carbonylation–oxidation sequence.[6] Thus, hydroboration of 2



(3)

equiv of cyclopentene with $MeBH_2$, followed by carbonylation–oxidation, cleanly gives 1,1-dicyclopentyl-1-ethanol, or hydroboration of 1 equiv of cyclopentene, followed by 1-octene, gives, after carbonylation–oxidation, 2-cyclopentyl-2-decanol (eq 4).



(4)

Therefore, $MeBH_2$, although sterically nonhindered, is capable of controlling the hydroboration of alkenes in THF to a degree previously attained only by the much more sterically demanding monoorganylborane 2,3-dimethyl-3-butylborane (thexylborane, $ThxBH_2$).[7] Moreover, whereas the latter fails in the controlled hydroboration of terminal alkenes, giving mixtures of mono- and dialkylated products, $MeBH_2$ cleanly furnishes the monoalkylated products, even with these reactive alkenes. Thus, $MeBH_2$, the simplest monoorganylborane, on one hand, and $ThxBH_2$, on the other, can each control the hydroboration of alkenes in a predictable manner. This suggests that other monoorganylboranes should exhibit varying degrees of monohydroboration of alkenes and offer a convenient means of introducing alkyl moities heretofore unobtainable via hy-

(1) Present address: Department of Chemistry, San Diego State University, San Diego, CA 92182-0328.
(2) Brown, H. C.; Cole, T. E.; Srebnik, M. *J. Org. Chem.* **1986**, *51*, 4925.
(3) Srebnik, M.; Cole, T. E.; Brown, H. C. *Tetrahedron Lett.* **1987**, *33*, 3771.
(4) For a discussion of the hydroboration reaction, see ref 36.
(5) Carlson, B. A.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 6876.
(6) Brown, H. C.; Rathke, M. W. *J. Am. Chem. Soc.* **1967**, *89*, 2737.
(7) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 1241. (b) Brown, H. C.; Negishi, E.; Katz, J.-J. *Ibid.* **1975**, *97*, 2791. (c) Brown, H. C.; Katz, J.-J.; Lane, C. F.; Negishi, E. *Ibid.* 2799.

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Table I. ^{11}B NMR Spectral Properties of Monoorganylboranes in THF

borane	^{11}B NMR, ppm			
	RBH_2	RBH_2·THF	RBH_2·SMe_2[b]	RBH_2·Py
$MeBH_2$[a]	21.9 (dt), 129.45	15.5	−10.3 (12–15)	5.8 (t), 97.0
i-$PrBH_2$	23.6 (d), 125.1	10.5		−1.0 (t), 95.4
n-$BuBH_2$	22.8 (d), 121.1	10.86		
s-$BuBH_2$	23.9 (d), 123.8	12.64	4.5 (6)	−1.66 (t), 95.7
t-$BuBH_2$	23.8 (d), 129.8	12.89	−1.02 (4)	0.61 (t), 98.3
$IpcBH_2$	23.1 (br, s)	10.26	−2.74 (5)	−1.00 (t),[c] 89

[a] Data from ref 3. [b] Number of equivalents of Me_2S needed to obtain the RBH_2·SMe_2 complex. [c] Partially resolved triplet.

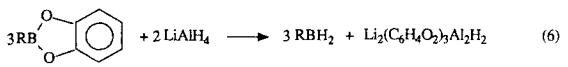
droboration in a controlled and rational manner. To test this hypothesis, we have now prepared a series of monoorganylboranes in THF: isopropylborane (*i*-$PrBH_2$), *n*-butylborane (*n*-$BuBH_2$), *sec*-butylborane (*s*-$BuBH_2$), and *tert*-butylborane (*t*-$BuBH_2$). We have also included in this study the important chiral hydroborating reagent monoisopinocampheylborane ($IpcBH_2$)[8] and for the sake of completeness, included our earlier results with $MeBH_2$.[3] These monoorganylboranes were reacted in THF with representative alkenes in a 1:1 molar ratio. In select cases, we then treated the newly formed mixed boranes, R^1R^2BH, with a different alkene to obtain mixed trialkylboranes, $R^1R^2R^3B$. In addition, we investigated the positional selectivity in the first and second stages of the hydroboration of representative alkenes.

Results and Discussion

Preparation of Monoorganylboranes. Monoorganylboranes have been prepared as their trialkylamine complexes by the reaction of trialkylboroxines[9] with excess lithium aluminum hydride ($LiAlH_4$), followed by treatment with water (eq 5). These amine complexes require ele-

$$(RBO)_3 \xrightarrow[2.\ H_2O]{1.\ LiAlH_4,NR^1_3} 3RBH_2{\cdot}NR^1_3 \qquad (5)$$

vated temperatures (50–60 °C) for hydroboration.[10] No attempt was made to liberate the free parent monoorganylborane from the amine complex. In a related synthesis, the reaction of 2-organyl-1,3,2-benzodioxaboroles with either $LiAlH_4$ (eq 6) or aluminum hydride (eq 7)



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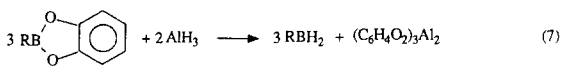
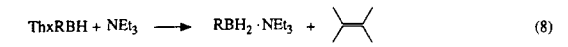


(7)

yielded the corresponding monoorganylboranes.[11] This reaction is limited to the preparation of monoorganylboranes available by hydroboration. In a conceptually different approach, thexylmonoalkylboranes have been dehydroborated with triethylamine to furnish monoorganylboranes as their triethylamine complexes[12] (eq 8).



(8)

The free boranes are then obtained by the action of boron trifluoride etherate. This reaction sequence is also limited to the alkyl groups obtainable via hydroboration. In another approach, reduction of organylboron dihalides with metal hydride is reported to result in the formation of a mixture of organoboron products.[13] Mikhailov has found that the equilibration of diarylborinates with diborane leads to the free monoorganoborane[14] (eq 9). But under

$$3Ar_2BO\text{-}n\text{-}Bu + 2B_2H_6 \rightarrow 3(ArBH_2)_2 + B(O\text{-}n\text{-}Bu)_3 \qquad (9)$$

the conditions of their preparation, these monoorganylboranes undergo rapid redistribution in the presence of alkenes.[15]

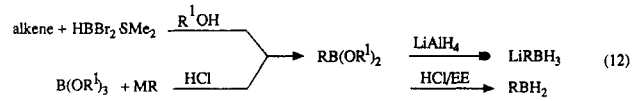
Recently we developed a general method for the preparation of lithium monoorganylborohydrides[16] from the reaction of $LiAlH_4$ with organylboronic acids or esters (eq 10). The borohydrides are obtained cleanly and are easily

$$RB(OR^1)_2 + LiAlH_4 \xrightarrow[0\ °C]{\text{pentane,EE}} LiRBH_3 + HAl(OR^1)_2\downarrow \qquad (10)$$

isolated from the relatively insoluble dialkoxyalanes. They are stable in solution for at least 1 year with no discernible changes in their ^{11}B NMR spectra. Treatment of these borohydrides with inter alia ethereal hydrogen chloride[17] liberates the free monoorganylboranes (eq 11). These borohydrides can therefore be viewed as stable forms of the monoorganylboranes.

$$2LiRBH_3 + 2HCl \rightarrow (RBH_2)_2 + 2LiCl + 4H_2 \qquad (11)$$

Since the requisite boronic acids and esters are readily available, either by the hydroboration of an appropriate alkene with dibromoborane methyl sulfide, followed by solvolysis,[18] or by treatment of an organometallic reagent and a borate,[19] this reaction sequence provides a general and rational synthesis of monoorganylboranes (eq 12).



(12)

Utilizing this sequence, we prepared a series of representative monoorganylboranes in THF. The spectral properties of these boranes are summarized in Table I.

In general, the monoorganylboranes $MeBH_2$, *i*-$PrBH_2$, *n*-BuBH, and *s*-$BuBH_2$ are stable in THF for at least 3–5

(8) (a) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, *37*, 3547. (b) Brown, H. C.; Jadhav, P. K.; Singaram, B. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer Verlag: Berlin, 1986.
(9) Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 831.
(10) (a) Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 748; (b) **1961**, *83*, 2541.
(11) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1971**, *93*, 4062.
(12) Brown, H. C.; Negishi, E.; Katz, J.-J. *J. Am. Chem. Soc.* **1972**, *94*, 5893.
(13) Long, L. H.; Wallbridge, M. G. H. *J. Chem. Soc.* **1965**, 3513.
(14) Mikhailov, B. M.; Dorokhov, V. A. *Dokl. Akad. Nauk SSSR* **1960**, *130*, 782 (*Engl. Transl.*, p 137).
(15) Mikhailov, B. M.; Dorokhov, V. A. *Dokl. Akad. Nauk SSSR* **1960**, *133*, 119 (*Engl. Transl.*, p 743). We have also found that $PhBH_2$, liberated from $LiPhBH_3$ with HCl, is highly labile toward disproportionation and in fact cannot be used effectively in monohydroborations, even in the presence of coordinating ligands, e.g., SMe_2, NEt_3, etc.
(16) Singaram, B.; Cole, T. E.; Brown, H. C. *Organometallics* **1984**, *3*, 774.
(17) Cole, T. E.; Bakshi, R. K.; Srebnik, M.; Singaram, B.; Brown, H. C. *Organometallics* **1986**, *5*, 2303.
(18) Brown, H. C.; Bhat, N. G.; Somayaji, V. *Organometallics* **1983**, *2*, 1311.
(19) (a) Brown, H. C.; Cole, T. E. *Organometallics* **1983**, *2*, 1316. (b) Brown, H. C.; Srebnik, M.; Cole, T. E. *Ibid.* **1986**, *5*, 2300.

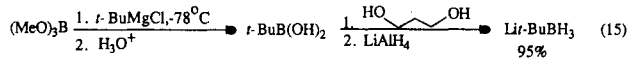
h at room temperature. (However, see Discussion.) After this time, a discernible redistribution occurs, as evidenced by ^{11}B NMR spectroscopy. Although these monoorganylboranes exist primarily as dimers in solution (δ 21–23), they form varying amounts of monomer·THF adducts (δ 10–15). The amount of monomer·THF varies with the steric bulk of the organyl moiety. Thus, $MeBH_2$, the simplest monoorganylborane, exists almost entirely as a dimer, >97%, whereas, $IpcBH_2$ and t-$BuBH_2$ show appreciable amounts of monomer·THF adducts, 37% and 20%, respectively. This suggests that the $(MeBH_2)_2$ dimer is relatively "tight". Evidence for this is the sharp doublet of triplets exhibited by $MeBH_2$ in the ^{11}B NMR spectrum[20] (Table I), whereas the other boranes generally give ill-defined doublets. $IpcBH_2$ shows a broad singlet. The extent of the "tightness" of the dimers can be gauged by the number of equivalents of methyl sulfide, Me_2S, needed to form the monoorganylborane·SMe_2 complex cleanly. Thus, while $MeBH_2$ requires up to 15 equiv of Me_2S, t-$BuBH_2$ needs only 4 equiv (eq 13 and 14). This is to be

$$(MeBH_2)_2 + 30Me_2S \rightarrow 2MeBH_2{\cdot}SMe_2 + 28Me_2S \quad (13)$$

$$(t\text{-}BuBH_2)_2 + 8Me_2S \rightarrow 2t\text{-}BuBH_2{\cdot}SMe_2 + 6Me_2S \quad (14)$$

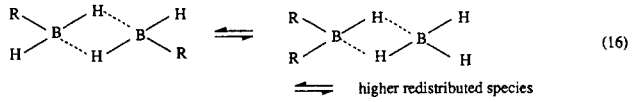
expected since in the dimeric species the greater steric bulk of the *tert*-butyl groups would favor the formation of the monomer·ligand complexes.

Stability of t-$BuBH_2$ in THF. It has been suggested that t-$BuBH_2$ ought to be a good substitute for the relatively expensive and unstable $ThxBH_2$.[21] We concur. Accordingly, we undertook a more thorough investigation of t-$BuBH_2$ in THF. In addition, owing to the potential importance of t-$BuBH_2$, we required a convenient synthesis of the precursor boronic ester, t-$BuB(OR)_2$. Previously, we had shown that t-$BuB(O\text{-}i\text{-}Pr)_2$[19] could be prepared by the reaction of *tert*-butyllithium and triisopropoxyborane at −100 °C, followed by treatment with ethereal HCl. The very low temperatures required and the relatively expensive lithium reagent make the preparation unattractive. After some experimentation, we found that treatment of 1 equiv of trimethoxyborane in EE at −78 °C with *tert*-butylmagnesium chloride in EE, followed by treatment with aqueous HCl, cleanly afforded *tert*-butylboronic acid in up to 75% yield.[22] The boronic acid in pentane was then treated with 1,3-propanediol[18] to yield 2-*tert*-butyl-1,3,2-dioxaborinane in quantitative yield, which, without further purification, was converted into lithium *tert*-butylborohydride in greater than 95% yield (eq 15).



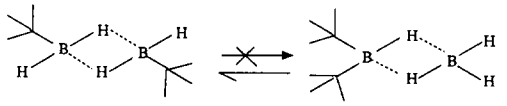
(15)

Although Hawthorne prepared t-$BuBH_2$ as the trimethylamine complex,[9,10] the stability of the free borane in solution has not been previously reported.[23] We have found that 1 M solutions of t-$BuBH_2$ in THF at 0 °C are very stable indeed. No discernible changes are evident for at least 1 week (^{11}B NMR). Why is t-$BuBH_2$ so stable in THF? Redistribution of boranes take place in the bridging dimeric species (eq 16). In the case of t-$BuBH_2$, the



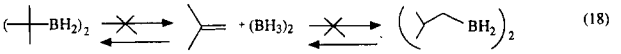
(16)

redistribution of the *tert*-butyl groups would lead to a di-*tert*-butylborane–borane dimer (eq 17). Apparently the


(17)

steric crowding of two geminal *tert*-butyl groups on boron makes this an unfavorable process. The other monoorganoboranes investigated, viz., $MeBH_2$, i-$PrBH_2$, n-$BuBH_2$, and s-$BuBH_2$ being less sterically demanding, can accommodate more readily two or more groups on boron. In fact, as mentioned before, redistribution is discernible for $MeBH_2$ and i-$PrBH_2$ after 3–5 h.

Analysis of the alcohol(s) obtained after oxidation of t-$BuBH_2$ reveals only t-BuOH, indicating that no isomerization, i.e., dehydroboration–rehydroboration, has occurred (eq 18). Otherwise, we should have observed significant amounts of isobutyl alcohol.


(18)

The *tert*-butyl group should exhibit similarly low migratory aptitude as the thexyl group in many reactions, and in radical reactions it should migrate preferentially. Therefore, the t-$BuBH_2$ reagent should offer advantages over $ThxBH_2$ since the latter must be prepared freshly prior to use and has a tendency to dehydroborate readily at 0 °C and isomerize.

Hydroborations with Monoorganylboranes in THF in a 1:1 Molar Ratio. Approximately 1 M solutions of the lithium borohydrides were prepared and treated with 1 equiv of ethereal HCl at 0 °C, followed by the addition of 1.1 equiv of alkene. After stirring for an appropriate length of time, the reaction was quenched with excess methanol, and the solution analyzed. The product distribution was determined by either peak heights (^{11}B NMR) or integration of peak areas. Both methods give good mass balance, ±5%.

Methylborane ($MeBH_2$). The results with $MeBH_2$ have already been reported[3] and are presented in Table II for the sake of comparison. $MeBH_2$ in THF is the only monoorganylborane to date capable of controlled hydroboration of all classes of alkenes.

***n*-Butylborane (*n*-$BuBH_2$).** This monoorganylborane behaves similarly to i-$PrBH_2$ in the hydroboration of mono- and disubstituted terminal alkenes, but unlike $MeBH_2$, with one noticeable exception. The monohydroboration of 3,3-dimethyl-1-butene at −25 °C can be cleanly stopped (Table III).

In a like manner, the hydroboration of styrene can be controlled to give the monoalkylated product. Terminal disubstituted alkenes cannot generally be monoalkylated. Although the major products are the monoalkylated compound, these are always accompanied to varying degrees by dialkylated materials. In one case, 2-ethyl-1-butene, we could cleanly obtain the monohydroborated product, although accompanied by considerable amounts of starting material (Table III).

As was the case with i-$PrBH_2$, the monohydroboration of internal alkenes can be successfully controlled with n-$BuBH_2$. The rates of hydroboration vary considerably with the steric requirements of the alkene (Table III).

(20) Williams, R. E.; Fisher, H. D.; Wilson, C. O. *J. Phys, Chem.* **1960**, *64*, 1583. However, there is no simple relationship between the extent of dimer formation of the monoalkylboranes and their rates of reaction with alkenes (see text).

(21) Pelter, A.; Smith, K. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, p 737. Thexylene is a relatively expensive olefin and is required in at least 50% excess to make $ThxBH_2$. In addition, $ThxBH_2$ is prone to redistribution and cannot be used at 25 °C. On the other hand, t-$BuBH_2$ can be stored as a stock solution.

(22) For an earlier procedure, see: Brown, H. C.; Park, W. S.; Cha, J. S.; Cho, B. T.; Brown, C. A. *J. Org. Chem.* **1986**, *51*, 337.

(23) See, however, ref 17 for a spectral characterization of t-$BuBH_2$.

Table II. Reaction of $MeBH_2$ with Representative Alkenes in 1:1 Molar Ratio in THF[a]

alkene	time, min	temp, °C	product distribution, %		
			$MeB(OMe)_2$	MeRBOMe	MeR_2B
Terminal					
1-hexene	1	−25	5	95	0
styrene	60	0	5	95	0
2-methyl-1-pentene	1	0	7	88	5
Internal					
cis-4-methyl-2-pentene	5	0	4	96	0
trans-4-methyl-2-pentene	5	0	2	98	0
2-methyl-2-butene	5	0	2	98	0
2,3-dimethyl-2-butene	30	0	2	98	0
cyclopentene	5	0	2	98	0
1-methylcyclopentene	5	0	2	98	0
1-phenylcyclopentene	90	0	4	96	0
1-methylcyclohexene	10	0	2	98	0
norbornene	5	−25	3	97	0
α-pinene	10	0	2	98	0

[a] Data taken from ref 3.

Table III. Reaction of n-$BuBH_2$ with Representative Alkenes in a 1:1 Molar Ratio in THF

alkene	time, min	temp, °C	product distribution, %		
			n-$BuB(OMe)_2$	n-BuRBOMe	n-BuR_2B
Terminal					
1-hexene	30	−25	55	38	7
	120	−40	75	25	0
3,3-dimethyl-1-butene	20	−25	4	96	0
2-methyl-1-pentene	10	−25	43	53	4
	60	−30	52	43	4
	180	−40	51	46	3
2-ethyl-1-butene	2	−25	48	49	3
	5	−25	45	55	0
	10	−25	26	68	6
2,3-dimethyl-1-butene	12	−10	22	58	10
styrene	50	25	1	99	0
Internal					
trans-2-hexene	50	0	1	99	0
trans-4-methyl-2-pentene	150	0	5	95	0
cyclopentene	30	−25	1	99	0
1-methylcyclopentene	10	0	4	96	0
cyclohexene	120	0	3	97	0
1-methylcyclohexene	150	25	3	97	0

Thus, n-$BuBH_2$ may prove to be a useful reagent in the selective hydroboration of compounds with multiple double bonds.

Isopropylborane (i-$PrBH_2$). The hydroboration of mono- and disubstituted terminal alkenes could not generally be controlled with i-$PrBH_2$. Even at −25 °C, mixtures are obtained from the hydroboration of 1-hexene. Increasing the steric bulk of the alkenes, i.e., 3,3-dimethyl-1-butene, and lowering the temperature to −25 °C enables the selective formation of monoalkylated product, although accompanied by large amounts of starting material. Styrene, however, can be selectively monohydroborated at 0 °C, with only residual amounts of starting material detectable (<2%). Disubstituted terminal alkenes, such as 2-methyl-1-pentene, cannot be monohydroborated. Mixtures of mono- and dialkylated products are obtained, accompanied by considerable amounts of starting borane. The more sterically demanding 2,3-dimethyl-1-butene yields the monohydroborated product, but only at low conversion of starting borane. The results are summarized in Table IV.

However, di- and trisubstituted alkenes are different. Hydroboration of these alkanes with i-$PrBH_2$ can be cleanly stopped after the first hydroboration to yield the monoisopropylalkylboranes. The results are summarized in Table IV. The rates of hydroboration with i-$PrBH_2$ are slower than with $MeBH_2$ and are more sensitive to the steric requirements of the alkene. Thus, whereas monohydroboration of 1-methylcyclohexene and α-pinene with $MeBH_2$ are complete within 10 min, the hydroboration of these alkenes with i-$PrBH_2$ requires 90 and 180 min, respectively (Table IV).

***sec*-Butylborane (s-$BuBH_2$).** This reagent hydroborates mono- and disubstituted terminal alkenes in a manner similar to i-$PrBH_2$ and n-$BuBH_2$. The results are summarized in Table V. Internal alkenes are cleanly monohydroborated, the rates varying with the steric requirements of the alkene, although to a lesser degree than that observed with n-$BuBH_2$.

***tert*-Butylborane (t-$BuBH_2$).** This reagent cleanly monohydroborated styrene but not 1-hexene and therefore behaves similarly to the other monoorganylboranes (except $MeBH_2$) with monosubstituted terminal alkenes. However, like $MeBH_2$ and $ThxBH_2$ but unlike the other monoorganylboranes studied t-$BuBH_2$ reacts with 1 equiv of 2-methyl-1-pentene to give the monoalkylated product (Table VI). Thus, the dividing line for steric requirements in the 1:1 monohydroboration of 2-substituted-1-alkenes occurs in the transition from $IpcBH_2$ to t-$BuBH_2$. In a manner analogous to the other reagents investigated, t-$BuBH_2$ cleanly monohydroborates internal alkenes (Table VI). The rates for these hydroborations are generally faster than those observed for s-$BuBH_2$ and much faster than n-$BuBH_2$.

Isopinocampheylborane ($IpcBH_2$). $IpcBH_2$ is similar to i-$PrBH_2$, n-$BuBH_2$, i-$BuBH_2$, and $ThxBH_2$ and cannot

Table IV. Reaction of *i*-PrBH$_2$ with Representative Alkenes in a 1:1 Molar Ratio in THF

alkene	time, min	temp, °C	product distribution, %		
			i-PrB(OMe)	*i*-PrRBOMe	*i*-PrR$_2$B
Terminal					
1-hexene	10	−25	72	20	8
3,3-dimethyl-1-butene	10	0	26	68	6
	25	−10	2	66	
	40	−25	43	54	
2-methyl-1-pentene	10	0	50	46	4
	30	−25	64	29	7
2,3-dimethyl-1-butene	20	−10	52	39	9
	60	−25	59	33	8
styrene	50	0	<2	>98	0
Internal					
trans-2-hexene	10	0	>3	>97	0
trans-4-methyl-2-pentene	25	0	<1	>99	0
cyclopentene	10	0	<1	>99	0
1-methylcyclopentene	10	0	<2	>98	0
α-pinene	180	0	<1	>99	0

Table V. Reaction of *s*-BuBH$_2$ with Representative Alkenes in 1:1 Molar Ratio in THF

alkene	time, min	temp, °C	product distribution, %		
			s-BuB(OMe)$_2$	*s*-BuRBOMe	*s*-BuR$_2$B
Terminal					
3-methyl-1-butene	5	0	20	76	4
	5	−25	39	61	0
2-methyl-1-pentene	20	−10	71	23	6
2,3-dimethyl-1-butene	20	−10	71	24	5
styrene	90	0	5	95	0
Internal					
trans-2-hexene	30	0	4	96	0
trans-4-methyl-2-pentene	50	0	<1	>99	0
2-methyl-2-butene	60	0	2	98	0
cyclopentene	10	0	6	90	4
	15	−10	3	97	0
1-methylcyclopentene	10	0	2	98	0
cyclohexene	30	0	4	96	0
1-methylcyclohexene	120	0	<1	>99	0
α-pinene	150	0	5	95	0

Table VI. Reaction of *t*-BuBH$_2$ with Representative Alkenes in a 1:1 Molar Ratio in THF

alkene	time, min	temp, °C	product distribution, %		
			t-BuB(OMe)$_2$	*t*-BuRBOMe	*t*-BuR$_2$B
Terminal					
1-hexene	5	0	48	1,	34
	5	−25	41	27	32
2-methyl-1-pentene	5	0	<1	>99	0
styrene	10	0	5	95	0
Internal					
trans-2-hexene	5	0	2	98	0
trans-4-methyl-2-pentene	30	0	5	98	0
cyclopentene	7	0	5	98	0
2-methyl-2-butene	10	0	2	98	0
α-pinene	150	0	<2	>98	0

Table VII. Reaction of IpcBH$_2$ with Representative Alkenes in 1:1 Molar Ratio in THF

alkene	time, min	temp, °C	product distribution, %		
			IpcB(OMe)$_2$	IpcRBOMe	IpcR$_2$B
1-hexene	1	0	61	39	0
2-methyl-1-pentene	1	0	40	56	4
	25	−25	44	51	5
trans-2-hexene	60	0	5	95	0
trans-4-methytl-2-pentene	10	0	10	90	0
2-methyl-2-butene	50	0	2	98	0
cyclopentene	8	0	4	96	0

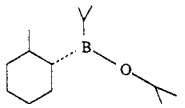
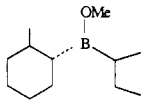
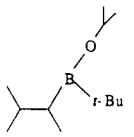
readily monohydroborate mono- and disubstituted terminal alkenes.[24] However, monohydroboration of internal alkenes[8] is readily achieved (Table VII).

(24) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *J. Org. Chem.* **1982**, *47*, 5074. In the present study, no attempt was made to determine the enantiomeric excess.

Isolation of Dialkylborinic Esters (R^{1}R^{2}RBOR^3). Dialkylboranes are generally labile compounds. To ascertain that no redistribution occurred during hydroboration, we converted these boranes into their esters by reaction with an alcohol (eq 19). Isolation was accom-

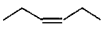
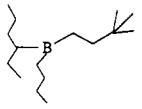
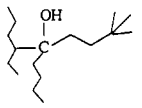
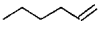
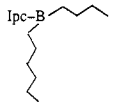
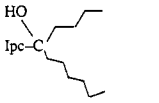
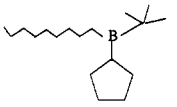
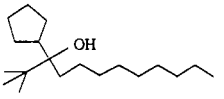
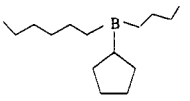
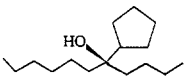
$$(R^1R^2BH)_2 + 2R^3OH \rightarrow 2R^1R^2BOR^3 + 2H_2 \quad (19)$$

Table VIII. Preparation of Borinic Esters Obtained from the Hydroboration of Alkenes with Monoorganylboranes

alkene	mono-organyl-borane	borinate	^{11}B NMR, δ	bp, °C (mmHg)	yield,[a] %
	i-PrBH$_2$		53.8	88–90 (12)	71
	s-BuBH$_2$		54.4	104–106 (12)	62
	t-BuBH$_2$		51.8	74–76 (14)	81

[a] Isolated yield.

Table IX. Preparation of Mixed Tertiary Alcohols by the Hydroboration–Carbonylation–Oxidation of Alkenes with Monoorganylboranes

alkene A	alkene B	mono-organylborane	trialkylborane	tertiary alcohol	yield, %
		n-BuBH$_2$			71
		n-BuBH$_2$			83
		t-BuBH$_2$			80
		BuBH$_2$			75

plished by removing all volatiles under reduced pressure, redissolving the borinic ester in pentane (to remove LiCl), and decanting the clear solution via a double-ended needle into a distillation flask. Simple distillation gave the borinic ester in good yield (Table VIII). The proposed structures of these borinic esters were corroborated by ^1H NMR spectroscopy and chemical ionization mass spectra. The latter gave the protonated molecular ion, $M^+ + H$ (see Experimental Section) as a major peak in most cases. Of equal importance is the fact that no higher molecular weight species were detected, reconfirming that no redistribution had occurred.

Reaction of Mixed Dialkylboranes with Representative Alkenes in THF in a 1:1 Molar Ratio. We have demonstrated with MeBH$_2$[3] that the ability to stop hydroboration at the first stage enables the addition of another alkene to the newly formed alkylmethylborane to give mixed dialkylmethylboranes, MeR^{1}R^{2}B (eq 3). We therefore next investigated the reaction of an appropriate alkene with an equimolar quantity of mixed dialkylboranes in THF at 0 °C. Each of these dialkylboranes was prepared as described above by the reaction of alkene A with an equimolar quantity of the monoorganylborane in THF at the appropriate temperature. The mixed dialkylboranes thus obtained were allowed to react with an equimolar quantity of a second alkene B at 0 °C, and the reaction mixture was stirred for the required period of time. Examination by ^{11}B NMR spectroscopy of an aliquot indicated the clean formation of a trialkylborane (δ 84), but owing to the intrinsic insensitivity of ^{11}B NMR to structurally similar compounds, the ^{11}B NMR spectrum does not establish whether this is the desired mixed trialkylborane or a mixture of various redistributed tiralkylboranes.

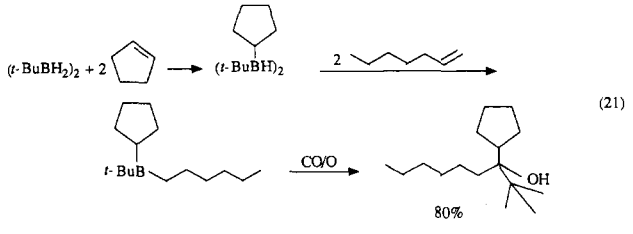
To examine the purity of the trialkylboranes present, it is necessary to convert these labile boron compounds into more stable carbon compounds that accurately reflect the structure of the trialkylboranes. It has been demonstrated that all three groups migrate from boron to carbon via carbonylation,[25] cyanidation,[26] and reaction with DCME,[27] forming the corresponding tertiary alcohol upon oxidation. Examination of the isomeric tertiary alcohols obtained reflects the isomeric purity of the trialkylborane. Inasmuch as we had previously observed incomplete transfer of the alkyl groups in the cyanidation and DCME reactions,[2] but complete transfer in carbonylation, we selected the latter reaction for the conversion of the trialkylboranes to the tertiary alcohols. The products of the hydroboration of alkene A and alkene B with the appropriate monoorganylborane were carbonylated (1000 psi, CO, 150 °C, 24 h) and oxidized (H_2O_2, OH^-) to yield the tertiary alkcohol (eq 20). These were purified by either bulb-to-bulb

(25) Brown, H. C. *Acc. Chem. Res.* **1969**, *2*, 65.
(26) Pelter, A.; Hutchings, M. G.; Smith, K. *Chem. Commun.* **1971**, 10.
(27) Brown, H. C.; Carlson, B. A. *J. Org. Chem.* **1973**, *38*, 2422.

$$R^1R^2R^3B \xrightarrow[2.\ H_2O_2,\ OH^-]{1.\ CO} R^1R^2R^3COH \qquad (20)$$

distillation or column chromatography. Analysis by capillary GC (methylsilicone, 50 M) showed the clean formation of the desired tertiary alcohols, indicating a clean formation of the parent mixed trialkylboranes. The results are summarized in Table IX. The proposed structures were corroborated by CIMS and, where applicable, by ^{13}C NMR spectroscopy. Importantly, no higher weight molecular species were observed in the mass spectra, indicating no redistribution reaction had occurred during the hydroboration. Thus, we have demonstrated that monoorganylboranes in THF can indeed hydroborate alkenes sequentially without redistribution to yield the totally mixed trialkylboranes.

The sequence of addition of alkenes to these monoorganylboranes to form trialkylboranes illustrates an important point. In general, terminal mono- and disubstituted alkenes cannot be successfully monohydroborated with these monoorganylboranes ($MeBH_2$ is the exception). However, it is still possible to fully utilize these reactive alkenes by an appropriate sequence of addition. For instance, t-$BuBH_2$ cannot cleanly monohydroborate 1-hexene, but cyclopentene is monohydroborated cleanly. Thus by simply adding cyclopentene first, followed by 1-hexene, the desired trialkylborane is obtained. The structure of the mixed trialkylborane was confirmed by conversion to the tertiary alcohol in 80% yield (eq 21).



(21)

The reverse addition would, of course, lead to mixtures.[7b,c] In a similar manner, reactive alkenes can be incorporated into the mixed trialkylboranes with i-$PrBH_2$ and n-$BuBH_2$.

Little selectivity is observed in the migratory aptitude of the various alkyl groups during carbonylation. In practical terms, this means that while carbonylation–oxidation serves admirably to determine the isomeric purity of triorganylboranes, the lack of any observed selectivity in the carbonylation step limits the present reaction sequence to the synthesis of tertiary alcohols with one asymmetric carbon. Thus, whereas 3-cyclopentyl-2-methyl-3-dodecanol and 3-cyclopentyl-2,2-dimethyl-3-nonanol are obtained as single compounds, 2,2-dimethyl-4-(3-hexyl)-4-octanol and 5-(2-isopinocampheyl)-5-undecanol are obtained as mixtures of diastereomers (Table IX).

Regioselectivity in the First and Second Stages of Hydroboration of Representative Alkenes with Monoorganylboranes in THF. Now that the hydroboration of alkenes with monoorganylboranes could be controlled to yield either the diorganylborane, R^1R^2BH, or the triorganylborane, $R^1R^2{}_2B$ (with 2 equiv of an alkene), selectively, it was of interest to examine the regioselectivity achieved in both stages of hydroboration. Previously, data were available only for the overall regioselectivity observed for mono- and dialkylboranes such as $ThxBH_2$,[7a] disiamylborane (Sia_2BH[28]), and 9-borabicyclo[3.3.1]nonane (9-BBN[29]) and the monohaloboranes, HBX_2·Ligand.[30]

In the present study, four representative alkenes, 1-hexene, *trans*-2-hexene, *trans*-4-methyl-2-pentene, and styrene, in 1:1 and 2:1 molar ratios in THF were hydroborated for the appropriate period of time with the follow-ign monoorganylboranes: i-$PrBH_2$, n-$BuBH_2$ s-$BuBH_2$, t-$BuBH_2$, and $IpcBH_2$. For the sake of completeness, we have also included the results of our earlier study with $MeBH_2$. The reaction of 1-hexene with the other monoorganylboranes was conducted with a large excess of the hydroborating reagent and short reaction times. Even under these conditions, we could obtain products of monohydroboration of 1-hexene with only n-$BuBH_2$ and $IpcBH_2$. After the first stage of hydroboration with 1 equiv of alkene, the dialkylborane was methanolyzed, the reaction mixture oxidized by alkaline H_2O_2 and the alcohol(s) formed analyzed by capillary GC (methylsilicone, 50 M) in the presence of an internal standard. After the second stage of hydroboration, the triorganylborane was directly oxidized with alkaline H_2O_2 and similarly examined. The second stage of hydroboration was estimated by the relation $2A - B$, where A represents the selectivity in percent obtained in the overall hydroboration and B represents the selectivity achieved in the first hydroboration. The results are summarized in Table X (see Experimental Section).

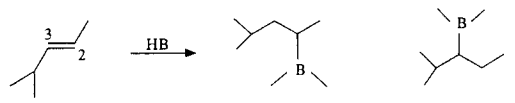
1-Hexene. Methylborane gives a C1/C2 distribution of alcohols in the first hydroboration of 1-hexene of 98.5:1.5 and an estimated selectivity of 100:0 in the second stage. This is comparable to the distribution realized in the hydroboration with chloroborane and bromoborane[30] but very different from the average distribution realized with thexylborane,[7a] 94:6. Similarly, n-$BuBH_2$ and $IpcBH_2$ show high positional selectivity in the first and second stages of the hydroboration of 1-hexene. Although the individual steps could not be determined for s-$BuBH_2$ and t-$BuBH_2$, the averaged distributions for these reagents are 97:3 and 98:2, respectively. These results are again very different from the values obtained for $ThxBH_2$.

***trans*-2-Hexene.** Very little selectivity is observed in either stage of hydroboration of this alkene. Strangely enough, $MeBH_2$ and n-$BuBH_2$, the least hindered of the monoorganylboranes investigated, give the best C2/C3 results in the second hydroboration step, 73:27 and 62:38, respectively. The reasons for this are not clear.

***trans*-4-Methyl-2-pentene.** The first hydroboration of *trans*-4-methyl-2-pentene with these monoorganylboranes proceeds with the same degree of indiscrimination as that obtained for the averaged value for borane, but the second hydroboration step, to a degree greater than that observed for styrene (vide infra), proceeds with very high positional selectivity. Thus, both t-$BuBH_2$ and $IpcBH_2$ achieve estimated values for C2/C3 of 100:0 in the second stage of hydroboration. The dramatic increase in positional selectivity in these cases can be accounted for in terms of the much higher steric requirements of the newly formed dialkylboranes derived from t-$BuBH_2$ or $IpcBH_2$ and 1 equiv of *trans*-4-methyl-2-pentene. The results are comparable to those of 9-BBN rather than borane (see listing below, where values in parentheses denote estimated positional selectivity for the second hydroboration step).

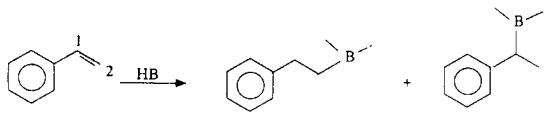
Styrene. In the first hydroboration of styrene with these monoorganylboranes, the positional selectivity, C2/C1, more closely resembles borane and is very different from that achieved by Sia_2BH or 9-BBN (see listing below,

(28) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 1241.
(29) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765.
(30) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1979**, *44*, 2417.
(31) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4708.
(32) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 1241.
(33) Brown, H. C.; Nelson, D. J.; Scouten, C. G. *J. Org. Chem.* **1983**, *48*, 641.



BH_3	57	43
Sia_2BH[32]	95	5
9-BBN[33]	93	7
$MeBH_2$	55 (97)	45 (3)
i-$PrBH_2$	53 (95)	47 (5)
n-$BuBH_2$	52 (94)	38 (6)
s-$BuBH_2$	53 (99)	47 (1)
t-$BuBH_2$	68 (100)	32 (0)
$IpcBH_2$	50 (100)	50 (0)

where values in parentheses are the estimated positional selectivity of the second hydroboration).



BH_3	81	19
Sia_2BH	98	2
9-BBN	98.5	1.5
$MeBH_2$	83 (87)	17 (13)
n-$BuBH_2$	86 (90)	14 (10)
s-$BuBH_2$	87 (91)	13 (9)
t-$BuBH_2$	88 (96)	12 (4)
i-$PrBH_2$	90 (94)	10 (6)
$IpcBH_2$	90 (94)	10 (6)

The regioselectivity of the second hydroboration is more profoundly influenced by the newly formed dialkylborane, R^1R^2BH. Being more sterically demanding, the positional selectivity of this hydroboration step should be much greater. Indeed, in the second hydroboration of styrene, there is a steady increase in selectivity from $MeBH_2$ to t-$BuBH_2$, with the latter reagent approaching values achieved with Sia_2BH.

Conclusions and Speculations

We have demonstrated that monoorganylboranes of different steric requirements $MeBH_2$, n-$BuBH_2$, i-$PrBH_2$, s-$BuBH_2$, and t-$BuBH_2$ all cleanly monohydroborate internal alkenes to yield mixed dialkylboranes, R^1R^2BH. $MeBH_2$ is the only monoorganylborane to date which can successfully hydroborate monosubstituted terminal alkenes such as 1-hexene. $ThxBH_2$, t-$BuBH_2$, and $MeBH_2$ cleanly monohydroborate 2-methyl-1-pentene. These results are summarized in Table XI.

In addition, we have discovered that t-$BuBH_2$, unlike $ThxBH_2$, is extraordinarily stable in THF, at both 0 °C and room temperature. No decomposition is evident as determined by hydride estimation, nor redistribution (^{11}B NMR), or isomerization as determined by oxidation and analysis by capillary GC. These attributes, together with the convenient syntheses we have developed and the relative inexpensiveness of the reagent, should make t-$BuBH_2$ an excellent and accessible hydroborating reagent.

The ability to cleanly monohydroborate a large variety of alkenes now makes mixed dialkylboranes R^1R^2BH readily available. These can in turn be used as new hydroborating agents or transformed into other useful organoborane intermediates such as borinic esters.

In addition, the reaction with a different alkene furnished the totally mixed trialkylboranes, $R^1R^2R^3B$, which can be converted into hitherto unavailable tertiary alcohols.

The ability to control hydroboration of alkenes with monoorganylboranes also suggests that new hydroborating reagents could be tailor-made to achieve high positional selectivity. For instance, in the hydroboration of *trans*-4-methyl-2-pentene with $IpcBH_2$,[24] boron is placed almost equally in both positions. This makes separation of the alcohols tedious.

On the other hand, Ipc_2BH does not give satisfactory optical induction with *trans*-alkenes.[8b] It should in theory be possible to reconcile these differences by constructing a molecule that will retain the high optical inductions realized in the hydroboration of *trans*-alkenes with $IpcBH_2$ and at the same time increase the positional selectivity of the hydroboration to enable the practical synthesis of alcohols. If this is achieved, a class of alkenes hitherto neglected due to low positional selectivity would be amenable to asymmetric hydroboration. With this in mind, we prepared the series listed in Table XII.

Thus, in the hydroboration of *trans*-4-methyl-2-pentene, simply replacing one hydride of $IpcBH_2$ by a methyl group increases the positional selectivity from 50:50 for $IpcBH_2$ to 85:15 for IpcMeBH. Further increase in the steric bulk of the alkyl group causes a steady increase of the selectivity until a maximum is reached with Ipc(*s*-Bu)BH, 95:5.

It will be of interest also in the future to see whether these and other new asymmetric hydroborating reagents will surpass the high asymmetric induction now realized with Ipc_2BH and $IpcBH_2$.

Experimental Section

All glassware, syringes, and needles were oven-dried at 150 °C prior to use. The glassware was assembled hot and cooled under a flow of nitrogen. A small positive pressure of nitrogen was maintained by using a mercury bubbler as a pressure relief valve. The syringes were fitted with needles while hot and then cooled under nitrogen.

Spectra. ^{11}B NMR spectra were obtained on a Varian FT-80A spectrometer (25.517 MHz) relative to BF_3·OEt_2. ^1H NMR spectra were obtained on a Varian T-60 instrument relative to TMS. ^{13}C NMR spectra were recorded on a Varian FT-80A spectrometer (20.000 MHz) relative to TMS. ^{27}Al NMR spectra were obtained on a Varian FT-80A spectrometer (20.725 MHz). IR spectra were recorded using a Perkin-Elmer 1420 ratio recording IR spectrometer. Mass spectra were obtained on a Finnigan Model 4000 gas chromatograph mass spectrometer.

GC Analysis. GC analyses of the alcohols were carried out on a Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The analysis was performed on a 50-m methylsilicone capillary column at appropriate temperatures.

Materials. Anhydrous diethyl ether (Mallinckrodt) and pentane (Phillips) were stored over 4-Å molecular sieves under nitrogen and used without further purification. THF was distilled from benzophenone ketyl and stored under nitrogen in an ampule. Borane–methyl sulfide (BMS), $LiAlH_4$ in diethyl ether (EE), MeLi in diethyl ether, *tert*-butylmagnesium chloride in diethyl ether, triisopropoxyborane, trimethoxyborane, 1,3-propanediol, and tetramethylethylenediamine were obtained from Aldrich Chemical Co. The alkenes were obtained from Aldrich Chemical Co. or Wiley Organics and were distilled from $LiAlH_4$ or used as received. Isopropyllithium was prepared by using the literature procedure.[34] Anhydrous ethereal hydrogen chloride (~3 M) was prepared using a Brown[□] apparatus from hydrochloric acid and sulfuric acid.[35] The solutions were standardized by hydrolyzing an aliquot with water and titrating with a standard solution of sodium hydroxide in the presence of phenolphthalein. Techniques for handling air-sensitive compounds have been previously described.[36]

Preparation of Lithium Monoorganylborohydrides in THF. The preparation of Li-t-$BuBH_3$ is representative.[16,38] A

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Table X. Product Distribution from the Hydroboration–Oxidation of Representative Alkenes with RBH_2 in THF in 1:1 and 2:1 Molar Ratio at 0 °C[a]

alkene	alcohol	product distribution,[b] % RR'BH	product distribution,[b] % RR'_2B	est regioselectivity for second hydroboration
		$MeBH_2$		
1-hexene	1-hexanol	98.5	99.5	100
		1.5	0.5	0
trans-2-hexene	2-hexanol	53	63	73
	3-hexanol	47	37	27
trans-4-methyl-2-pentene	4-methyl-2-pentanol	55	76	97
	2-methyl-3-pentanol	45	24	3
styrene	2-phenylethanol	83	85	87
	1-phenylethanol	17	15	13
		i-$PrBH_2$		
trans-2-hexene	2-hexanol		45	
	3-hexanol		55	
trans-4-methyl-2-pentene	4-methyl-2-pentanol	53	74	95
	2-methyl-3-pentanol	47	26	5
styrene	2-phenylethanol	90	92	94
	1-phenylethanol	10	8	6
		n-$BuBH_2$		
1-hexene	1-hexanol	96	97	98
	2-hexanol	4	3	2
trans-2-hexene	2-hexanol	44	53	98
	3-hexanol	56	47	2
trans-4-methyl-2-pentene	4-methyl-2-pentanol	62	78	94
	2-methyl-3-pentanol	38	22	6
styrene	2-phenylethanol	86	88	90
	1-phenylethanol	14	12	10
		s-$BuBH_2$		
1-hexene	1-hexanol		97	
	2-hexanol		13	
trans-2-hexene	2-hexanol	48	52	56
	3-hexanol	52	48	44
trans-4-methyl-2-pentene	4-methyl-2-pentanol	87	89	91
	2-methyl-3-pentanol	13	11	9
styrene	2-phenylethanol	53	76	99
	1-phenylethanol	47	24	1
		t-$BuBH_2$		
1-hexene	1-hexanol		98	
	2-hexanol		2	
trans-2-hexene	2-hexanol	47	53	59
	3-hexanol	53	47	41
trans-4-methyl-2-pentene	4-methyl-2-pentanol	68	84	100
	2-methyl-3-pentanol	32	16	0
styrene	2-phenylethanol	88	92	96
	1-phenylethanol	12	8	4
		$IpcBH_2$		
1-hexene	1-hexanol	98	98.5	99
	2-hexanol	2	1.5	1
trans-2-hexene	2-hexanol	43	49	55
	3-hexanol	57	51	45
trans-4-methyl-2-pentene	4-methyl-2-pentanol	50	75	100
	2-methyl-3-pentanol	50	25	0
styrene	2-phenylethanol	90	92	94
	1-phenylethanol	10	8	6

[a] Yields are all ≥95% based on an internal standard. [b] Reproducibility is ±1%. [c] Data are from ref 3.

Table XI. Steric Requirements for the Reaction of RBH_2 with Representative Alkenes in 1:1 Molar Ratio in THF at 0 °C

RBH_2	1-hexene	2-methyl-1-pentene	*trans*-2-hexene	cyclopentene	2-methyl-2-butene
$MeBH_2$[a]	1:1[b]	1:1	1:1	1:1	1:1
n-$BuBH_2$	>1:1	>1:1	1:1	1:1	1:1
i-$PrBH_2$	>1:1	>1:1	1:1	1:1	1:1
s-$BuBH_2$	>1:1	>1:1	1:1	1:1	1:1
$IpcBH_2$	>1:1	>1:1	1:1	1:1	1:1
t-$BuBH_2$	>1:1	1:1	1:1	1:1	1:1
$ThxBH_2$	>1:1	1:1			

[a] Data from ref 3. [b] Reaction temperature −25 °C.

500-mL round-bottom flask fitted with a sidearm and containing a stirring bar was charged with 2-*tert*-butyl-1,3,2-dioxaborinane (21.3 g, 150 mmol) and pentane (150 mL). The solution was cooled to 0 °C and $LiAlH_4$ in EE (150 mL of 1 M, 150 mmol) was added. During the addition, a heavy white precipitate was formed. The reaction mixture was stirred an additional 15 min at 0 °C, allowed to warm to room temperature, and filtered through a filter chamber under nitrogen pressure. The white precipitate was

Table XII. Regioselectivity in the Hydroboration of *trans*-4-Methyl-2-pentene with IpcRBH in a 1:1 Molar Ratio in THF at 0 °C

IpcRBH R	positional distribution of alcohols obtained after oxidation	
	4-methyl-2-pentanol	2-methyl-2-pentanol
H	50	50
Me	85	15
cyclopentyl	87	13
sec-butyl	95	5

washed with pentane (3 × 150 mL). ^{11}B NMR indicated the clean formation of Li-*t*-BuBH$_3$ (δ −21, q, J = 76 Hz. ^{27}Al NMR showed a trace amount of aluminum salts present, i.e., <1%. The solvents were removed in vacuo, and the solid, which crystallized, was dissolved in pentane to precipitate the residual aluminum salt. The latter was removed by centrifuging and transferring the clear supernatant solution to a calibrated ampule. The pentane was removed in vacuo as before. The solid was cooled to 0 °C, and the THF (~150 mL) was slowly added. (The solvation is exothermic and care should be taken.) The solution of Li-*t*-BuBH$_3$ in THF was standardized by hydrolyzing an accurate aliquot and measuring the amount of hydrogen liberated, yield 85–90%.

Preparation of Lithium Isopropylborohydride. This reagent was prepared from 2-isopropyl-1,3,2-dioxaborinane (19.2 g, 150 mmol) and LiAlH$_4$ (150 mmol) by using a procedure similar to the above, yield 82%; ^{11}B NMR δ −23.5 (q J = 73.3 Hz); IR ν_{max} (THF) 2168 (B–H) cm^{-1}.

Preparation of Lithium *n*-Butylborohydride.[16] The reagent was prepared from 2-*n*-butyl-1,3,2-dioxaborinane (18.3 g, 129 mmol) and LiAlH$_4$ (129 mmol) by using the standard procedure given above, yield 80%; ^{11}B NMR δ (THF)–29.2 (q, J = 76.0 Hz).

Preparation of Lithium *sec*-Butylborohydride.[16] With the standard procedure given above, the reagent weas prepared from 2-(2-butyl)-1,3,2-dioxaborinane (26.1 g, 184 mmol) and LiAlH$_4$ (184 mmol), yield 87%; ^{11}B NMR δ (THF)–25.8 (q, J = 75 Hz).

Improved Procedure for the Preparation of LiIpcBH$_3$ from (IpcBH$_2$)$_2$·TMEDA.[37] For small-scale reactions, we have found it more convenient to prepare IpcBH$_2$ from the lithium borohydride and HCl in EE rather than from 2IpcBH$_2$·TMED and BF$_3$·OEt$_2$. The 2IpcBH$_2$·TMED adduct (21.0 g, 50.4 mmol) was suspended in EE (100 mL). LiAlH$_4$ in EE (100 mL, 100 mmol) was added at room temperature. The reaction mixture was stirred for 1 h during which time the solid dissolved with the concomitant formation of a gel. All volatiles were removed under reduced pressure. The white solid was washed with pentane (2 × 200 mL) and filtered through a filter chamber. ^{27}A NMR indicated only traces of aluminum compounds present. The volatiles were removed under reduced pressure and the viscous solid was dissolved in THF (50 mL). Hydride estimation showed a yield of 95%. ^{11}B NMR δ (THF) − 23 (q, J = 76.6 Hz); IR ν_{max} (THF) 2164 (B–H) cm^{-1}.

Improved Procedure for the Preparation of Butylboronic Acid.[22] A 1-L flask fitted with a septum-capped sidearm and containign a magnetic stirrer was charged with trimethoxyborane (34 mL, 300 mmol). Diethyl ether (300 mL) was then added, and the flask cooled to −78 °C. *tert*-Butylmagnesium chloride in EE (150 mL, 300 mmol) was added dropwise while stirring, using a double-ended needle. After the addition was over, the reaction mixture was stirred for an additional 2 h at −78 °C and then warmed to room temperature. Aqueous HCl (excess) was then added and stirred for 1 h. The organic phase was separated, and the aqueous phase was extracted with EE (2 × 100 mL). The combined extracts were dried (MgSO$_4$), and the solvent was removed in vacuo to obtain *tert*-butylboronic acid, yield 50–75%.

Improved Procedure for the Preparation of 2-*tert*-Butyl-1,3,2-dioxaborinane.[22] *tert*-Butylboronic acid (20.4 g, 200 mmol) was added to a 500-mL round-bottom flask fitted with a septum-capped sidearm and containing a magnetic stirring bar. While this was stirring, pentane (200 mL) was added to the flask, followed by 1,3-propanediol (15 mL, 210 mmol). The solid boronic acid goes into solution within 10 min and the water separates. The pentane layer was separated and dried (MgSO$_4$), and the solvent removed in vacuo to obtain 2-*tert*-butyl-1,3,2-dioxaborinane (crude yield, quantitative) as a syrupy liquid, which was used as such for the preparation of Li-*t*-BuBH$_3$; ^{11}B NMR δ 32 (s).

Reaction of Alkenes with Monoorganylboranes in THF in a Molar Ratio of 1:1. LiRBH$_3$ in THF (5 mmol) was added to a 50-mL centrifuge tube capped with a rubber septum and containing a stirring bar. The solution was cooled to 0 °C, and ethereal HCl (5 mmol) was added. The reaction mixture was then maintained at the appropriate temperature (Tables II–XII), and the alkene (5.5 mmol) was added neat via syringe. After this stirred for the requisite time (Tables II–XIII), either methanol or ispropyl alcohol was added in excess, and the reaction mixture maintained at the reaction temperature until all evolution of hydrogen had ceased (~15–20 min). The reaction mixture was allowed to warm to room temperature, during which time LiCl precipitated out. This was either allowed to settle or centrifuged to obtain a clear supernatant. An aliquot was examined by ^{11}B NMR to determine product distribution by peak heights.

General Procedure for the Determination of Regioselectivity in the Hydroboration of Representative Alkenes by RBH$_2$ in Molar Ratios of 1:1 and 2:1. The hydroboration in a 1:1 or 2:1 molar ratio of alkene and RBH$_2$ was done as above, except that an internal standard was added prior to the addition of the alcohol. To the borinic ester was added NaOH (4.5 mL, 7.5 mmol), and the reaction was cooled to 0 °C, followed by the addition of H$_2$O$_2$ (30%, 1.7 mL). The reaction mixture was then heated to 50–60 °C for at least 2 h, anhydrous K$_2$CO$_3$ was added to the aqueous phase to near saturation, and the ether layer was separated and dried over MgSO$_4$. This was analyzed for alcohols by capillary GC (Table X).

Isolation of Borinic Esters Obtained from the Reaction of Alkenes with Monoorganylboranes in THF in a Molar Ratio of 1:1. The preparation of *tert*-butyl(2-methylbutyl)isopropoxyborane is typical. Li-*t*-BuH$_3$ in THF (14.3 mL, 15 mmol) was cooled to 0 °C, and ethereal HCl (4.7 mL, 15 mmol) was added. After the evolution of H$_2$ had ceased, 2-methyl-2-butene (1.62 mL, 15 mmol) was added via a syringe. The reaction was stirred for 10 min, quenched with isopropyl alcohol (2.3 mL, 30 mmol), and stirred until the evolution of H$_2$ had ceased (10 min). The THF was removed at reduced pressure (12 mmHg), and pentane was added. After the LiCl had settled, the clear supernatant was transferred to a distillation apparatus. The pentane was removed under vacuum (12 mmHg), and the product distilled, yield 2.53 g (12.76 mmol, 81%); bp 74–76 °C (14 mmHg); $n^{20}$$_D$ 1.4145; MS (chemical ionization, isobutene), m/z 199 (M$^+$ + H, 1.97), 157 (M$^+$ − C$_3$H$_6$, 48.7), 71 (C$_5$H$_{11}^+$, 100); MS (electron impact), m/z 182 (M$^+$ − CH$_4$, 0.2), 157 (M$^+$ − C$_3$H$_7$, 7.0), 71 (C$_5$H$_{11}^+$, 16.7), 57 (C$_4$H$_9^+$, 100), 43 (C$_3$H$_7^+$, 60.66); ^{11}B NMR δ (neat) 51.8 (s); IR ν_{max} (neat) 1320 (B–O) cm^{-1}.

Preparation of (*trans*-2-Methylcyclohexyl)-2-butylmethoxyborane. *s*-BuBH$_2$ was liberated from Li-*s*-BuBH$_3$ (12.7 mL, 15 mmol) by using HCl in EE (4.7 mL, 15 mmol) at 0 °C. 1-methylcyclohexene was added at 0 °C and stirred for 2 h. The reaction was quenched with methanol and worked up as above, yield 1.82 g, 62%; bp 104–106 °C (12 mmHg); ^{11}B NMR δ (neat) 54 (s); ^{1}H NMR δ (CDCl$_3$) 3.7 (s, 3 H); $n^{20}$$_D$ 1.4476; MS (chemical ionization, isobutene), m/z 197 (M$^+$ + H, 100), 97, (95.2); MS (electron impact), m/z 196 (M$^+$, <1), 139 (M$^+$ − C$_4$H$_9$, 46.5), 57 (C$_4$H$_9$, 100), 43 (C$_3$H$_7^+$, 98.6); IR ν_{max} (neat) 1363 (B–O) cm^{-1}.

Preparation of Isopropyl(*trans*-2-methylcyclopentyl)-isopropoxyborane. With the standard procedure given above, this compound was prepared from Li-*i*-PrBH$_3$ (13.6 mL, 20 mmol), HCl in EE (6.3 mL, 20 mmol), and 1-methylcyclopentene (2.43 mL, 22 mmol) at 0 °C, stirring for 10 min and quenching with excess isopropyl alcohol, yield 2.78 g (14.2 mmol, 71%); bp 88–90 °C (15 mmHg); $n^{20}$$_D$ 1.4275; ^{11}B NMR δ (neat) 53 (s); ^{1}H NMR δ (CDCl$_3$) 4.5 (septet, 1 H), 2.33, 1.68 (m, 7 H), 1.4–1.03 (m, 17 H); MS (chemical ionization, isobutene), m/z (%) 197 (M$^+$ + H, 35), 155 (29), 131 (320), 113 (8), 99 (41), 83 (C$_6$H$_{11}^+$, 100); MS (electron impact), m/z 83 (C$_6$H$_{11}^+$, 67), 69 (61), 61 (12), 55 (28), 43 (C$_6$H$_7^+$, 100).

Carbonylation–Oxidation of the Products Obtained from the Sequential Addition of Alkene A and Alkene B to a Solution of Monoorganylboranes in THF. The preparation of 2,2-dimethyl-3-cyclopentylnonan-3-ol is typical. In a 100-mL flask equipped with a septum-capped sidearm, magnetic stirring bar, and gas inlet adaptor was added Li-*t*-BuBH$_3$ in THF (14.3

mL, 15 mmol). The reaction was cooled to 0 °C and treated with HCl in EE (4.7 mL, 15 mmol). The reaction was cooled to 0 °C and treated with HCl in EE (4.7 mL, 15 mmol). Cyclopentene (1.32 mL, 15 mmol) was then added, and the reaction stirred for 5 min, followed by the addition of 1-hexene (1.88 mL, 15 mmol). The reaction was stirred for 20 min. ^{11}B NMR at this point showed a single peak at δ +83. The lithium chloride was allowed to settle, and the clear supernatant decanted via a double-ended needle into a nitrogen-flushed Paar "mini" reactor. The remaining solid LiCl was washed with THF (2 × 5 mL) and added to the pressure reactor along with ethylene glycol (1.25 mL, 22.5 mmol). The Paar reactor was sealed and pressurized to 1000 psi with CO and heated to 150 °C for 36 h. After cooling and carefully venting the reactor, the contents were transferred to a 100-mL flask fitted with a septum-capped sidearm and a reflux condenser and containing a magnetic stirring bar. The ^{11}B NMR of the mixture showed a singlet at δ +35, indicating a clean formation of the boronic ester. Ethanol (5 mL) was added as cosolvent, and NaOH solution 5.5 mL, 33 mmol) was added, followed by careful dropwise addition of H_2O_2 (30%, 5.5 mL). The reaction mixture was heated to 50–60 °C for at least 2 h to ensure complete oxidation. K_2CO_3 was added to the aqueous fraction to near saturation, and the organic layer separated. The aqueous portion was extracted with pentane. The combined organic fractions were dried ($MgSO_4$), and the solvents removed in vacuo (12 mmHg) to obtain the crude alcohol. This material was purified by medium-pressure liquid chromatography (MPLC) using an FMI pump and E Merck prepacked silica columns (Lobar, 40–63 μm) and eluting with a hexane–ether mixture (97:3), yield 2.59 g (10.8 mmol, 72%). This material was pure by capillary GC. ^{13}C NMR δ ($CDCl_3$) 78.37, 46.7, 39.6, 35.22, 31.92, 30.71, 29.05, 28.94, 26.92, 25.77, 25.58, 25.34, 22.77, 14.07; n^{20}_D 1.4697; IR ν_{max} (neat) 3523 (O–H) cm^{-1}.

Preparation of 5-Isopinocampheyldodecan-5-ol. *n*-$BuBH_2$ was liberated from Li-*n*-$BuBH_3$ (23.8 mL, 10 mmol) by using HCl in EE (10 mmol), and α-pinene (1.6 mL, 10 mmol) was hydroborated by using this at 0 °C (reaction time 20 min). 1-Hexene (1.25 mL, 10 mmol) was added to this mixture at 0 °C and stirred for 20 min. ^{11}B NMR (δ 82.4) showed the clean formation of a trialkylborane, which was carbonylated and oxidized by using the representative procedure given above, yield 2.55 g (8.2 mmol, 82%); n^{20}_D 1.4808; IR ν_{max} (neat) cm^{-1}: 3473 (O-H) cm^{-1}; ^{13}C NMR δ ($CDCl_3$) 77.30, 49.34, 42.71, 41.67, 38.86, 37.39, 37.04, 36.66, 36.15, 35.81, 32.11, 31.92, 30.32, 2..16, 27.94, 26.40, 25.12, 24, 24.12, 23.91, 23.66, 23.55, 22.93, 14.31; MS (chemical ionization, isobutene), *m/z* 291 ($M^+ + H - H_2O$, 100), 263 (58), 137 (28), 123 (12), 109 (3); MS (electron impact), *m/z* 291 (67), 263 (21), 235 (24), 171 (100), 143 (32), 137 (44), 123 (24), 109 (10), 95 (23), 81 (37), 69 (54), 55 (66), 41 (63).

Preparation of 2,2-Dimethyl-5-(3-hexyl)nonan-5-ol. *trans*-3-Hexene (1.24 mL, 10 mmol) was hydroborated by *n*-$BuBH_2$ liberated from Li-*n*-$BuBH_3$ (23.8 mL, 10 mmol) by using HCl in EE (2.92 mL, 10 mmol) at 0 °C in THF (reaction time 50 min). The dialkylborane formed was used to hydroborate 3,3-dimethyl-1-butene (1.29 mL, 10 mmol) at 0 °C (40 min). The reaction mixture was carbonylated and oxidized by using the standard procedure to yield 1.84 g (7.1 mmol, 71%) of the alcohol; n^{20}_D 1.4828; IR ν_{max} (neat) 3487 (OH) cm^{-1}; ^{13}C NMR δ ($CDCl_3$) 77.2, 47.18, 37.28, 36.84, 32.53, 31.46, 30.39, 29.61, 25.80, 23.14, 22.97, 14.97, 14.34, 14.07; MS (chemical ionization, isobutene), *m/z* 239 ($M^+ + H - H_2O$, 100), 155 (11), 141 (7), 127 (5), 113 (4), 99 (3), 85 (2), 71 (1); MS (electron impact), *m/z* 239 (100), 199 (11), 171 (39), 155 (18), 141 (12), 127 (10), 113 (9), 97 (9), 85 (12), 69 (14), 57 (45), 43 (37).

Preparation of 3-Cyclopentyl-2-methyldodecan-3-ol. *i*-$PrBH_2$ was liberated from Li-*i*-$PrBH_3$ in THF (10 mL, 6.8 mmol) by using HCl in EE (2.0 mL, 6.8 mmol) and was used to hydroborate cyclopentene (0.6 mL, 6.8 mmol) (reaction time, 10 min) at 0 °C. The dialkylborane thus formed was used to hydroborate 1-nonene (1.17 mL, 6.8 mmol) and the reaction mixture was carbonylated–oxidized by using standard procedure, yield of alcohol 1.45 g (5.4 mmol, 79%); n^{21}_D 1.4707; IR ν_{max} (neat) 3488 (OH) cm^{-1}; ^{13}C NMR δ ($CDCl_3$) 76.96, 46.63, 36.31, 36.14, 32.1, 31.06, 29.79, 29.51, 27.28, 26.68, 25.75, 25.63, 24.59, 22.83, 18.17, 17.81, 14.21; MS (chemical ionization), *m/z* 252 (17), 251 ($M^+ + H - H_2O$, 100); MS (electron impact), *m/z* 252 (10), 251 ($M^+ + H - H_2O$, 100), 225 (17), 199 (15), 193 (5), 181 (2), 169 (5), 155 (4), 141 (33), 123 (22), 111 (16), 97 (24), 81 (23), 69 (30), 55 (24), 43 (82).

Acknowledgment. We thank the National Science Foundation (Grant CHE 79-18881) and the Lady Davis Fellowship Foundation from the Hebrew University of Jerusalem for financial support, which made this study possible.

Registry No. Li-*t*-$BuBH_3$, 76826-51-2; $\overline{OB(t\text{-}Bu)O(CH_2)_2CH_2}$, 63689-73-6; $LiAlH_4$, 16853-85-3; Li-*i*-$PrBH_3$, 84280-38-6; $\overline{Pr)O(CH_2)_2CH_2}$, 62930-27-2; Li-*n*-$BuBH_3$, 82111-98-6; $\overline{OB(n\text{-}Bu)O(CH_2)_2CH_2}$, 30169-71-2; Li-*s*-$BuBH_3$, 84280-33-1; $\overline{OB(s\text{-}Bu)O(CH_2)_2CH_2}$, 30169-72-3; LiIpc$BH_3$, 94062-97-2; (Ipc$BH_2$)$_2$·TMEDA, 67826-92-0; $B(OMe)_3$, 121-43-7; *t*-BuGmCl, 677-22-5; $HO(CH_2)_3OH$, 62930-27-2; *t*-$BuB(OH)_2$, 86253-12-5; $MeBH_2$, 12538-96-4; *i*-$PrBH_2$, 17643-29-7; *n*-$BuBH_2$, 44210-73-3; *s*-$BuBH_2$, 44149-91-9; *t*-$BuBH_2$, 43795-48-8; IpcBH_2, 64234-27-1; *t*-$BuBH_2$·THF, 84470-68-8; IpcBH_2·THF, 123569-93-7; *n*-$BuB(OMe)_2$, 2117-94-4; *n*-BuB(OMe)(1-hexyl), 123568-63-8; *n*-BuB(OMe)(3,3-dimethyl-1-butyl), 123568-64-9; *n*-BuB(OMe)(3,3-dimethyl-2-butyl), 123568-65-0; *n*-BuB(OMe)(2-methyl-1-pentyl), 123568-66-1; *n*-BuB(OMe)(2-ethyl-1-butyl), 123568-67-2; *n*-BuB(OMe)(2,3-dimethyl-1-butyl), 123568-68-3; *n*-BuB(OMe)(2-phenylethyl), 123568-69-4; *n*-BuB(OMe)(1-phenylethyl), 123568-70-7; *n*-BuB(OMe)(2-hexyl), 123568-71-8; *n*-BuB(OMe)(3-hexyl), 123568-72-9; *n*-BuB(OMe)(4-methyl-2-pentyl), 123568-73-0; *n*-BuB(OMe)(2-methyl-3-pentyl), 123568-74-1; *n*-BuB(OMe)(cyclopentyl), 123593-25-9; *n*-BuB(OMe)(2-methyl-1-cyclopentyl), 123568-75-2; *n*-BuB(OMe)(cyclohexyl), 123568-76-3; *n*-BuB(OMe)(2-methyl-1-cyclohexyl), 123568-77-4; *n*-BuB(1-hexyl)$_2$, 123568-78-5; *n*-BuB(2-methyl-1-pentyl)$_2$, 123568-79-6; *n*-BuB(2-ethyl-1-butyl)$_2$, 123568-80-9; *n*-BuB(2,3-dimethyl-1-butyl)$_2$, 123568-81-0; *i*-PrB$(OMe)_2$, 95093-89-3; *i*-PrB(OMe)(1-hexyl), 123568-82-1; *i*-PrB(OMe)(3,3-dimethyl-1-butyl), 123568-83-2; *i*-PrB(OMe)(3,3-dimethyl-2-butyl), 123568-84-3; *i*-PrB(OMe)(2-methyl-1-pentyl), 123568-85-4; *i*-PrB(OMe)(2,3-dimethyl-1-butyl), 123568-86-5; *i*-PrB(OMe)(2-phenylethyl), 123568-87-6; *i*-PrB(OMe)(1-phenylethyl), 123568-88-7; *i*-PrB(OMe)(2-hexyl), 123568-89-8; *i*-PrB(OMe)(3-hexyl), 123568-90-1; *i*-PrB(OMe)(4-methyl-2-pentyl), 123568-91-2; *i*-PrB(OMe)(4-methyl-3-pentyl), 123568-92-3; *i*-PrB(OMe)(cyclopentyl), 123568-93-4; *i*-PrB(OMe)(2-methylcyclopentyl), 123568-94-5; *i*-PrB(OMe)(Ipc), 123568-95-6; *i*-PrB(1-hexyl)$_2$, 123568-96-7; *i*-PrB(3,3-dimethyl-1-butyl)$_2$, 123568-97-8; *i*-PrB(3,3-dimethyl-2-butyl)$_2$, 123593-26-0; *i*-PrB(3,3-dimethyl-1-butyl)(3,3-dimethyl-2-butyl), 123568-98-9; *i*-PrB(2-methyl-1-pentyl)$_2$, 123568-99-0; *i*-PrB(2,3-dimethyl-1-butyl)$_2$, 123569-00-6; *s*-BuB$(OMe)_2$, 41156-58-5; *s*-BuB(OMe)(3-methyl-1-butyl), 123569-01-7; *s*-BuB(OMe)(2-methyl-1-pentyl), 123569-02-8; *s*-BuB(OMe)(2,3-dimethyl-1-butyl), 123569-03-9; *s*-BuB(OMe)(2-phenylethyl), 123569-04-0; *s*-BuB(OMe)(1-phenylethyl), 123569-05-1; *s*-BuB(OMe)(2-hexyl), 123593-27-1; *s*-BuB(OMe)(3-hexyl), 123593-28-2; *s*-BuB(OMe)(4-methyl-2-pentyl), 123569-06-2; *s*-BuB(OMe)(2-methyl-3-pentyl), 123569-07-3; *s*-BuB(OMe)(3-methyl-2-butyl), 123569-08-4; *s*-BuB(OMe)(cyclopentyl), 123593-29-3; *s*-BuB(OMe)(2-methyl-1-cyclopentyl), 123569-09-5; *s*-BuB(OMe)(cyclohexyl), 123569-10-8; *s*-BuB(OMe)(2-methyl-1-cyclohexyl), 123569-11-9; *s*-BuB(OMe)(Ipc), 123569-12-0; *s*-BuB(3-methyl-1-butyl)$_2$, 123569-13-1; *s*-BuB(3-methyl-2-butyl)$_2$, 90791-96-1; *s*-BuB(3-methyl-1-butyl)(3-methyl-2-butyl), 123569-14-2; *s*-BuB(2-methyl-1-pentyl)$_2$, 123593-30-6; *s*-BuB(2,3-dimethyl-1-butyl)$_2$, 123569-15-3; *s*-BuB(cyclopentyl)$_2$, 123593-31-7; *t*-BuB$(OMe)_2$, 37490-36-1; *t*-BuB(OMe)(1-hexyl), 123569-16-4; *t*-BuB(OMe)(2-methyl-1-pentyl), 123569-17-5; *t*-BuB(OMe)(2-phenylethyl), 123569-18-6; *t*-BuB(OMe)(1-phenylethyl), 123569-19-7; *t*-BuB(OMe)(2-hexyl), 123569-20-0; *t*-BuB(OMe)(3-hexyl), 123569-21-1; *t*-BuB(OMe)(4-methyl-2-pentyl), 123569-22-2; *t*-BuB(OMe)(2-methyl-3-pentyl), 123569-23-3; *t*-BuB(OMe)(cyclopentyl), 123569-24-4; *t*-BuB(OMe)(3-methyl-2-butyl), 123569-25-5; *t*-BuB(OMe)(Ipc), 123593-32-8; *t*-BuB(1-hexyl)$_2$, 32327-54-1; Ipc$B(OMe)_2$, 68165-34-4; IpcB(OMe)(1-hexyl), 123569-26-6; IpcB(OMe)(2-methyl-1-pentyl), 123569-27-7; IpcB(OMe)(2-hexyl), 123569-28-8; IpcB(OMe)(3-hexyl), 123569-29-9; IpcB(OMe)(4-methyl-2-pentyl), 123569-30-2;

IpcB(OMe)(2-methyl-3-pentyl), 123569-31-3; IpcB(OMe)(3-methyl-2-butyl), 123593-33-9; IpcB(OMe)(cyclopentyl), 123569-32-4; IpcB(2-methyl-1-pentyl)$_2$, 123569-33-5; *i*-PrB(OPr-*i*)(2-methylcyclohexyl), 123569-34-6; *t*-BuB(OPr-*i*)(3-methyl-2-butyl), 123569-35-7; $CH_3CH_2CH{=}CHCH_2CH_3$, 592-47-2; $CH_2{=}CH(CH_2)_6CH_3$, 124-11-8; BuB(3,3-dimethyl-1-butyl)(3-hexyl), 123593-34-0; IpcB(*n*-Bu)(1-hexyl), 123569-36-8; *t*-BuB(cyclopentyl)(1-nonyl), 123569-37-9; *n*-BuB(cyclopentyl)(1-hexyl), 123569-38-0; *n*-BuC(OH)(3,3-dimethyl-1-butyl)(3-hexyl) isomer I, 123569-39-1; *n*-BuC(OH)(3,3-dimethyl-1-butyl)(3-hexyl) isomer II, 123569-91-5; IpcC(OH)(*n*-Bu)(1-hexyl) isomer I, 123569-40-4; IpcC(OH)(*n*-Bu)(1-hexyl) isomer II, 123569-92-6; *t*-BuC(OH)(cyclopentyl)(1-nonyl), 123569-41-5; *n*-BuC(OH)(cyclopentyl)(1-hexyl), 123569-42-6; IpcMeBH, 123569-43-7; Ipc(cyclopentyl)BH, 123569-44-8; Ipc(*s*-Bu)BH, 123569-45-9; *i*-PrBH(4-methyl-2-pentyl), 123569-46-0; *i*-PrBH(2-methyl-3-pentyl), 123569-47-1; *i*-PrBH(2-phenylethyl), 123569-48-2; *i*-PrBH(1-phenylethyl), 123569-49-3; *i*-PrB(2-hexyl)$_2$, 123569-53-9; *i*-PrB(3-hexyl)$_2$, 123569-54-0; *i*-PrB(4-methyl-2-pentyl)$_2$, 123569-55-1; *i*-PrB(2-methyl-3-pentyl)$_2$, 123569-56-2; *i*-PrB(4-methyl-2-pentyl)(2-methyl-3-pentyl), 123569-57-3; *i*-PrB(2-phenylethyl)$_2$, 123569-58-4; *i*-PrB(1-phenylethyl)$_2$, 123569-59-5; *i*-PrB(2-phenylethyl)(1-phenylethyl), 123569-60-8; *n*-BuBH(1-hexyl), 123569-50-6; *n*-BuBH(2-hexyl), 123569-51-7; *n*-BuBH(3-hexyl), 123569-52-8; *n*-BuB(2-hexyl)$_2$, 123569-61-9; *n*-BuB(3-hexyl)$_2$, 123569-62-0; *n*-BuB(4-methyl-2-pentyl)$_2$, 123569-63-1; *n*-BuB(2-methyl-3-pentyl)$_2$, 123569-64-2; *n*-BuB(4-methyl-2-pentyl)(2-methyl-3-pentyl), 123569-65-3; *n*-BuB(2-phenylethyl)$_2$, 123569-66-4; *n*-BuB(1-phenylethyl)$_2$, 123569-67-5; *n*-BuB(2-phenylethyl)(1-phenylethyl), 123569-68-6; *n*-BuBH(4-methyl-2-pentyl), 123569-94-8; *n*-BuBH(2-methyl-3-pentyl), 123569-95-9; *n*-BuBH(2-phenylethyl), 123569-96-0; *n*-BuBH(1-phenylethyl), 123569-97-1; *s*-BuBH(2-hexyl), 123569-98-2; *s*-BuBH(1-hexyl), 123569-99-3; *s*-BuBH(4-methyl-2-pentyl), 123570-00-3; *s*-BuBH(2-methyl-3-pentyl), 123570-01-4; *s*-BuBH(2-phenylethyl), 123570-02-5; *s*-BuBH(1-phenylethyl), 123570-03-6; *s*-BuB(1-hexyl)$_2$, 123569-69-7; *s*-BuB(2-hexyl)$_2$, 123569-70-0; *s*-BuB(3-hexyl)$_2$, 123569-71-1; *s*-BuB(2-hexyl)(3-hexyl), 123569-72-2; *s*-BuB(4-methyl-2-pentyl)$_2$, 123569-73-3; *s*-BuB(2-methyl-3-pentyl)$_2$, 123569-74-4; *s*-BuB(4-methyl-2-pentyl)(2-methyl-3-pentyl), 123569-75-5; *s*-BuB(2-phenylethyl)$_2$, 123569-76-6; *s*-BuB(1-phenylethyl)$_2$, 123569-77-7; *t*-BuBH(2-hexyl), 123570-04-7; *t*-BuBH(3-hexyl), 123570-05-8; *t*-BuBH(4-methyl-2-pentyl), 123570-06-9; *t*-BuBH(2-methyl-3-pentyl), 123570-07-0; *t*-BuBH(2-phenylethyl), 123570-08-1; *t*-BuBH(1-phenylethyl), 123570-09-2; *t*-BuB(2-hexyl)$_2$, 123569-78-8; *t*-BuB(3-hexyl)$_2$, 123569-79-9; *t*-BuB(2-hexyl)(3-hexyl), 123569-80-2; *t*-BuB(4-methyl-2-pentyl)$_2$, 123569-81-3; *t*-BuB(2-methyl-3-pentyl)$_2$, 123569-82-4; *t*-BuB(2-phenylethyl)$_2$, 123569-83-5; *t*-BuB(1-phenylethyl)$_2$, 123569-84-6; IpcBH(1-hexyl), 123570-10-5; IpcBH(2-hexyl), 123570-11-6; IpcBH(3-hexyl), 123570-12-7; IpcBH(4-methyl-2-pentyl), 123570-13-8; IpcBH(2-methyl-3-pentyl), 123570-14-9; IpcBH(2-phenylethyl), 123570-15-0; IpcBH(1-phenylethyl), 123570-16-1; IpcB(1-hexyl)$_2$, 123569-85-7; IpcB(2-hexyl)$_2$, 123569-86-8; IpcB(3-hexyl)$_2$, 123569-87-9; IpcB(2-hexyl)(3-hexyl), 123569-88-0; IpcB(4-methyl-2-pentyl)$_2$, 123569-89-1; IpcB(2-methyl-3-pentyl)$_2$, 123569-90-4; IpcB(2-phenylethyl)$_2$, 123593-35-1; IpcB(1-phenylethyl)$_2$, 123593-36-2; IpcB(2-phenylethyl)(1-phenylethyl), 123593-37-3; $MeBH_2{\cdot}SMe_2$, 84470-72-4; $t\text{-}BuBH_2{\cdot}SMe_2$, 84280-41-1; 1-hexene, 592-41-6; 3,3-dimethyl-1-butene, 558-37-2; 2-methyl-1-pentene, 763-29-1; 2-ethyl-1-butene, 760-21-4; 2,3-dimethyl-1-butene, 563-78-0; styrene, 100-42-5; *trans*-2-hexene, 4050-45-7; *trans*-4-methyl-2-pentene, 674-76-0; cyclopentene, 142-29-0; 1-methylcyclopentene, 693-89-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; α-pinene, 80-56-8; 3-methyl-1-butene, 563-45-1; 2-methyl-2-butene, 513-35-9; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; 3-hexanol, 623-37-0; 4-methyl-2-pentanol, 108-11-2; 2-methyl-3-pentanol, 565-67-3; 2-phenylethanol, 60-12-8; 1-phenylethanol, 98-85-1.

Supplementary Material Available: Mass, IR, and ^{13}C NMR spectra for selected compounds (25 pages). Ordering information is given on any current masthead page.

Trispiro[2.1.2.1.2.1]dodecane-4,8,12-trione and Other Oligomers of Carbonylcyclopropane. The Organozinc Route

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Received February 21, 1989

1-Bromocyclopropanecarboxylic acid (**8**) and its chloride (**9**) were prepared from γ-butyrolactone on a 20–100-g scale. Dehalogenation of **9** with zinc–copper couple in acetonitrile gave not only the known dispiro[2.1.2.1]octane-4,8-dione (**3**) but also the aesthetically pleasing title compound **10** and 6-cyclopropylidene-5-oxaspiro[2.3]hexan-4-one (**11**) as well as tetracyclic α-alkylidene-γ-butyrolactone **12**, i.e., 3-(oxodispiro[2.1.2.1]octan-4-ylidene)tetrahydro-2-furanone. "Zinc carbon enolate" **13a** is considered to be an important intermediate en route to **10** in solvent acetonitrile. The X-ray crystal structure of **10** shows the molecule to be nearly planar with very short distal cyclopropane carbon–carbon bonds [1.437 (4)–1.452 (4) Å].

Carbonylcyclopropane (other names, dimethyleneketene or cyclopropylidenemethanone) (**2**) is a reactive ketene that has been generated by Brown and his co-workers when they submitted the spiroannulated Meldrum acid **1** to flash vapor thermolysis (FVT).[1a] Carbonylcyclopropane has

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‖ X-ray analysis of **10**.
⊥ X-ray analysis of **12**.

(1) (a) Baxter, G. J.; Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. *Tetrahedron Lett.* **1975**, 4283. (b) Brown, R. F. C. *Chem. Brit.* **1987**, 1189. See also: Brown, R. F. C. *Chem. Brit.* **1988**, 770. (c) See also: Ripoll, J. L. *Tetrahedron* **1977**, *33*, 389. Bock, H.; Hirabayashi, T.; Mohmand, S. *Chem. Ber.* **1981**, *114*, 2595.

0022-3263/89/1954-6096$01.50/0