# Hydroboration. XXXVII. Structural Study of the Hydroboration of Olefins with Thexylborane in the Molar Ratio of 1:1. A Convenient Synthesis of Thexylmonoalkylboranes and Their Ready Conversion to Monoalkylboranes[1]

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Abstract: Twelve representative olefins were hydroborated with thexylborane in the molar ratio of 1:1, and the products were examined by residual hydride analysis, ir, GLC analysis of olefins, and GLC and ^{1}H NMR analyses of the methanolysis products. The GLC-^{1}H NMR examination provides a convenient means of analyzing mixtures of mono- and dimethoxyorganoboranes. In all cases examined, the methoxy protons of monomethoxydialkylboranes appear downfield (δ 3.7–3.96 ppm) relative to those of dimethoxymonoalkylboranes (δ 3.5–3.65 ppm). The reaction of monosubstituted terminal olefins, such as 1-pentene, with thexylborane produces preferentially thexyldi-*n*-pentylborane. On the other hand, thexylmonoalkylboranes can be prepared in excellent yields ($\geq$ 90%) from a wide variety of olefins, such as isobutylene, 2-methyl-1-pentene, *cis*-2-butene, cyclopentene, cyclohexene, norbornene, and 1-methylcyclopentene. In most cases, it is desirable to maintain the temperature of the reaction mixture at ca. −25° to minimize dehydroboration of tetramethylethylene (TME). The yields of thexylmonoalkylboranes from 1-methylcyclohexene and α-pinene are 80 and <75%, respectively. Complete dehydroboration of tetramethylethylene can be achieved by treating thexylmonoalkylboranes with a fourfold excess of triethylamine. This reaction provides the basis for a new general synthesis of the monoalkylboranes as the triethylaminates. The monoalkylborane-triethylamine complexes obtained are readily converted to alkylboronates on alcoholysis or to mixed trialkylboranes RR'$_2$B on reaction with appropriate olefins. The reaction of TME with thexylborane in the ratio of 1:1 produces a mixture consisting largely of 1,1,2-trithexyldiborane. However, the reaction of TME with borane in the ratio of 16:1 produces in 95% yield dithexylborane, exhibiting a characteristic ir band at 2470 cm^{-1} (ν_{B-D} 1820 cm^{-1}) and existing as the unassociated monomer. Methoxydithexylborane can be prepared from dithexylborane and isolated by distillation (85% yield). Thexylmonoalkylboranes exhibit ir bands at 2470 and 1570–1540 cm^{-1}. The ratio of these two bands increases in the following order: isobutylene < cyclopentene < 2-butene < 1-methylcyclopentene < norbornene < 2-methyl-2-butene. The results suggest that the thexylmonoalkylboranes exist as the monomer–dimer equilibrium mixture.

Organoboranes have become one of the most significant classes of organometallics in organic synthesis.[3] Successful applications of the organoboranes to organic synthesis often hinge on the availability of organoboranes with definite structures. Simple hydroboration of olefins with borane is satisfactory, in the majority of cases, for the preparation of trialkylboranes containing three identical alkyl groups, R$_3$B.[4] On the other hand, the synthesis of "mixed" organoboranes often requires more elaborate procedures. Recently, various applications of thexylborane[5] (2,3-dimethyl-2-butylborane) derivatives, as readily available "mixed" organoboranes, to organic synthesis have been demonstrated.[6] These synthetic possibilities have made it highly desirable to be able to synthesize thexylmonoalkylboranes (1) in high yields and in high purities. Indeed, in certain reactions utilizing the thexylmonoalkylboranes (1), the yields of organic products were sometimes low, and these appeared to be attributable to the low yields of 1.

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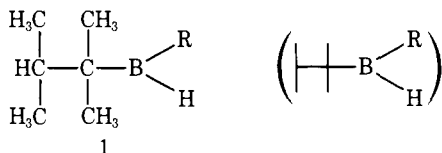
In our earlier study[5c] of the hydroboration of olefins with thexylborane, a representative series of olefins was reacted with the stoichiometric amount of thexylborane (olefin: thexylborane = 2:1), and the rates and directive effects in these reactions were established. However, the structures of the organoborane products were not investigated. Accordingly, we decided to investigate the hydroboration of olefins with thexylborane in the molar ratio of 1:1 with the following objectives: (1) to establish the precise nature of the

products obtained by the hydroboration of olefins with thexylborane in the molar ratio of 1:1; (2) to clarify the course of the hydroboration reaction; and finally, (3) to define reaction conditions to produce thexylmonoalkylboranes cleanly and quantitatively.

Results and Discussion

Methods of Analyses. Combination of GLC and ^{1}H NMR Examinations of *B*-Methoxyboranes. Twelve representative olefins were selected for the present study. Each olefin was hydroborated with an equimolar quantity of thexylborane (0.5 M in olefin and thexylborane), and the reaction was followed by analysis for residual olefin. At the completion of the olefin uptake, the reaction mixture was examined by GLC analysis (SE-30, 2 ft) of the methanolysis product[7] and ^{1}H NMR analysis of the THF-free methanolysis product. More routine examinations utilizing residual hydride analysis and ir and GLC analysis (CW-20M or adiponitrile) for tetramethylethylene (TME) were also performed. We have found that the combination of GLC and ^{1}H NMR examinations provides a simple means of examining the methanolyzed hydroboration mixtures. The GLC examination of the methanolysis product readily permits us to identify dimethoxyalkylboranes and monomethoxydialkylboranes derived from symmetrically substituted dialkylboranes using authentic samples prepared by the previously reported procedures.[5a,8] It also permits a qualitative analysis of methoxythexylmonoalkylboranes which, in most cases, eluted satisfactorily. The ^{1}H NMR examination of the methanolysis product, after evaporation of THF and methanol [25° (15 mm), 1–2 hr], provides a convenient means of determining the quantities of monomethoxy and dimethoxyboranes. In all cases examined, the methoxy pro-

Table I. Reaction of Monosubstituted Terminal Olefins with Thexylborane or Triethylamine–Thexylborane in the Molar Ratio of 1:1 (10 mmol Scale)

Olefin	Hydro-borating agent[a]	Temp, °C	Time, hr	TME,[b] mmol	Residual olefin,[b] mmol	$\vdash\!\!\vdash$—BH$_2$,[c] mmol	$\vdash\!\!\vdash$—BHR,[c] mmol	$\vdash\!\!\vdash$—BR$_2$,[c] mmol
1-Pentene	A	0	1	Trace	0	3.8 (4.0)[d]	2.4 (2.0)[d]	(3.7)[d]
	A	−25	1	0	0	(4.5)[d]	(0.7)[d]	(4.6)[d]
	B	0	0.25		0	(4.9)[d]	(0.3)[d]	(4.8)[d]
3,3-Dimethyl-1-butene	A	0	1	0.3	0	3.0	4.3	[2.7][e]
	A	−25	1	Trace	Trace	2.4	5.2	[2.4][e]
Styrene	A	0	1	0.4	0	2.2	5.2	[2.2][e]
	A	−25	1	Trace	Trace	2.0	6.1	[1.9][e]

[a] A = thexylborane. B = triethylamine–thexylborane. [b] By GLC on a CW-20M or adiponitrile column. [c] By GLC (SE-30) and ^{1}H NMR examinations of the methanolysis product. [d] Numbers in parentheses are based on the results of carbonylation experiments after the addition of 10 mmol of 1-hexene. [e] Numbers in brackets are based on the material balance.

tons of monomethoxydialkylboranes appear downfield (δ 3.7–3.96 ppm) relative to those of dimethoxymonoalkylboranes (δ 3.5–3.65 ppm). It also permits us to identify methoxythexylmonoalkylboranes whenever these are formed as essentially single products in nearly quantitative yields. Thus, without isolating methoxythexylmonoalkylboranes, their identity and quantities can be conveniently determined.
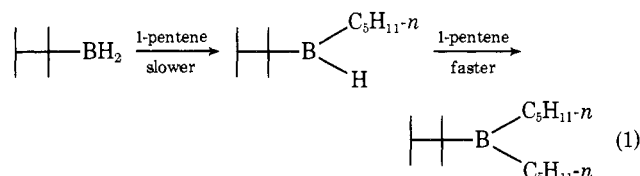
Monosubstituted Terminal Olefins. As representative monosubstituted terminal olefins, 1-pentene, 3,3-dimethyl-1-pentene, and styrene were selected. The hydroboration of these olefins with thexylborane were carried out as described above. The experimental results with these olefins are summarized in Table I.

As shown in Table I, the hydroboration of 10.0 mmol of 1-pentene with 10.0 mmol of thexylborane produces only 2.4 mmol of thexyl-n-pentylborane, with 3.8 mmol of thexylborane remaining unreacted. Since the hydroboration of 1-pentene is complete, and since no dehydroboration of tetramethylethylene has taken place, the fate of the remaining 3.8 mmol of thexylborane must be accounted for by the formation of thexyldi-n-pentylborane. In order to clarify this point, 10.0 mmol of 1-hexene was added to the hydroboration mixture, and the product was carbonylated at 150° and 1000 psi in the presence of ethylene glycol.[9] GLC examination (SE-30 or CW-20M) of the carbonylated mixture indicated the presence of 4.0 mmol of **2**, 2.0 mmol of **3**, and 3.7 mmol of **4**.

2   **3**   **4**
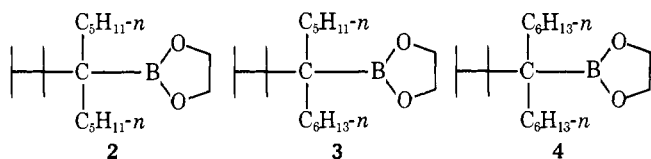
The formation of thexyldi-n-pentylborane can be accounted for either by the competitive hydroboration of 1-pentene with thexyl-n-pentylborane or by the disproportionation of thexyl-n-pentylborane. This last hypothesis was ruled out on the basis of the following two observations: (1) the reaction mixture obtained by adding 1 equiv of 1-pentene to 1 equiv of thexylborane at 0° did not show any change (by ir) when maintained for 72 hr at 25° followed by 1 hr at 65°; (2) in lowering the hydroboration temperature to −25°, the product of the same experiment consisted of 45% of thexylborane, only 7% of thexyl-n-pentylborane, and 46% of thexyldi-n-pentylborane. Clearly, the results support the following mechanism in which thexyl-n-pentylborane favorably competes with thexylborane for 1-pentene (eq 1).

Attempts to apply thexylborane–aminates were unsuccessful. Neither trimethylamine–thexylborane[4a] nor pyridine–thexylborane reacted with 1-pentene at a measurable rate at 25°. On the other hand, triethylamine–thexylborane


(1)

reacted smoothly even at 0°. However, the product contained only 3% of the desired thexyl-n-pentylborane.

Results with 3,3-dimethyl-1-pentene and styrene are more favorable. However, no clean formation of the corresponding thexylmonoalkylboranes was achieved.

Disubstituted Terminal and Internal Olefins. In, marked contrast with monosubstituted terminal olefins, disubstituted olefins (either terminal or internal) react with thexylborane in the molar ratio of 1:1 to produce predominantly the corresponding thexylmonoalkylboranes. The experimental results with these olefins are summarized in Table II.

In all of the cases examined, no more than trace quantities of thexylborane were detected as dimethoxythexylborane. When the reaction was carried out at 0°, dehydroboration of tetramethylethylene (TME) took place to the extent of 5–25%. Moreover, the amount of TME roughly corresponded to that of the monoalkylborane derived from the olefin used. These results strongly suggest the following reaction path (eq 2).

(2)
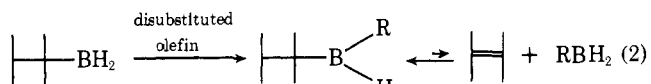
Fortunately, we discovered that the dehydroboration could be essentially prevented by maintaining the temperature of hydroboration at −25°. At this temperature, all of the disubstituted olefins examined can be converted to the corresponding thexylmonoalkylboranes as essentially single products.
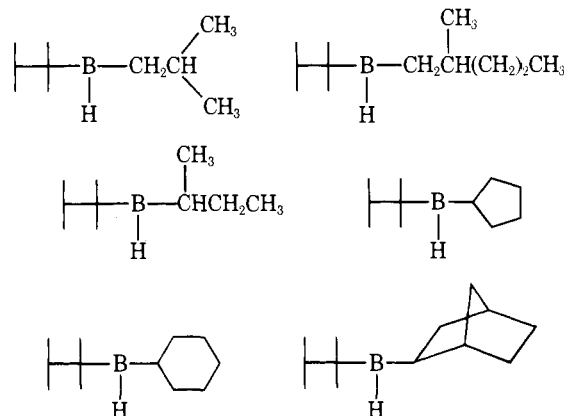
Trisubstituted Olefins. The more reactive of the trisubstituted olefins, such as 2-methyl-2-butene and 1-methylcyclo-

Table II. Reaction of Disubstituted Olefins with Thexylborane in the Molar Ratio of 1 : 1 (10 mmol Scale)[a]

| Olefin	Temp, °C	TME,[b] mmol	Residual olefin,[b] mmol	$\vdash\!\!\!-BH_2$,[c] mmol	RBH_2,[c] mmol	$\vdash\!\!\!-BHR$,[c] mmol
Isobutylene	0	0.5	0	0	0.6	9.2
	−25	<0.1	0	0	0.1	9.5
2-Methyl-	0	0.8	0	0	0.7	8.7
1-pentene	−25	0.1	0	0		9.3
cis-2-	0	1.8	0	0	1.6	8.0
Butene	−25	0.2	Trace	0	0.7	9.2
Cyclo-	0	0.8	0	0	1.2	8.8
pentene	−25	<0.1	Trace	0	0.3	9.3
Cyclo-	0	2.5	0	0	2.8	7.1
hexene	−25	0.6	Trace		0.5	9.1
Norbornene	0	0.7	Trace	0	2.3	7.7
	−25	<0.1	Trace	0	0.7	9.2

[a] At 1 hr, the reaction mixture was quenched with methanol. [b] By GLC analyses (CW-20M or adiponitrile). [c] By GLC (SE-30) and [1]H .NMR examinations of the methanolysis product. The alkyl group (R) corresponds to the olefin used.

Table III. Reaction of 2-Methyl-2-butene and 1-Methylcyclopentene with Thexylborane in the Molar Ratio of 1:1 (10 mmol Scale)[a]

Olefin	Temp, °C	TME,[b] mmol	Residual olefin,[b] mmol	$\vdash\!\!\!-BH_2$,[c] mmol	RBH_2,[c] mmol	$\vdash\!\!\!-BHR$,[c] mmol
2-Methyl-2-	0	1.5	Trace			
butene	−25	0.7	0.5	Trace	0.2	9.1
1-Methyl-	0	2.1	Trace			
cyclopentene	−25	0.5	0.3	Trace	0.6	8.8

[a-c] See the corresponding footnotes of Table II.

pentene, can be hydroborated with thexylborane in the molar ratio of 1:1 at −25° to form the corresponding thexylmonoalkylboranes in ∼90% yields (Table III).

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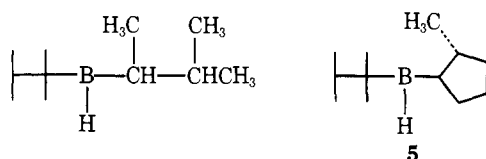
That the dehydroboration involves an equilibrium reaction was demonstrated with 1-methylcyclopentene. At 0° its hydroboration with thexylborane was followed with time. The results are summarized in Table IV. Significantly, at no time is the reaction mixture as clean as that obtained at −25°.

With the less reactive of the trisubstituted olefins, such as 1-methylcyclohexene and α-pinene, the rate of hydroboration is quite slow, requiring ∼24 hr to reach a plateau of 93–94% completion at −25°. The dehydroboration process competes with the hydroboration reaction even at −25°. The experimental results are summarized in Table V. The GLC-^{1}H NMR examination of the methanolyzed product derived from 1-methylcyclohexene at 24 hr indicates that thexyl(2-methylcyclohexyl)borane is formed in 80% yield. The yield of thexylisopinocampheylborane was not determined. However, it cannot exceed 75% based on the GLC analysis of TME and the residual α-pinene.

Reaction of Thexylmonoalkylboranes with Triethylamine. A New Synthesis of Monoalkylboranes. If the reaction path outlined in eq 2 is indeed operative, a mere shift of the equilibrium should provide a simple route to monoalkylboranes. Thexyl(2-methylcyclopentyl)borane (5) was therefore selected for exploratory experiments because of the relatively high amount (21%) of TME dehydroborated during its preparation at 0°. In order to avoid any side reactions, 5 was prepared at −20° and then, after warming up to 0°, aspirator vacuum was applied for 1 hr. Analysis of the trapped materials by GLC revealed the presence of 6% of TME. Further evaporation at 0° (0.3 mm Hg) for another hour resulted in an additional 19% of TME. Although

Table IV. Reaction of 1-Methylcyclopentene with Thexylborane at 0° in the Molar Ratio of 1:1 (10 mmol Scale)

Time, min	TME, mmol	1-Methylcyclopentene, mmol
1	Trace	1.6
5	0.4	1.3
15	0.8	0.9
30	1.3	0.4
60	2.3	Trace
1440	3.0	0
2880	2.7	0
4320	2.7	0

Table V. Reaction of 1-Methylcyclohexene and α-Pinene with Thexylborane at −25° in the Molar Ratio of 1:1 (10 mmol Scale)

Olefin	Time, hr	TME,[a] mmol	Residual olefin,[a] mmol	Residual hydride, mmol
1-Methylcyclohexene	3	Trace	4.8	16.2
	18	1.1	0.6	11.8
	24	1.2	0.7	11.8
α-Pinene	1	Trace	6.8	
	2.5	0.5	4.4	
	6	1.2	2.7	
	20	1.6		
	24	2.5	0.7	

[a] By GLC analysis (CW-20M or adiponitrile).

dehydroboration occurred to some extent, it was felt that this procedure was not sufficiently promising to justify investigation in greater detail.

Another possible means of shifting the equilibrium is selective complexation of the monoalkylborane. To this end 2.5 mmol of 5 were treated with 2.5 mmol of pyridine at 0°. The reaction was conveniently followed by ir. Within 1 hr, free pyridine and all free B–H species had disappeared. Analysis of an aliquot after methanolysis indicated the presence of only 11% of TME. After 5 days at room temperature, the increase in dehydroboration was only 2%. Clearly, pyridine quenches the entire reaction mixture by coordinating with 5. However, when triethylamine was added to a THF solution of 5, a rapid dehydroboration occurred with formation of TME.

Table VI. Reaction of Thexyl(*trans*-2-methylcyclopentyl)borane with Triethylamine

Time,	TME dehydroborated, %		
hr	Reaction ratio: 1:1	1:2	1:4
0.25	75	88	
0.5	75	84	94
1	78	84	98
3		86	98

ranes, RR'_2B, by this procedure is quite simple, opening a convenient new route to tertiary alcohols. The complete experimental results are summarized in Table VII.

Dithexylborane. A Monomeric Dialkylborane. It has been previously established that the hydroboration of tetramethylethylene (TME) with borane in the molar ratio of 1:1 produces thexylborane as the dimer[4a] (eq 4). We also studied the reaction in the molar ratio of 3:1 (TME:borane) in diglyme.[5b] At 25°, 1.78 mol of TME was consumed per mole

Table VII. Preparation and Characterization of Triethylamine–Monoalkylboranes[a]

	Triethylamine–monoalkylborane[b]		Dimethyl alkaneboronate[e]			
Olefin	Alcohol,[c,d] mmol	TME dehydroborated,[c] mmol	Yield, % GLC	Isolated	Bp, °C (mm Hg)	$n^{20}D$
trans-3-Hexene	10.0	9.5	96	75	52–53 (15)	1.407
2-Methyl-1-pentene	9.3	8.8	90	70	56–57 (15)	1.409
Cyclopentene	9.6	10.0	98			
Cyclohexene	9.8	10.0	95	77	75–76 (17)[f]	1.437
2-Methyl-2-butene	9.5	9.5			[g]	
1-Methylcyclopentene	9.7	9.8	93	80	60–61 (15)	1.429

[a] Prepared by the reaction of 10 mmol of thexylmonoalkylborane and 40 mmol of triethylamine. [b] All exhibit a strong, broad ir absorption centered at ca. 2350 cm⁻¹ and satisfactory ¹H NMR spectra. The GLC yield of triethylamine 100–105%. [c] By GLC. [d] Alcohol corresponds to the olefin used. Less than 0.5 mmol of 2,3-dimethyl-2-butanol and less than 0.1 mmol of 2,3-dimethyl-1-butanol observed except with 2-methyl-1-pentene. In the case of 2-methyl-1-pentene, 1.0 mmol of 2,3-dimethyl-2-butanol observed. [e] Satisfactory ¹H NMR and ir data obtained. On oxidation, the corresponding alcohol was obtained in 100 ± 5% yields. [f] Triethylamine–cyclopentylborane was identified by conversion in 70% yield to 2-(cyclopentyldi-*n*-penthylcarbinyl)-2-bora-1,3-dioxolane, bp 127–128° (0.7 mm); $n^{20}D$ 1.4675. [g] Triethylamine–(3-methyl-2-butyl)borane was identified by conversion in 72% yield to 2-[(3'-methyl-2'-butyl)dicyclopentylcarbinyl]-2-bora-1,3-dioxolane, bp 130–131° (0.8 mm); $n^{20}D$ 1.4996.

By using 100% excess of triethylamine, 84% of TME was recovered within 1 hr at 25°. This value went up to 94% after 21 hr. Addition of 4 equiv of triethylamine achieved complete TME dehydroboration *without* the concurrent formation of 1-methylcyclopentene within 1 hr at 25°. The results are summarized in Table VI.

Alkaline hydrogen peroxide oxidation of the hydrolyzed reaction mixture provided *trans*-2-methylcyclopentanol in 97% yield. Evaporation of the volatile substances produced triethylamine-(2-methylcyclopentyl)borane in quantitative yield. Clearly the present synthesis is exceedingly simple and convenient. It was successfully extended to other thexylmonoalkylboranes. The experimental results are summarized in Table VII.

The triethylamine–monoalkylboranes (**6**) function as monoalkylboranes in disguise. They can be readily methanolyzed with 100% excess methanol. A quantitative amount of hydrogen is generated within 30 min at 25°, thus indicating the presence of 2 equiv of hydride per boron. GLC analysis reveals the presence of the corresponding dimethyl alkylboronates (**7**) as the sole products (eq 3). Unlike free

$$RBH_2 \cdot NEt_3 \xrightarrow[25°]{CH_3OH} 2H_2 + RB(OCH_3)_2 + NEt_3 \quad (3)$$
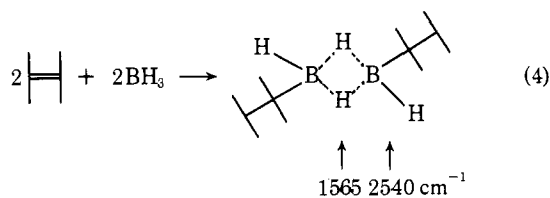
6   **7**
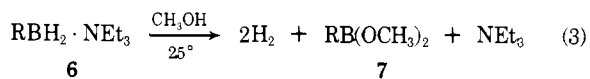
monoalkylboranes,[8d] triethylamine–monoalkylboranes appear quite stable to disproportionation. A sample of **6** (R = 2-methylcyclopentyl) did not show any sign of disproportionation for at least a week at room temperature. In sharp contrast with the trimethylamine or pyridine complexes, which show very little tendency to hydroborate at room temperature, triethylamine–monoalkylboranes react with olefins at reasonable rates at 25° (Table VIII).

Addition of boron trifluoride etherate to a THF solution of triethylamine-(2-methylcyclopentyl)borane does not appear to generate the free borane since little or no acceleration of the reaction was observed (Table IX). However, in hexane solvent, addition of boron trifluoride etherate does appear to generate free monoalkylboranes, at least as an intermediate. Nearly 90% of 1-octene was taken up within 30 min at 25° (Table IX). The synthesis of mixed trialkylbo-

$$2 \mathord{\Vert} + 2BH_3 \longrightarrow$$

(structure of dithexylborane dimer)

↑ ↑
1565 2540 cm⁻¹

(4)

of borane in 24 hr. It has not been established whether the reaction could be pushed further. With the hope of synthesizing dithexylborane, we decided to investigate the reaction in more detail. First, the reaction was carried out in the molar ratio (TME:borane) of 1.5:1, 2:1, and 4:1 and followed by analysis for residual hydride with time and GLC examination of the oxidation products (Table X). The re-

Table VIII. Hydroboration of 1-Octene with Triethylamine–*trans*-2-Methylcyclopentylborane at 25° in the Molar Ratio of 2:1

Time, hr	1-Octene consumed, %
0	0
0.5	49
1	58
2	71
3	79
6	86
21	90

Table IX. Hydroboration of 1-Octene with Triethylamine–*trans*-2-Methylcyclopentylborane at 25° in the Molar Ratio of 2:1 in the Presence of Boron Trifluoride Etherate

Time, hr	1-Octene consumed, %	
	In THF	In hexane
0	0	0
0.25	43	72
0.5	46	86
1	55	85
3	72	88
6	82	88
18	85	88

Table X. Reaction of Tetramethylethylene with Borane in THF at 25°[a]

| | TME:BH$_3$ | | | | | | | | |
| | 1.5:1 | | | 2:1 | | | 4:1 | | |
Time, hr	TA,[b] mmol	I,[b] mmol	Residual hydride, mmol	TA,[b] mmol	I,[b] mmol	Residual hydride, mmol	TA,[b] mmol	I,[b] mmol	Residual hydride, mmol
0	0	0	300	0	0	300	0	0	300
1	107	Trace	192	123	Trace	167			145
24	125	Trace	165	145	3	151	181	4	107
48	124	4	166	142	8	146	174	11	
72	126	6	162				171	18	107
96				128	15	151			
120	122	13	163						

[a]The scale and concentration were 100 mmol and 1.0 M in borane, respectively. [b]TA = thexyl alcohol; I = 2,3-dimethyl-1-butanol.

sults clearly indicate that the reaction involves an equilibrium. Moreover, it is further complicated by a relatively fast isomerization of the 2,3-dimethyl-2-butyl group. The amount of the 2,3-dimethyl-1-butyl group in the product is not negligible beyond 24 hr at 25°.

When the thexyl to boron ratio in the product is 3:2 (reactant ratio, 2:1), the ir features are basically the same as those of 1,2-dithexyldiborane, except that the intensity of the 2540 cm^{-1} band has diminished, and a very minor band appears at 2470 cm^{-1}. No noticeable change in intensity of the 1565 cm^{-1} band is observed (Figure 1). These observations indicate that the product exists essentially as 1,1,2-trithexyldiborane (eq 5).

$$ \text{[structure]} + \text{[structure]} \rightleftharpoons \text{[structure]} \quad (5) $$
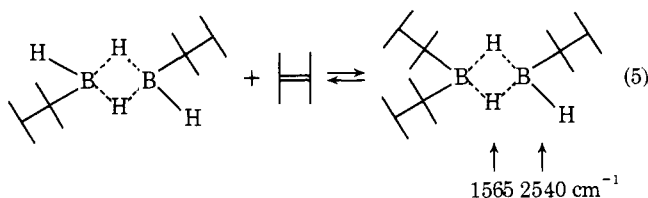
1565 2540 cm^{-1}

A dramatic change in ir spectra takes place as the reaction proceeds beyond the formation of 1,1,2-trithexyldiborane. The two original bands at 1565 and 2540 cm^{-1} diminish, and the minor band at 2470 cm^{-1} increases. When the ratio of TME to borane is 16:1, the ir spectrum of the reaction mixture (0.5 M in B) at 3 hr and 25° shows only the 2470 cm^{-1} band in the 2600–2400 cm^{-1} region, and practically no absorption is observed in the 1600–1500 cm^{-1} region (Figure 1). The amount of residual hydride corresponds to the formation of a dialkylborane (active hydride: B = 1.01), and GLC examination of the oxidation product indicates the formation of 1.96 mol of thexyl alcohol[10] per mole of borane. These observations are consistent only with the formation of monomeric dithexylborane (eq 6).

$$ \text{[structure]} + \text{[structure]} \rightleftharpoons \text{[structure]} \;\;B\!-\!H \quad (6) $$

2470 cm^{-1}
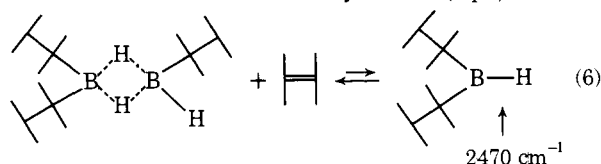
Treatment of the 16:1 reaction mixture with a 100% excess of methanol followed by evaporation of the volatile substances at 25° (0.5 mm) provides ~95% pure[11] methoxydithexylborane in 95% yield, purified by distillation (85% yield by isolation).

The assignment of the band at 2470 cm^{-1} was further confirmed by treating tetramethylethylene with deuterioborane (BD$_3$) in THF to produce the deuterium analogs of 1,2-dithexyldiborane (8) and dithexylborane (9) and observing the infrared shifts produced by the introduction of the deuterium atoms. The shift from 2540 cm^{-1} for the terminal B–H stretching to 1870 cm^{-1} for the corresponding B–D stretching is in agreement with the predicted effect of
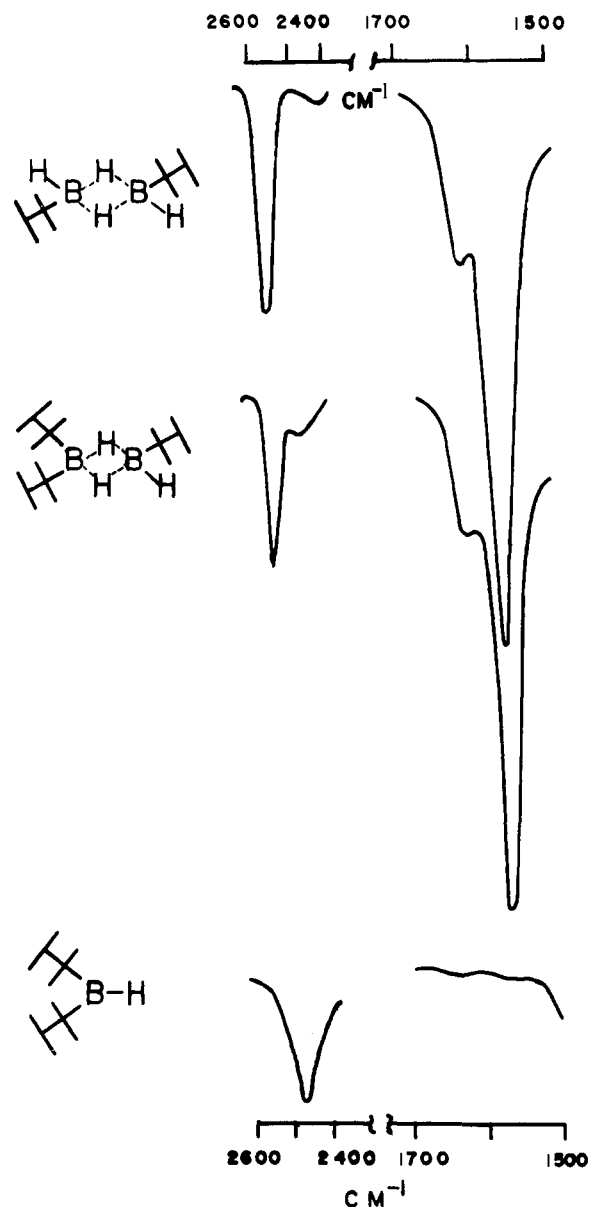

Figure 1. Infrared spectra of dithexyldiborane, trithexyldiborane, and dithexylborane.

the heavier isotope.[12] The similar shift, from 2470 cm^{-1} for dithexylborane to 1820 cm^{-1} for the corresponding deuterium derivative 6 supports the assignment of these absorptions to the stretching frequencies for the monomeric species. The monomeric nature of dithexylborane was further established by ^{11}B NMR, which exhibits a doublet centered at 81.3 ppm (J = 110 Hz) downfield relative to boron trifluoride etherate.

$$1150 \quad 1870 \, cm^{-1}$$
8

$$1820 \, cm^{-1}$$
9
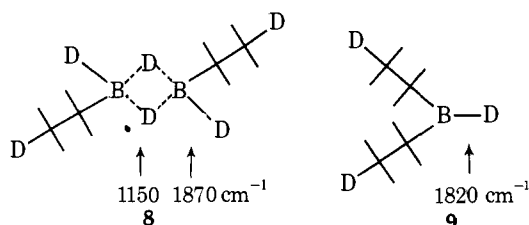
That dithexylborane exists as an unassociated monomer rather than the THF complex was established by its synthesis in the absence of THF. The reaction of TME with performed neat dithexyldiborane in the 30:1 molar ratio (TME:B = 16:1) produced slowly (24 hr) at 25° dithexylborane which exhibits the same ir features in the 2600–2400 and 1600–1500 cm^{-1} regions as the sample prepared in THF. The molecular weight of the product in TME, determined by osmometry, was 185, in excellent agreement with the theoretical value 182 for the monomer.

All dialkylboranes studied previously exist as the dimers, i.e., as the tetraalkyldiboranes, either under neat conditions or in various solvents, such as cyclohexane and tetrahydrofuran. Thus, pure dialkylboranes, such as dimethylborane,[12] di-n-butylborane,[13] diisobutylborane,[13] disiamylborane,[5a] dicyclohexylborane,[5a] bis(2-methylcyclohexyl)borane,[5a] diisopinocampheylborane,[5a] borinane,[14a] 3,5-dimethylborinane,[14b] and 9-borabicyclo[3.3.1]nonane,[15] all exhibit the strong absorption characteristic of the B–H–B stretching in the 1600–1500 cm^{-1} region and no absorption characteristic of the terminal B–H stretching in the 2600–2400 cm^{-1} region.[16] Thus, this study represents the first identification of a monomeric dialkylborane. Interestingly, examination of the ir spectra of the thexylmonoalkylboranes described in the present study reveals the presence of the ir band at 2470 cm^{-1} attributable to monomeric dialkylboranes in varying intensities. The ratio of intensities of the band at 2470 cm^{-1} to that in the 1600–1500 cm^{-1} region increases in the following order and seems to correlate with the steric requirements of olefins: isobutylene < cyclopentene < 2-butene < 1-methylcyclopentene < 1-methylcyclopentene < norbornene < 2-methyl-2-butene. These results strongly suggest that these thexylmonoalkylboranes exist as the monomer–dimer equilibria (eq 7), and that the large steric requirements of the two alkyl groups are primarily responsible for the existence of such monomeric dialkylboranes.
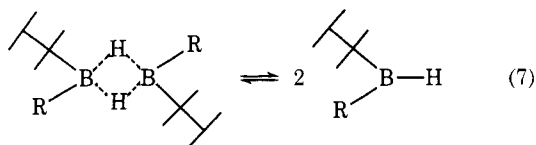
$$\rightleftharpoons 2 \qquad (7)$$

ments of the two alkyl groups are primarily responsible for the existence of such monomeric dialkylboranes.

Experimental Section

The organoboranes were always handled under nitrogen. ^{1}H NMR, ^{11}B NMR, and ir spectra were obtained with a Varian T-60, a Varian XL-100, and a Perkin-Elmer 700, respectively.

Materials. The preparation of borane[17] and thexylborane[18] in THF were carried out as described previously. Commercially available olefins, straight-chain hydrocarbons (internal standards), methanol, and trialkylamines were used without additional purification after checking the purities.

Reaction of Olefins with Thexylborane at 0° in the Molar Ratio of 1:1. The following procedure is representative. In a 50-ml flask, equipped with a septum inlet and a condenser connected to a mercury bubbler, was added 5.75 ml (10 mmol) of a 1.74 M solution of thexylborane in THF. To this was added, at 0°, 14.25 ml of a THF solution containing 10 mmol of cyclopentene and 5 mmol of n-decane. A 1-ml aliquot was hydrolyzed at 1 hr with a 1:1:1 mixture of water, glycerol, and THF, and the amount of hydrogen evolved was measured. Another 1-ml aliquot (0.5 mmol) was methanolyzed with 1 mmol (0.04 ml) of methanol and analyzed for

TME and the residual olefin on a 6-ft CW-20M (or an adiponitrile) column. GLC examination of the same mixture carried out on a 2-ft SE-30 indicated the absence of dimethoxythexylborane.[19] A major peak and a minor peak were observed. The minor peak was identified as dimethoxycyclopentylborane.[19] The major peak was tentatively assigned to methoxythexylcyclopentylborane. A third 5-mmol aliquot was methanolyzed (0.4 ml, 10 mmol), evaporated under diminished pressure [25° (15–20 mm)], and examined by ^{1}H NMR after adding 0.22 ml (2.5 mmol) of benzene as an internal standard. This established the amounts of methoxythexylcyclopentylborane and dimethoxycyclopentylborane. The methoxy protons of most of the methoxythexylmonoalkylboranes prepared in the present study appeared in the 3.7–3.8 ppm region. Methoxydithexylborane exhibits a peak at 3.96 ppm for the methoxy protons. The methoxy protons of the dimethoxyalkylboranes described in the present study appeared in the 3.5–3.65 ppm region. The final identification of methoxythexylcyclopentylborane is described in the following experiment. An aliquot of the hydroboration mixture was also examined by ir. A strong broad band appeared at 1540 cm^{-1}. A weak band at 2540 cm^{-1} and a weak but somewhat stronger band at 2470 cm^{-1} were observed in the 2600–2400 cm^{-1} region. The experimental results of the hydroboration of olefins with thexylborane at 0° are summarized in Tables I–IV.

Reaction of Olefins with Thexylborane at −25° in the Molar Ratio of 1:1. The experiments were carried out in a manner similar to the one described above. A commercially available low-temperature bath (Neslab, Inc.) was used to maintain the reaction temperature at −25°. In the favorable cases, neat samples of methoxythexylalkylboranes were prepared in the absence of an internal standard and identified by ^{1}H NMR examination. The experimental results are summarized in Tables I–IV.

The case of methoxythexylcyclopentylborane is representative: ^{1}H NMR (CCl$_4$, Me$_4$Si) δ 0.76 (t, J = 4 Hz, 12 H), 1.3–2.0 (singlet-like m, 10 H), 3.75 (s, 3 H) ppm.

Carbonylation of the Product Obtained by the Hydroboration of 1-Pentene with Thexylborane Followed by the Addition of 1-Hexene. To a 10-mmol hydroboration mixture derived from 1-pentene and thexylborane as described above was added 1-hexene (1.25 ml, 10 mmol) at 0° (or −25°). The reaction mixture was stirred for 1 hr at this temperature and then for 2–3 hr at 25°. After the addition of 1.8 ml (30 mmol) of ethylene glycol, the reaction mixture was carbonylated as described previously.[6g] The carbonylated products were analyzed by GLC on a SE-30. In each case, at least three peaks were observed in the expected region. Two were identified as 2[19] and 4.[19] A peak between those for 2 and 4 was assigned to 3. The GLC response factor of 3 was assumed to be the arithmetic mean of those of 2 and 4.

Preparation of Trimethylamine–Thexylborane. The compound was prepared by the procedure described previously.[5a]

Preparation of Pyridine–Thexylborane. To 28.3 ml (50 mmol) of 1.77 M thexylborane in THF was added, at 0°, 4.0 ml (50 mmol) of pyridine. Evaporation of the volatile compounds produced an orange solid. After recrystallization from pentane, a colorless solid was obtained: mp 38–39°; ir (Nujol) 2330 (s) and 1620 (s) cm^{-1}; ^{1}H NMR (CCl$_4$, Me$_4$Si); δ 0.53 (s, 6 H), 0.83 (d, J = 6 Hz, 6 H), 1.1–1.6 (m, 1 H), 7.35–7.75 (triplet-like m, 2 H), 7.81–8.18 (doublet-like m, 1 H), and 8.45–8.65 ppm (doublet-like m, 2 H).

Anal. Calcd for C$_{11}$H$_{20}$BN: C, 74.59; H, 11.38; B, 6.11; N, 7.91. Found: C, 74.40; H, 11.36; B, 6.01; N, 8.00. The compound appeared to be quite insensitive to air and moisture.

Preparation of Triethylamine–Thexylborane. To 10 mmol of thexylborane (5.75 ml of 1.74 M solution) was added 20 mmol of triethylamine. The ir spectrum of the product exhibited a strong broad band at 2400–2380 cm^{-1}. The bands at 2540 and 1565 cm^{-1} attributable to free thexylborane were virtually absent. When the ratio of triethylamine to thexylborane was 1.5, the bands at 2540 and 1565 cm^{-1} were present in addition to the band at 2400–2380 cm^{-1}.

Hydroboration of Olefins with Trialkylamine–Thexylborane. The reaction of 1-octene with either trimethylamine–thexylborane or pyridine–thexylborane did not take place to any measurable extent in 1 hr at 25°. Hydroboration of 1-octene with triethylamine–thexylborane in the molar ratio of 1:1 at 0° was fast and over in 15 min. The reaction in the molar ratio of 2:1 at 0° required 30 min for completion. Based on these results, 10 mmol of 1-pentene was

reacted with 10 mmol of triethylamine-thexylborane for 15 min at 0°. To this was added 10 mmol of 1-hexene. After stirring for 30 min at 0°, the reaction mixture was carbonylated as described above and analyzed by GLC (SE-30).

Attempted Synthesis of *trans*-2-Methylcyclopentylborane by the Dehydroboration of Tetramethylethylene from Thexyl(*trans*-2-methylpentyl)borane under Reduced Pressure. Evaporation of a solution containing 100 mmol of **5** was carried out at 0° (~15 mm) for 1 hr. GLC examination of the trapped material (in 150 ml of THF in a Dry Ice trap) indicated the presence of 6 mmol of TME. The pressure was lowered to 0.3 mmHg and maintained an additional hour. The amount of TME dehydroborated had increased to 25 mmol. The residue was quenched at 0° with 16 ml (400 mmol) of methanol. GLC examination of the mixture on a 2 ft × 0.125 in. 10% SE-30 indicated the presence of 15 mmol of *trans*-2-methylcyclopentylborane (decane was used as internal standard). It was found that a small amount of bis(2-methylcyclopentyl)borane was also formed. As pointed out in the Discussion, no further attempts were made.

Reaction of Thexyl(2-methylcyclopentyl)borane with Pyridine. To a 5-ml aliquot of 0.5 *M* thexyl(2-methylcyclopentyl)borane (2.5 mmol) prepared at −25° was added 0.2 ml (2.5 mmol) of pyridine at 0°. After stirring for 1 hr, ir examination of a 0.4-ml aliquot indicated the disappearance of bands at 1580 cm⁻¹ for pyridine and at 1550 cm⁻¹ for thexyl(2-methylcyclopentyl)borane. A broad band at 2340 cm⁻¹ and a sharp band at 1620 cm⁻¹ indicated the formation of pyridine–alkylborane complexes. GLC examination on a CW-20M of an aliquot after methanolysis (using 100% excess of dry methanol) revealed that 11% of TME had been dehydroborated. The cooling bath was removed, and the temperature of the mixture was allowed to rise to 25°. Even after 5 days of standing at 25°, the amount of TME dehydroborated was only 13%. The 5-day-old reaction mixture was then refluxed for 1 hr. The amount of TME increased to only 19%. When a 0.5-mmol aliquot of the refluxed mixture was hydrolyzed with a 1:1 mixture of water and glycerol, 0.48 mmol of active hydride was evolved within 15 min at 25°.

Reaction of Thexylmonoalkylborane with Triethylamine. The following experiment is representative. To 11.3 ml (20 mmol) of 1.77 *M* thexylborane in THF was added, at −25°, 2.1 ml (20 mmol) of 1-methylcyclopentene. After stirring the mixture for 1 hr at −25°, 2.8 ml (20 mmol), 5.6 ml (40 mmol), or 11.2 ml (80 mmol) of triethylamine was added at −25°. The temperature of the mixture was raised to 25°, and the reaction was followed by GLC analysis (CW-20M) of TME. The results are summarized in Table VII.

Preparation of Triethylamine–Monoalkylboranes. The following preparation of triethylamine-*trans*-2-methylcyclopentylborane is representative. The preparation of 20 mmol of thexyl(2-methylcyclopentyl)borane was carried out as described above. To this was added 11.2 ml (80 mmol) of triethylamine at −25°. The temperature of the mixture was raised to 25°, and the mixture was stirred for 1 hr. For most purposes, this reaction mixture was directly used as described later. Evaporation of the volatile substances at 15 mm for 2 hr produced triethylamine-*trans*-2-methylcyclopentylborane: ¹H NMR (benzene, Me₄Si) δ 0.86 (t, *J* = 7 Hz, 9 H), 1.28 (d, *J* = 6 Hz, 3 H), 1.40–2.2 (m, ca. 8 H), and 2.46 (q, *J* = 7 Hz, 6 H) ppm; ir (neat) 2350 cm⁻¹ (s). The product was further characterized by its conversion into dimethyl *trans*-2-methylcyclopentylboronate. An aliquot of the reaction mixture obtained by using 80 mmol of triethylamine was oxidized with alkaline hydrogen peroxide. [*Caution!* Hydrogen peroxide (30%) should be added after completing the destruction of active hydride (25°, 0.5–1 hr) with 3 *N* sodium hydroxide. Premature addition of hydrogen peroxide can cause minor explosions.] GLC examination on a CW-20M indicated the presence of *trans*-2-methylcyclopentanol (97% yield) along with traces (≤1% each) of the cis isomer, 2,3-dimethyl-1-butanol, and 2,3-dimethyl-2-butanol.

Preparation of Dimethyl Alkaneboronates. The following preparation of dimethyl *trans*-2-methylcyclopentaneboronate is representative. A mixture containing 20 mmol of triethylamine-*trans*-2-methylcyclopentylborane was prepared as described in the previous experiment. To this was added 40 mmol (100% excess) of dry methanol. Evolution of 19.8 mmol (99%) of hydrogen was observed within 30 min at 25°. GLC examination of the methanolysis product on a 2-ft SE-30 indicated the presence of 18.6 mmol (93%)

of dimethyl *trans*-2-methylcyclopentaneboronate. Distillation provided 2.5 g (80%) of the product: bp 60–61° (15 mm); $n^{20}D$ 1.4290; ¹H NMR (CCl₄, Me₄Si); δ 0.7–1.2 (m with a sharp doublet centered at 0.95, *J* = 6 Hz, 4 H), 1.3–2.2 (m, 7 H), and 3.52 (s, 6 H) ppm; ir (neat) 2970 (s), 2890 (s), 1475 (s), 1360 (s), 1325 (s), 1020 cm⁻¹ (s). Oxidation of the product yielded *trans*-2-methylcyclopentanol in 98% yield along with traces of impurities.

In a separate run, a mixture containing triethylamine-*trans*-2-methylcyclopentylborane was stored at 25° under nitrogen and periodically methanolyzed. The products were analyzed by GLC. Practically no change in the yield of dimethyl *trans*-2-methylcyclopentaneboronate was observed for 1 week.

Hydroboration of Olefins with Triethylamine–Monoalkylboranes in the Absence of Boron Trifluoride Etherate. The following experiment on the reaction of 1-octene with triethylamine-*trans*-2-methylcyclopentylborane is representative. To 25 ml (20 mmol) of 0.8 *M* triethylamine-*trans*-2-methylcyclopentylborane were added, at 25°, 15 ml of a THF solution containing 4.48 g (40 mmol) of 1-octene and 10 mmol of *n*-nonane. At appropriate times, aliquots were quenched with methanol and analyzed by GLC (SE-30). The experimental results are summarized in Table VIII.

Hydroboration of Olefins with Triethylamine–Monoalkylboranes in the Presence of Boron Trifluoride Etherate. (a) In THF. This experiment was carried out in essentially the same manner as described in the previous experiment except that 11.28 g (80 mmol) of boron trifluoride etherate was added immediately after the addition of 1-octene. The results are summarized in Table IX. Practically no acceleration of the rate was observed.

(b) In Hexane. Triethylamine-*trans*-2-methylcyclopentylborane (20 mmol) was prepared as described earlier in this section. After evaporation of the volatile substances [25° (15 mm), 1–2 hr], 30 ml of hexane, 10 mmol of *n*-nonane, 4.48 g (40 mmol) of 1-octene, and 2.82 g (20 mmol) of boron trifluoride etherate were added in this order at 25°. At appropriate times, aliquots were analyzed by GLC after treatment with water. The results are summarized in Table IX.

Preparation of "Mixed" Trialkylboranes by the Hydroboration of Olefins with Triethylamine–Monoalkylboranes and Their Carbonylation. The following experiment is representative. A mixture containing 10 mmol of triethylamine-cyclopentylborane was obtained as described earlier in this section. 1-Pentene (1.4 g, 20 mmol) was added at 25°, and the reaction mixture was stirred for 16 hr. GLC examination indicated that 94% of 1-pentene had been consumed. After the addition of 1.86 g (30 mmol) of ethylene glycol, the mixture was carbonylated at 150° (70 atm) in the same manner as reported previously.[10] GLC examination (SE-30) of the product indicated the presence of 7.0 mmol (70% yield) of 2-(cyclopentyldi-*n*-pentylcarbinyl)-2-bora-1,3-dioxolane contaminated with an apparently isomeric product (~5%). The product was isolated by distillation: bp 127–128° (0.7 mm); $n^{20}D$ 1.4675; ¹H NMR (CCl₄, Me₄Si) δ 0.6–2.1 (m, with peaks at 0.9, 1.27, and 1.47, 31 H) and 4.1 ppm (s, 4 H) ppm; ir (neat) 2950 (s), 1460 (s), 1390 (s), 1265 (s), 1240 (s), 1210 (s), 1030 (s), 950 cm⁻¹ (s).

Anal. Calcd for C₁₈H₃₅BO₂: C, 73.46; H, 11.99; B, 3.67. Found: C, 73.62; H, 12.22; B, 3.72.

Reaction of Tetramethylethylene with Borane in THF in the Molar Ratio of 1.5:1, 2:1, or 4:1 at 25°. To 44.5 ml (100 mmol) of 2.25 *M* borane in THF were added, at 25°, 150, 200, or 400 mmol of TME and 3.9 ml (20 mmol) of *n*-decane. The total volume was adjusted by the addition of THF so that the concentration of boron in each case was 1.0 *M*. At appropriate times, aliquots were examined by ir, residual hydride analysis, and GLC analysis of the oxidation product. The results are summarized in Table X.

Hydroboration of Tetramethylethylene with Borane at 25° in the Molar Ratio of 16:1. Ten millimoles of thexylborane in THF was evaporated. To this was added 19.2 ml (160 mmol) of TME and 1 ml of THF. The mixture was stirred at 25° and analyzed at appropriate times as described in the previous experiments. At 3 hr, the ir spectrum showed only the band at 2470 cm⁻¹ in the 2600–2400 cm⁻¹ region and practically no absorption was observed in the 1600–1500 cm⁻¹ region. The active hydride analysis indicated the presence of 10.1 mmol of active hydride. An aliquot was oxidized using 6 *N* sodium hydroxide and 30% hydrogen peroxide. Ethanol was also used as a cosolvent. GLC examination of the oxidation product on a CW-20 indicated the formation of 1.96 mol of thexyl alcohol and 0.02 mol of 2,3-dimethyl-1-butanol per mole of bo-

rane. Another 5-mmol aliquot was treated with 0.4 ml (10 mmol) of dry methanol, evaporated [25° (0.5 mm)], and examined by ^{1}H NMR with benzene as a standard. There were formed 0.90 mol of methoxydithexylborane and 0.05 mol of dimethoxythexylborane per mole of borane.

Preparation of Methoxydithexylborane. The preparation of dithexylborane described above was repeated on a 20 mmol scale. After quenching the reaction mixture with 1.6 ml (40 mmol) of dry methanol, distillation provided 3.6 g (85% yield) of methoxydithexylborane: bp 50–52° (0.25 mm); n^{20}D 1.4515; ^{1}H NMR (CCl$_4$, Me$_4$Si): δ 0.79 (d, J = 7 Hz, 24 H), 1.70–2.30 (septet, J = 7 Hz, 2 H), and 3.96 ppm (s, 3 H); ir (neat) 1310 (s), 980 cm^{-1} (s).

Anal. Calcd for C$_{13}$H$_{29}$BO: C, 73.58; H, 13.78; B, 5.10. Found: C, 73.77; H, 13.76; B, 5.28. Oxidation of 1 mmol of the distilled product yielded 1.98 mmol (99%) of thexyl alcohol. A trace amount (0.02 mmol) of 2,3-dimethyl-1-butanol was also observed.

Preparation of Dithexylborane in the Absence of THF. Ten millimoles of thexylborane was evaporated. ^{1}H NMR examination of an aliquot indicated the absence of THF. To the remaining residue was added 19.2 ml (160 mmol) of TME, and the mixture was stirred at 25°. The reaction was slow, requiring 24 hr for completion. The ir spectrum taken at 24 hr showed the same patterns in the 2600–2400 and 1600–1500 cm^{-1} region.

Reaction of Tetramethylethylene with Deuterioborane in the Molar Ratio of 16:1. To a flask of a small set-up for the generation of borane[17] containing 0.64 g (15 mmol) of sodium borodeuteride and 1 ml of diglyme was added, at 25°, 2.54 ml (20 mmol) of boron trifluoride etherate over a period of 5–10 min. Deuterioborane thus formed was absorbed in a flask containing 20 ml of THF. The reaction mixture was stirred for 30 min at 25° and then heated for 2 hr at 50–60°. The concentration of deuterioborane in THF was 0.33 M. A 16-ml aliquot (5.3 mmol) of deuterioborane in THF was reacted with 0.64 ml (5.3 mmol) of TME. The concentration was adjusted to 0.5 M in boron by the addition of THF. An aliquot was examined by ir. The volatile substances were then evaporated at 25° (15 mm), and 9.6 ml (80 mmol) of TME and 0.6 ml of THF were added to the residue. The product was examined by ir. The results are described in the main text.

References and Notes

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(2) (a) Postdoctoral research associate on a research grant, DA 31-134 ARO(D) 453, supported by the U.S. Army Research Office (Durham); (b) graduate assistant on a research grant, GM 10937, supported by the National Institutes of Health.
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(8) (a) H. C. Brown and S. K. Gupta, *J. Am. Chem Soc.*, **92**, 6983 (1970); (b) *ibid.*, **93**, 1816, 2802 (1971); (c) *ibid.*, **93**, 4062 (1971); (d) unpublished results by S. K. Gupta.
(9) For carbonylation conditions, see H. C. Brown. E. Negishi, and S. K. Gupta, *J. Am. Chem. Soc.*, **92**, 6648 (1970).
(10) A trace quantity (<1 to ~2%) of 2,3-dimethyl-1-butanol was observed.
(11) By ^{1}H NMR. The crude product contained ~5% of dimethoxythexylborane.
(12) W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, **17**, 396 (1961), and references cited therein.
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(16) The ir spectrum of tetramethyldiborane reported in the literature shows a minor absorption at 2500 cm^{-1}. However, the authors concluded that it is due to trimethyldiborane present as an impurity: W. J. Lehmann, C. O. Wilson, J. F. Ditter, and I. Shapiro, *Adv. Chem. Ser.*, **No. 32**, 139 (1961).
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(19) Authentic samples of these compounds were available in our laboratories.