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## Hydroboration. XVI. The Hydroboration of Olefins, Acetylenes and Dienes with Thexylborane

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**RECEIVED DECEMBER 15, 1962** 

The hydroboration of 2,3-dimethyl-2-butene yields 2,3-dimethyl-2-butylborane (thexylborane). The large steric requirements of thexylborane permit some control of the addition of the boron-hydrogen bond to the carbon-carbon double bond. Thus, the hydroboration of styrene with thexylborane yields 96% of the primary and only 4% of the secondary derivative, as compared to 20% secondary realized with diborane. Moreover, the reagent exhibits major differences in its rate of reaction with internal olefins, thus providing a convenient means of removing the more reactive *cis* from the *trans* isomer. Thexylborane readily converts both internal and terminal acetylenes into the corresponding monothexyldivinylboranes, which undergo protonolysis to the corresponding olefins, or oxidation to the corresponding aldehydes or ketones. Dihydroboration of 1,3-butadiene and 1,4-pentadiene with thexylborane avoids the formation of insoluble polymeric organoboranes and facilitates transformation of the intermediate organoborane, yields 85% *trans*- and 15% *cis*-1,3-cyclopentanediol with diborane, 87% *trans*- and 13% *cis*- with thexylborane, and 97% *trans*- and 35% *cis*- with disiamylborane. A convenient procedure has been developed for the separation of isomeric *cis*-*trans* cyclic diols involving esterification of the diol mixture with *n*-butylboroxine, followed by distillation of the volatile *cis* cyclic diols involving esterification of the diol mixture with *n*-butylboroxine, followed by distillation is readily ob-tained from cyclopentadiene *via* the hydroboration reaction.

The hydroboration of simple olefins with diborane proceeds to the trialkylborane stage. However, more hindered olefins yield the dialkylborane derivative.<sup>1</sup> Thus, hydroboration of 2-methyl-2-butene yields bis-3methyl-2-butylborane (disiamylborane). In exploring the scope of the hydroboration of olefins with disiamylborane, it was observed that the reagent exhibits a remarkable selectivity for certain olefinic structures.<sup>2</sup>

With a more hindered olefin, such as 2,3-dimethyl-2butene, the hydroboration proceeds to the monoalkylborane stage, yielding 2,3-dimethyl-2-butylborane (thexylborane).<sup>3,4</sup>

Preliminary experiments indicated that this reagent exhibits interesting characteristics as a hydroborating agent. Consequently, a study was initiated to examine the relative rates of reaction of thexylborane with various olefins and its utility as a selective hydroborating agent for olefins, acetylenes and dienes.<sup>5</sup>

#### Results and Discussion

**Preparation of Thexylborane.**—It has been established that the hydroboration of 2,3-dimethyl-2-butene with borane in the ratio of 1 to 1 proceeds cleanly to the monoalkylborane stage.<sup>3,4</sup> At  $0^{\circ}$ , the conversion of the olefin to thexylborane in diglyme and in tetrahydrofuran is complete in 1–2 hr.

$$\begin{array}{cccc} H_{3}C & CH_{3} & H_{3}C & CH_{3} \\ | & | & | \\ C = C + BH_{3} & \xrightarrow{0^{\circ}} H - C - BH_{2} \\ | & | & | \\ H_{3}C & CH_{3} & H_{3}C & CH_{3} \end{array}$$
(1)

Solutions of the xylborane in these solvents are stable at room temperature over long periods of time. Thus, an approximately 0.8~M solution of the xylborane did not undergo significant change in the "hydride" concentration in 16 days. Moreover, oxidation of the the xylborane indicated that isomerization of the tertiary boron to the primary position was slow: 3% after 8 days and 8-9% after 16 days (Table I).

Rates of Reaction with Various Olefins.—In order to determine the selectivity of thexylborane for various olefinic structures, a number of representative olefins

(1) H. C. Brown and B. C. Subba Rao, J. Am. Chem. Soc., 81, 6428 (1959).

(2) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961); H. C. Brown and A. W. Moerikofer, *ibid.*, **83**, 3417 (1961).

(3) H. C. Brown and A. W. Moerikofer, *ibid.*, 84, 1478 (1962).

(4) H. C. Brown and G. J. Klender, Inorg. Chem., 1, 204 (1962).

(5) M. F. Hawthorne, J. Am. Chem. Soc., 83, 2541 (1961), has reported the preparation of trimethylamine-*i*-butylborane  $[(CH_3)_3 \stackrel{\circ}{\mathrm{M}}, \stackrel{\circ}{\mathrm{B}}H_2C(CH_3)_3]$ and its utility as a hydroborating agent for acetylenes and dienes.

TABLE I					
STABILITY	OF	Thexylborane at $2025^\circ$ in Diglyme (DG) and			
in Tetrahydrofuran (THF)					

Time,		Molarity in	Alcohol di after oxid	stribution ation, %
days	Solvent	''hydride''	$2 - 01^a$	1-01 <sup>6</sup>
0	DG	1.66	99	1
	THF	1.62	99	1
8	DG	1.64	97	3
	THF	1.60	97	3
16	DG	1.67	92	8
	THF	1.64	91	9

<sup>a</sup> 2,3-Dimethyl-2-butanol. <sup>b</sup> 2,3-Dimethyl-1-butanol.

(25 mmoles) were hydroborated with the reagent (12.5 mmoles) at 0° in diglyme solution. The rate of disappearance of the olefin was followed by gas chromatographic analysis.

Terminal olefins, such as 1-hexene, 2-methyl-1-pentene and styrene, reacted rapidly, utilizing both hydrides of the thexylborane.<sup>2</sup>

$$\begin{array}{c} HC \stackrel{-}{\overset{-}{\underset{c}{\leftarrow}}} -BH_{2} + 2RCH = CH_{2} \longrightarrow \\ H_{3}C \quad CH_{3} \qquad H_{3}C \quad CH_{3} \\ HC \stackrel{-}{\underset{c}{\leftarrow}} -B \ (CH_{2}CH_{2}R)_{2} \quad (2) \\ H_{3}C \quad CH_{3} \end{array}$$

However, disubstituted internal olefins, such as *cis*- and *trans*-2-hexene, *cis*- and *trans*-4-methyl-2-pentene and cyclohexene, showed an unusual feature. The reaction proceeded rapidly to the dialkylborane stage.<sup>3</sup> The utilization of the remaining hydride of the thexylborane occurred at a much slower rate.<sup>4</sup> H<sub>2</sub>C  $_{\rm CH}$ 

Moreover, analysis of the reaction mixture revealed the presence of essentially pure 2,3-dimethyl-2-butene. Evidently, the complete reaction of thexylborane with more hindered olefins involves a prior elimination of 2,3-dimethyl-2-butene. It is noteworthy that acyclic *cis*-olefins react faster than the corresponding *trans* compounds. With the exception of 1-methylcyclohexene, trisubstituted olefins, such as 2-methyl-2-butene and 1-methylcyclopentene, react at a rate comparable to the acyclic *trans*-olefins.

The order of reactivity observed corresponds to that reported for disiamylborane.<sup>2</sup> The experimental results are summarized in Table II.

TABLE II

# Reaction of Various Olefins with Thexylborane in Diglyme at $0^{\circ}$

		Olefi	n reacte	d, %—-		Displace- ment <sup>b</sup> of 2,3-di- methyl-2- butene,
Olefin <sup>a</sup>	0.5 hr.	1.0 hr.	2 hr.	4 hr.	24 hr.	mmoles
1-Hexene	72	87	95			Trace
2-Methyl-1-pentene	69	86	92			Trace
Styrene	73	91	94			Trace
cis-2-Hexene	76	84	90	96		2.6
trans-2-Hexene	56	61	72	84		6.4
cis-4-Methyl-2-						
pentene	55	73	85	95		3.8
trans-4-Methyl-2-						
pentene	53	60	68	80		8.0
Cyclohexene	53	62	73	79	90	7.1
2-Methyl-2-butene	46	59	66	76	94	8.1
1-Methylcyclo-						
pentene	59	<b>64</b>	73	85		6.6
1-Methylcyclo-						
hexene	18	32	41	53	77	6.2

 $^{\alpha}$  Sample consisted of 12.5 mmoles of the xylborane and 25 mmoles of olefin.  $^{b}$  Yield of 2,3-dimethyl-2-but ene is based on the last olefin analysis.

The observation that the hydroboration of internal olefins occurs partially by displacement of 2,3-dimethyl-2-butene suggested a more quantitative exploration of this phenomenon. Consequently, *cis*- and *trans*-2hexene were hydroborated with thexylborane in the ratio of 2 to 1. Samples were withdrawn at different time intervals and analyzed by gas chromatography for unreacted 2-hexene and 2,3-dimethyl-2-butene. The experimental data obtained are shown in Table III.

TABLE III

Hydroboration of *cis*- and *trans*-2-Hexene with Thexylborane at 0° in Diglyme<sup>a</sup>

		is-2-Hexen	e	tı	ans-2-Hexe	ne
Time, min.	Olefin reacted, mmoles	Displaced 2,3-di- methyl- 2-butene, mmoles	Hydrogen evolved on hy- drolysis, mmoles	Olefin reacted, mmoles	Displaced 2,3-di- methyl- 2-butene, mmoles	Hydrogen evolved on hy- drolysis, mmoles
<b>3</b> 0	19.0	0.7		14.0	0.7	
<b>6</b> 0	21.0	0.8		15.3	1.7	
120	22.5	<b>2</b> . 0		18.0	2.8	
240	24.0	2.1	2.6	21.0	4.3	
<b>48</b> 0				23.8	6.4	6.8

 $^a$  Sample consisted of 12.5 mm oles of the xylborane and 25 mm oles of olefin.

Previous reports on the displacement of olefins from organoboranes indicated that the reaction required elevated temperatures.<sup>6</sup> However, it has been shown

(6) H. C. Brown and B. C. Subba Rao, J. Am. Chem. Soc., 81, 6434 (1959); H. C. Brown and M. V. Bhatt, *ibid.*, 22, 2074 (1960).

that the elimination of a boron-hydrogen bond from an organoborane is markedly catalyzed by boron-hydrogen moieties already present in the reaction mixture.<sup>7</sup> In the usual displacement experiments, the excess boron-hydrogen moieties from the initial hydroboration reaction are destroyed by the displacing olefin. Consequently, both the large steric requirements of the dialkylborane (RR'BH) containing a thexyl group and the presence of boron-hydrogen bonds should assist in the displacement of the thexyl group.

$$\begin{array}{ccccccc} H_3C & CH_3 & H & H_3C & CH_3 \\ \downarrow & \downarrow & & \\ H_C & -C - B & & -5^{\circ} & \downarrow & \downarrow \\ \downarrow & & & \\ H_3C & CH_3 & R' & H_3C & CH_3 \end{array}$$
(5)

The monoalkylborane thus obtained can now react further, either to the di- or trialkylborane stage, depending on the structure of the olefin (Table II).

It has been shown that acyclic *cis*-olefins react faster with disiamylborane than the *trans* isomers.<sup>2</sup> Thus, treatment of a mixture of *cis*-*trans* olefin with the reagent results in a preferential conversion of the *cis*olefin into the corresponding organoborane; the remaining *trans* isomer can be isolated in high purity from the reaction mixture.<sup>2</sup> A similar selectivity was observed when an equimolar mixture of *cis*-*trans*-2hexene was hydroborated with thexylborane in the ratio of 2 to 1. It is noteworthy that the separation realized in this case exceeds that achieved by the use of disiamylborane. The experimental results obtained are shown in Table IV.

Table IV Hydroboration of cis-trans-2-Hexene with Thexylborane at  $0^{\circ a}$ 

		AL U		
Reaction time, hr.	-Residual olef cis	in, mmoles— trans	Produ cis	ct, %
0	24.5	25.5		
0.5	0.2	19.5	<b>2</b>	98
1	.15	16	1	99
$^{2}$	.15	13.5	1	99
4	.05	6.5	1	99

<sup>a</sup> Sample consisted of 25 mmoles of thexylborane and 50 mmoles of *cis-trans*-2-hexene.

Similarly, hydroboration of an equimolar mixture of 2-methyl-1-pentene and 4-methyl-1-pentene with thexyl-borane results in the preferential hydroboration of the sterically less hindered olefin. Gas chromatographic analysis indicated that 72% of 4-methyl-1-pentene and only 30% of 2-methyl-1-pentene had reacted.

Directive Effects in the Hydroboration of Olefins.-We had previously observed that disiamylborane is a highly selective hydroborating agent, providing a measure of control of the direction of addition of the boronhydrogen bond to the double bond.<sup>2</sup> It was of interest to determine whether a monoalkylborane would exhibit a directive effect similar to that observed with disiamylborane. Accordingly, we undertook a study of the hydroboration of unsymmetrically substituted olefins with thexylborane. In these experiments a 25-mmole sample of the olefin was hydroborated with 12.5 mmoles of the xylborane at  $0^{\circ}$ . The disappearance of the olefin was followed by gas chromatographic analysis. When all the olefin had reacted, the reaction mixture was oxidized with alkaline hydrogen peroxide, then analyzed by gas chromatography for isomeric alcohols. The experimental results obtained are summarized in Table

The hydroboration of 1-hexene with diborane places 6% of the boron at the secondary position; nearly the same distribution is observed with the ylborane. On

(7) H. C. Brown and G. Zweifel, to be published.

			2	Table V			
DIRECTIVE	Effects	IN	THE	Hydroboration	OF	OLEFINS	WITH
VARIOUS HYDROBORATING AGENTS							

	Hydroborating	Alcohol	distribution	1, %7
Olefin	agent	1-01	2-01	$3 - ol^d$
1-Hexene	$\mathrm{B}_{2}\mathrm{H}_{6}{}^{a}$	94	6	
	$Thexyl-BH_2$	94 - 95	5-6	
	Sia <sub>2</sub> BH <sup>b, c</sup>	99	1	
Styrene	$B_2H_6^a$	80	20	
	$Thexyl-BH_2$	94	6	
	$Sia_2BH^{b,c}$	98	$^{2}$	
trans-4-Methyl-2-	$\mathrm{B}_{2}\mathrm{H}_{6}{}^{a}$		57	43
pentene	$Thexyl-BH_2$		60	40
	Sia2BH <sup>b,c</sup>		95	5
cis-4-Methyl-2-pentene	$Thexyl-BH_2$		66	34
	Sia <sub>2</sub> BH <sup>a,b</sup>		97	3

 $^a$  Reference 8.  $^b$  Sia2BH = disiamyl<br/>borane.  $^c$  Reference 2.  $^d$  2-Methyl-3-pentanol.

the other hand, disiamylborane produces essentially only the primary derivative.

The addition of diborane to olefins must involve at least three stages<sup>8</sup> (not counting the dimeric species).



The results shown in Table V indicate that the first and the second stage have nearly the same selectivity for the terminal olefin, since the third stage is highly selective.<sup>2</sup> The large difference in selectivity in going from a monoalkylborane to the dialkylborane can be rationalized in the following manner. The *cis*-addition of the boron-hydrogen bond to an olefin has been discussed in terms of a four-center transition state.<sup>9</sup> The observed mode of addition of thexylborane and disiamylborane to 1-hexene is compatible with this mechanism.



Structure I represents the transition state for the addition of thexylborane to the secondary position of 1hexene and structure II the corresponding transition state for disiamylborane. In such a rigid transition state, the steric interaction of the boron alkyl substituent with the alkyl group of the olefin should be an important destabilizing factor. On this model, steric interference therefore will destabilize transition state II with respect to I and lead to a predominance of the primary organoborane in the case of disiamylborane. Similar arguments can be advanced to explain the observed isomer distribution in the case of *cis-* and *trans-*4methyl-2-pentene.

The hydroboration of styrene remains to be considered. The marked influence of the phenyl group in the hydroboration of styrene with diborane has been discussed earlier.<sup>8</sup> From the present study one can conclude that the 20% of the secondary derivative (Table V) is formed mainly in the initial stage of the hydroboration, since both thexylborane and disiamylborane exhibit a marked selectivity for the primary position of the styrene side chain.

Hydroboration of Acetylenes.—The addition of thexylborane to 1-hexyne in the ratio of 1 to 2 yields the corresponding vinylborane. Essentially no displacement of the thexyl group was observed. Protonolysis of the product with glacial acetic acid yielded 1-hexene in 91% yield (gas chromatographic analysis). Oxidation of the vinylborane with hydrogen peroxide under controlled conditions afforded hexaldehyde in 82% yield. Similarly, 2-hexyne was converted to the vinylborane. Protonolysis gave essentially pure *cis*-2-hexene.

The preparation of vinylboranes has been achieved previously by using disiamylborane.<sup>10</sup> Thexylborane represents an alternative reagent for the facile conversion of acetylenes into vinylboranes.

Hydroboration of Dienes.—The dihydroboration of terminal dienes, such as 1,4-pentadiene, with diborane yields after oxidation 62% of the 1,4- and 38% of the 1,5-pentanediol, whereas the monofunctional disiamylborane affords mainly the  $\alpha,\omega$ -diol (85%).<sup>11,12</sup> The difference in selectivity of the two reagents with terminal dienes has been rationalized in terms of a cyclization reaction which takes place in the case of diborane.<sup>11,12</sup> It was anticipated that the diffunctional thexylborane should also favor an intramolecular addition of the second B–H bond, and therefore yield an isomer distribution similar to that observed with diborane (9).



The results obtained are summarized in Table VI.

Т	ЪВ	LE	VI

Directive Effects in the Dihydroboration of 1,3-Butadiene and 1,4-Pentadiene with Various Hydroborating Agents

	Hydroborating	Dio	l distributior	ı, %—
Diene	agent	1,3-	1,4-	1,5-
1,3-Butadiene	${ m B_2H_6}^a$	<b>24</b>	76	
	Thexyl- $\mathrm{BH}_2^b$	21	79	
	Sia₂BH <sup>°, d</sup>	10	90	
1,4-Pentadiene	$B_2H_6^a$		62	38
	Thexyl-BH2 <sup>b</sup>		70	<b>30</b>
	${ m Sia_2BH}^{c,d}$		15	85

<sup>a</sup> Reference 11. <sup>b</sup> 1 Thexylborane to 1 diene. <sup>c</sup> Sia<sub>2</sub>BH = disiamylborane. <sup>d</sup> Reference 12.

It had been reported that bis-hydroboration of cyclopentadiene with diborane gave, after oxidation, cis-1,3cyclopentanediol in 41% yield.<sup>13</sup> Since the preparation of cyclic diols by this method should find wide application, a more detailed study of the bis-hydroboration of cyclopentadiene with different hydroborating agents was initiated.

The predominant formation of the *cis* isomer in the hydroboration of cyclopentadiene suggested that the hydroboration must proceed preferentially through the formation of a bicyclic boron derivative (10). On this basis it could be predicted, that because of the well known

- (10) H. C. Brown and G. Zweifel, Bid., 83, 3834 (1961).
- (11) G. Zweifel, K. Nagase and H. C. Brown, ibid., 84, 183 (1962).
- (12) G. Zweifel, K. Nagase and H. C. Brown, ibid., 84, 190 (1962).
- (13) K. A. Saegebarth, J. Org. Chem., 25, 2212 (1960).

<sup>(8)</sup> H. C. Brown and G. Zweifel, J. Am. Chem. Soc., 82, 4708 (1960).

<sup>(9)</sup> H. C. Brown and G. Zweifel, ibid., 83, 2544 (1961).

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tendency of large bulky groups to favor ring formation, the use of thexylborane should favor the formation of the cis isomer. Contrary to this, the use of the monofunctional reagent, disiamylborane, was expected to favor the formation of the trans isomer.

However, the results were not in accord with these predictions. Thus, dihydroboration of cyclopentadiene with diborane (1 cyclopentadiene per BH<sub>3</sub>) yielded a polymeric material which was oxidized by alkaline hydrogen peroxide to the diol. Gas chromatographic analysis on a sorbitol-silicone column indicated the presence of two diols in the ratio of 15% to 85%. Following Saegebarth, the predominant product should have been the "cis" isomer.

However, thexylborane yielded the same two isomers in essentially the same ratio, 87% to 13%. Moreover, disiamylborane, which is incapable of forming a cyclic derivative, yielded a product which exhibited the same two peaks, this time in a ratio of 97:3.

These results are summarized in Table VII.

#### TABLE VII

HYDROBORATION OF CYCLOPENTADIENE IN TETRAHYDROFURAN Diol distribution

	after dist	illation, %		M.p. of
Hydroborating	cis-1,3-	trans-1,3-	Yield of	bis-phenyl-
agent	diol	diol	diol, %	urethan, °C.
$B_2H_6$	15	85	80	173 - 174
$Thexyl-BH_2$	13	87	71	172 - 173
$Sia_2BH^a$	3	97	70	172 - 174
4 Sto DU - d	isia marilha			

Sia2BH = disiamylborane.

Since there was no obvious way in which disiamylborane could lead to the formation of an almost pure cis derivative, we were led to re-examine the structural assignment made by Saegebarth.

The configurational assignment to the isomeric 1,3cyclopentanediols has been the subject of much controversy.<sup>14</sup> In view of this fact, we investigated the possibility of finding a simple method which would not only permit the separation of the isomeric diols, but also permit the configurational assignments. We discovered that esterification of the diols with a lower aliphatic boronic acid, such as n-butylboronic acid or *n*-butylboroxine, provides a suitable procedure.<sup>15</sup>

For example, cis-1,4-cyclohexanediol reacted with nbutylboroxine to form a product volatile at low pressure; the trans product did not distil under these conditions. Similarly, treatment of a mixture of cisand trans-1,3-cyclohexanediol resulted in the formation of a volatile boronic ester from the *cis* isomer, whereas the trans failed to distil. The boron is readily displaced by transesterification with ethylene glycol. In this way it was possible to obtain essentially pure cis- and pure trans-1,3-cyclohexanediol from the mixture.

Similarly, the crude 1,3-cyclopentanediol from the hydroboration of cyclopentadiene with diborane was treated with n-butylboroxine. The process removed the minor component (15%) as a volatile distillate, b.p. 80° at 10 mm., and yielded the major component as a non-volatile boronic ester. On this basis, the major

(14) (a) L. N. Owen and P. N. Smith, J. Chem. Soc., 4035 (1952); (b) A. C. Darby, H. B. Henbest and I. McCleanaghan, Chem. Ind. (London), 462 (1962)

(15) H. C. Brown and G. Zweifel, J. Org. Chem., 27, 4708 (1962).

product, m.p. of bis-phenylurethane 173-174°, is trans-1,3-cyclopentanediol, and the minor product, m.p. of bis-phenylurethane  $162-163^{\circ}$ , is the *cis* isomer. The assignment of the trans configuration to the diol was confirmed by the absence of a chelated hydroxyl group in the infrared spectrum at high dilution in carbon tetrachloride solution.

Consequently, hydroboration of cyclopentadiene with diborane, thexylborane and disiamylborane yields the trans-1,3-cyclopentanediol.

Nature of the Organoborane from the Hydroboration of Dienes.-Köster originally suggested that the product formed in treating 1,3-butadiene with diborane possesses the cyclic structure<sup>16</sup> (11). However, the

$$\begin{array}{ccc} HC = CH_{2} & \xrightarrow{2 \text{ BH}_{3}} \\ HC = CH_{2} & & \\ H_{2}C = CH_{2} & & \\ H_{2}C = CH_{2} & B & H_{2} & \\ H_{2}C = CH_{2} & B & H_{2} & \\ H_{2}C = CH_{2} & B & H_{2} & \\ H_{2}C = CH_{2} & B & H_{2} & \\ H_{2}C = CH_{2} & H_{2} & H_{2} & \\ H_{2}C & H_{2} & H_{2} & \\ H_{2}C & H_{2} & H_{2} & \\ H_{2}C & H_{2} & H_{2} & H_{2} & \\ H_{2}C & H_{2} & H_{2} & H_{2} & \\ H_{2} & H_{2} & H_{2} & H_{2} & H_{2} & \\ H_{2} & H_{2} & H_{2} & H_{2} & H_{2} & H_{2} & \\ H_{2} & H_{2}$$

properties described appear unusual for a substance with this structure. Consequently, we suggested that the reaction product realized by Köster possessed the alternative structure (12).<sup>11</sup> This proposal is supported



by a recent publication by Weiss, Lehmann and Shapiro.<sup>17</sup> These authors isolated a 1:1 product of diborane and 1,3-butadiene and report that n.m.r. and infrared data indicate the cyclic structure involving both boron atoms (13).



We explored the possibility that the reaction of thexylborane with dienes under controlled conditions might proceed in a similar manner (14).



Molecular weight determination and infrared spectra establish that thexylborane is dimeric (sym-dithexyldiborane) in tetrahydrofuran solution.<sup>4</sup> Consequently, if the reaction proceeded preferentially to give a cyclic derivative involving both carbon atoms, as shown in (14), then the product should show the strong absorption of the bridge hydrogens at 6.39  $\mu$ , and the absence Η



of the terminal >B absorption at  $3.98 \mu$ .



Accordingly, 2,3-dimethyl-1,3-butadiene and thexylborane were slowly added simultaneously to tetrahydrofuran, maintaining the reagents in low concentration to facilitate ring formation. The product was examined by infrared. The spectra exhibited two absorption bands: at  $4.02 \ \mu$  for the terminal >BHR; and at  $6.52 \ \mu$  for the bridge >BH<sub>2</sub>B<. The relative intensity of these two bands was

identical with that exhibited by solutions of dithexyl-

(16) R. Köster, Angew. Chem., 71, 520 (1959); 72, 626 (1960).

(17) H. C. Weiss, W. J. Lehmann and I. Shapiro, J. Am. Chem. Soc., 84, 3840 (1962).

#### TABLE VIII

RATE OF METHANOLYSIS OF DITHEXYLDIBORANE AND OF THE **REACTION MIXTURE FROM 1.4-CYCLOHEXADIENE** 

	Methanolysis of dithexyldiborane	Methanolysis of reactio mixture from 1,4- cyclohexadiene
Time, min.	Hydrogen evolved, mmoles	Hydrogen evolved, mmoles
15	48.8	55.1
60	64.4	65.0
120	75	73.4
180	80.5	83.0

diborane. Moreover, the observed concentration of dithexyldiborane revealed by the spectra was precisely half that of the original solution utilized in the reaction. This indicates that the reaction does not proceed as indicated in eq. 14, but proceeds instead via a path in which the 2,3-dimethyl-1,3-butadiene utilized all of the available hydride from one-half of the dithexyldiborane molecules, as shown in eq. 15. This was further confirmed by comparing the rate of methanolysis of the reaction mixture obtained from the reaction of 1,4-cyclohexadiene with dithexyldiborane with that of pure dithexyldiborane of one-half the original concentration.



or polymer

Consequently, the hydroboration of dienes with thexylborane appears to occur by an intermolecular reaction path.

It is possible that this failure to realize cyclization involving both boron atoms is the result of the large steric requirement of the thexyl groups. It is evident that a sym-dialkyldiborane should be capable of exist-ing in cis-trans isomeric forms. It is probable that the large steric requirements of the thexyl groups causes the trans arrangement to be far more stable than the cisarrangement. It is clear that if dithexyldiborane has the trans configuration, intramolecular addition of the boron-hydrogen bond to the unsaturated organoborane is sterically not possible (16).



It should be pointed out that the cyclic derivatives realized by Köster were obtained by distilling the initially polymeric product of diborane and 1,3-butadiene at low pressure and elevated temperature. Similarly, the cyclic product realized by Shapiro and co-workers was obtained in a gas phase reaction of diborane and 1,3-butadiene at 100°. Consequently, it appears that the initial product of the reaction of diborane and thexylborane with such dienes as 2,3-dimethyl-1,3butadiene and 1,4-cyclohexadiene at low temperature is predominantly the polymeric derivative. Presumably, these initially formed products could be transformed into cyclic derivatives by distillation under reduced pressure. However, we did not explore this possibility.

Conclusions .--- In summary, thexylborane appears to be a convenient reagent for the hydroboration of dienes, with the advantage over diborane of avoiding the formation of insoluble polymeric products. Moreover, the reagent offers major advantage over diborane in the conversion of acetylenes into vinylboranes, a transformation which previously required disiamylborane for satisfactory yields. Although thexylborane exhibits nearly the same selectivity towards different olefin structures as diborane, the reagent appears to be very promising for the separation of the *trans*-olefin from the faster reacting *cis* isomer in a mixture of both.

#### Experimental

Materials .- Diglyme, tetrahydrofuran and boron trifluoride etherate were purified as previously described. Sodium boro-hydride from Metal Hydrides, Inc. ( $\sim 98\%$  pure), was used without further purification.

The olefins, dienes and acetylenes used, their physical constants and source were reported in earlier papers. Cyclopenta-diene (b.p.  $40^{\circ}$  at 743 mm.,  $n^{20}$ D 1.4450) was obtained by depolymerization of dicyclopentadiene. 2,3-Dimethyl-2-butene of 99% purity was generously made available by the Phillips Petroleum Company.

Preparation of Thexylborane. (a) In Diglyme.—In a 100-ml. three-necked flask, fitted with a thermometer, a pressure equalizing funnel, a condenser and a side arm capped with a rubber septum to permit removal of samples, were placed 39.5 ml. of a 1 M solution of sodium borohydride (1.49 g.) and 4.2 g. of 2,3-dimethyl-2-butene (50 mmoles) in 10 ml. of diglyme. The flask was immersed in an ice bath and 6.7 ml. of boron trifluoride etherate (52.5 mmoles), diluted with 5 ml. of diglyme, was added over a period of 15 min. to the well stirred reaction mixture. After completion of the boron trifluoride addition, the flask was permitted to remain at  $20-25^\circ$ . At appropriate time intervals, 5-ml. samples were withdrawn and analyzed for hydride by treatment with ethylene glycol and measuring the hydrogen evolved. The organoborane was oxidized with alkaline hydrogen peroxide. The reaction mixture was extracted with hydrogen peroxide. The reaction mixture was extracted with ether, and the dried ether extract was analyzed for 2,3-dimethyl-2-butanol and 2,3-dimethyl-1-butanol by gas chromatography. The results obtained are summarized in Table I.
(b) In Tetrahydrofuran.—In a three-necked flask was placed 4.2 g. of 2,3-dimethyl-2-butene (50 mmoles) in 33 ml. of tetra-hydrofuran. The flask was cooled to -10°, then 27.5 ml. of a

 $0.91 \ M$  solution of diborane in tetrahydrofuran was added slowly 0.91 M solution of diborane in tetrahydrofuran was added slowly to the olefin. After completion of the diborane addition, the flask was maintained at 20–25°. At different time intervals 5-ml. samples were withdrawn and analyzed for residual hydride. The organoborane was oxidized with alkaline hydrogen peroxide. The reaction mixture was extracted with ether. The dried ether extract was analyzed for 2,3-dimethyl-2-butanol and 2,3-dimethyl-1-butanol by gas chromatography. The experimental results are summarized in Table I.

Rates of Reaction with Various Olefins .- In a 100-ml. flask Rates of Reaction with Various Olefins.—In a 100-ml. flask were placed 18 ml. of diglyme, 9.4 ml. of a 1 M solution of sodium borohydride in diglyme and 8.3 ml of a 1.5 M solution of 2,3-dimethyl-2-butene (12.5 mmoles) in diglyme. The flask was immersed in an ice bath, then 7.0 ml. of a 1.83 M solution of boron trifluoride diglymate<sup>2</sup> was added to the well stirred reaction mixture over a period of 15 min. The reaction was allowed to proceed for an additional hour at 0-3°. Gas chromatographic analysis indicated 2% of unreacted 2,3-dimethyl-2-butene. The thexylborane thus obtained (12.5 mmoles) was cooled to  $-15^\circ$ , then diluted with 25 mmoles of the olefin in 10 ml. diglyme

 $-15^{\circ}$ , then diluted with 25 mmoles of the olefin in 10 ml. diglyme solution, containing an internal standard. Samples (1-ml.) were withdrawn at different time intervals. In order to decompose residual hydride the samples were quenched in a saturated sodium chloride solution. The upper layer formed was analyzed by gas chromatography for unreacted olefin and for 2,3-dimethyl-2-butene, using the internal standard as reference. The remain-2-butene, using the internal standard as reference. ing reaction mixture was diluted with water and the hydrogen evolved was collected. The results of these investigations are reported in Tables II

and III.

Competitive Hydroboration of a Mixture of cis- and trans-2-Hexene.—In a 100-ml. three-necked flask were placed 19.6 ml. of a 1 M solution of sodium borohydride in diglyme and 25 mmoles of 2,3-dimethyl-2-butene (2.1 g.) in 10 ml. diglyme solution. The flask was immersed in an ice bath, then 7.2 ml. of a 3.65 M solution of boron trifluoride (26.2 mmoles) in diglyme was added to the well stimulation privities. the well stirred reaction mixture.

After standing for one hour at 0-3°, the reaction mixture was colled to  $-15^{\circ}$ , then diluted with 4.2 g. of a 51 to 49 mixture of *cis*- and *trans*-2-hexene (50 mmoles), containing an internal standard. The flask was permitted to remain at  $0-3^{\circ}$ . Samples were withdrawn and analyzed by gas chromatography for unreacted olefins as described above. At the end of the reaction the residual hydride was decomposed by adding water. There was collected 12.4 mmoles of hydrogen. The experimental results are summarized in Table IV.

Was collected 12.4 minutes of hydrogen. results are summarized in Table IV. Competitive Hydroboration of 2-Methyl-1-pentene and 4-Methyl-1-pentene.—Under similar experimental conditions as described above, an equimolar mixture of 2-methyl-1-pentene (50 mmoles) and 4-methyl-1-pentene (50 mmoles) was treated with thexylborane (25 mmoles) at 0°. The reaction mixture was permitted to remain for 2 hr. at 0°. Gas chromatographic analysis of the reaction mixture indicated that 30% of 2-methyl-1pentene and 72% of 4-methyl-1-pentene had reacted. Directive Effects in the Hydroboration of Olefins.—The or-

Directive Effects in the Hydroboration of Olefins.—The organoboranes obtained from the rate studies were oxidized with alkaline hydrogen peroxide in the usual way. The alcohols were extracted with ether. The dried ether extracts were analyzed by gas chromatography for isomeric alcohols. The results of these experiments are reported in Table V. Hydroboration of Acetylenes. (a) Protonolysis.—Thexyl-

Hydroboration of Acetylenes. (a) Protonolysis.—Thexylborane (10 mmoles) in 20 ml. of diglyme solution was added to 1.64 g. of 1-hexyne (20 mmoles) in 20 ml. of diglyme at  $-15^{\circ}$  over a period of 10 min. The reaction was kept for 2 hr. at  $0-3^{\circ}$ . Gas chromatographic analysis of the reaction mixture indicated 3% of unreacted 1-hexyne and practically no 2,3-dimethyl-2-butene. The organoborane thus obtained was diluted with 10 ml. of glacial acetic acid. The reaction mixture was kept for 3 hr. at  $20-25^{\circ}$ . Gas chromatographic analysis indicated a 91% yield of 1-hexene.

Similarly, 20 mmoles of 2-hexyne was hydroborated with 10 mmoles of thexylborane in diglyme. Gas chromatographic analysis indicated 4% of unreacted 2-hexyne and only a small amount of 2,3-dimethyl-2-butene. Protonolysis of the organoborane as described above yielded essentially pure *cis*-2-hexene in 86% yield.

(b) Oxidation.—Thexylborane (12.5 mmoles) in 20 ml. of diglyme was added to a solution of 1-hexyne (2.05 g., 25 mmoles) in diglyme at  $-15^{\circ}$ . The reaction mixture was permitted to remain for 3 hr. at  $0-3^{\circ}$ . The residual hydride was decomposed by adding a small amount of water. The flask was placed in an ice-sodium chloride bath.

The organoborane was oxidized by adding simultaneously 8 ml. of a 1.5 M solution of sodium hydroxide and 8 ml. of 15% hydrogen peroxide. During the oxidation, the pH of the reaction mixture was kept approximately at 7.

The reaction mixture was extracted with ether. Gas chromatographic analysis of the dried ether extract revealed an 82% yield of *n*-hexaldehyde contaminated with a small amount of 2-hexanone and 1-hexanol.

Hydroboration of Dienes.—Thexylborane (25 mmoles) was prepared by adding 16.1 ml. of a 0.78 M solution of diborane in tetrahydrofuran to 2.1 g. of 2,3-dimethyl-2-butene (25 mmoles) in 25 ml. of tetrahydrofuran solution. The thexylborane thus prepared was kept for 1 hr. at 0-3°, then diluted with 25 mmoles of 1,3-butadiene or 1,4-pentadiene in 10 ml. of tetrahydrofuran. After standing for 2 hr. at 0-3°, gas chromatographic analysis of the reaction mixture indicated that nearly all the diene had reacted. The organoborane was oxidized at 30-40° with alkaline hydrogen peroxide. The reaction mixture was saturated with solid potassium carbonate. The tetrahydrofuran layer formed was separated and the aqueous phase extracted once more with 50 ml. of tetrahydrofuran. The combined tetrahydrofuran extracts were dried over Drierite, then analyzed by gas chromatography on a silicon-sorbitol column for isomeric diols. The experimental results are summarized in Table VI.

Examination of the Utility of *n*-Butylboroxine for the Separation of Isomeric Cyclic Diols.—Esterification of *cis*-cycloalkanediols with *n*-butylboroxine yields volatile cyclic boronates, whereas *trans*-cycloalkanediols, in most cases, yield non-volatile polymeric products.<sup>15</sup> To 10.0 g. of a mixture (56 mmoles) of *cis-trans*-1,3-cyclohexanediol was added 28.7 mmoles of *n*butylboroxine.<sup>18</sup> Benzene was added and the water of esterification removed by azeotropic distillation. The viscous product was subjected to vacuum distillation. There was obtained 6.24 g. of distillate, b.p. 100–103° (13 mm.),  $n^{20}$ D 1.4572.

The distillate, 6.24 g., was treated with 0.10 mole of ethylene glycol. Distillation yielded the ethylene glycol boronate, b.p.  $48-52^{\circ}$  (13 mm.). Recrystallization of the residue from ethyl acetate yielded 2.8 g. of crystalline *cis*-1,3-cyclohexanediol, m.p.  $85-86^{\circ}$ .<sup>19</sup>

The residue, 7.3 g. was treated with ethylene glycol and transformed by the above procedure into 4.6 g. of *trans*-1,3-cyclo-hexanediol, m.p. 114-116°. The recovery was 74%. Gas chromatographic analysis indicated that the two products were essentially pure.

In the same way 5.0 g. of cis-, trans-1,4-cyclohexanediol was converted into 1.42 g. of cis-, m.p. 105-107°, and 2.25 g. of trans-diol m.p. 140-142°, <sup>30</sup> a recovery of 72%. Treatment of a mixture of 68% cis- and 32% trans-1,2-cyclo-

Treatment of a mixture of 68% cis- and 32% trans-1,2-cyclohexanediol with *n*-butylboroxine yielded a distillate containing both diols. Consequently, the simple separation of the 1,4- and 1,3-isomers cannot be extended to the 1,2-isomer. However, gas chromatographic examination of the distillate revealed that the first fraction contained 76% cis- and 24% trans-, whereas the second fraction contained 31% cis- and 69% trans-1,2-cyclohexanediol. Consequently, the use of an efficient fractionating column would make the separation of these isomeric diols possible.

Hydroboration of Cyclopentadiene. (a) With Diborane.— In a 1-1. flask was placed 13.2 g. of cyclopentadiene (0.20 mole) in 300 ml. of tetrahydrofuran. The flask was kept at 0°. A solution of diborane (0.10 mole) in tetrahydrofuran (93 ml.) was added slowly to the diene. During the diborane addition the reaction mixture turned into a gel. The reaction was permitted to proceed for 12 hr. at  $20-25^{\circ}$ .

The excess of hydride was decomposed by adding water. The organoborane was oxidized at 50–60° with alkaline hydrogen peroxide (44 ml. of 3 N sodium hydroxide followed by 44 ml. of 30% hydrogen peroxide). The aqueous phase was saturated with solid potassium carbonate. The tetrahydrofuran extract obtained was dried over Drierite. The solvent was removed and the residue obtained was distilled under vacuum. There was obtained 16.3 g. of diol (80% yield) b.p.  $95^{\circ}$  (0.5 mm). Gas chromatographic analysis of the distillate indicated 85% transand 15% cis-1,3-cyclopentanediol. A 10.2-g. portion of the diol mixture (0.10 mole) was treated with 33.3 mmoles of *n*-butylboroxine. The water formed was removed by azeotropic distillation with benzene. Distillation at reduced pressure yielded 1.77 g. of a volatile distillate, b.p.  $80^{\circ}$  (10 mm.), and 15.1 g. of non-volatile residue.

The boron was displaced from the volatile boronic ester by adding 1 ml. of ethylene glycol. The ethylene glycol boronate (b.p. 48-52° (13 mm.)) was removed by distillation. Gas chromatographic analysis of the residue on a sorbitol-silicone column indicated 95% of *cis*- and 5% of *trans*-1,3-cyclopentanediol, m.p. of bisphenylurethane 160-162°.

The non-volatile residue (15.5 g.) yielded after displacement of the boron with ethylene glycol (0.10 mole) 7.55 g. of diol, b.p. 95° (0.5 mm.), m.p. 28–30°, m.p. di-*p*-nitrobenzoate 186–187°, m.p. bisphenylurethane 173–174°, reported<sup>14b</sup> for *trans*-1,3cyclopentanediol di-*p*-nitrobenzoate m.p. 184–185°. The infrared spectrum of the diol at high dilution in carbon tetrachloride indicated no chelated hydroxyl group.

indicated no chelated hydroxyl group. (b) With Thexylborane.—In a 500-ml. flask was placed 90 ml. of tetrahydrofuran. The flask was immersed in an ice bath. A solution of thexylborane in tetrahydrofuran (90 ml., 0.10 mole) and a solution of cyclopentadiene in tetrahydrofuran (90 ml., 50 mmoles) were added simultaneously to the tetrahydrofuran at 0° over a period of 30 min. The clear reaction mixture was maintained for 12 hr. at 0°, then water was added to decompose residual hydride. The organoborane was oxidized at 40-60° by adding 21 ml. of 3 N sodium hydroxide followed by dropwise addition of 21 ml. of 30% hydrogen peroxide. The reaction mixture was worked up as described above. The solvent was removed and the residue obtained was distilled. There was obtained 3.62 g. of product (71% yield), b.p. 92-94° (0.9 mm.), m.p. 27-30°. Gas chromatographic analysis of the distillate indicated 87% trans- and 13% -cis-1,3-cyclopentanediol, m.p. of bis-phenylurethane after recrystallization from benzene 172-173°.

(c) With Disiamylborane.—In a 300-ml. flask was placed 15.4 g, of 2-methyl-2-butene (0.22 mole) in 25 ml. of tetrahydrofuran. The flask was cooled to  $-15^{\circ}$ , then 58.8 ml. of a 0.935 M solution of diborane in tetrahydrofuran was added. The reaction mixture was allowed to remain overnight at 0°.

To 3.3 g. of cyclopentadiene (50 mmoles) in 50 ml. of tetrahydrofuran was added disiamylborane (0.11 mole) at 0°. The reaction mixture was kept 24 hr. at 0°, then water was added to decompose residual hydride. The organoborane was oxidized by adding 32 ml. of 3 N sodium hydroxide followed by 32 ml. 30% hydrogen peroxide. The reaction mixture was worked up in the usual way. Distillation yielded 3.57 g. of diol, b.p. 88-90° (0.5 mm)., m.p. bisphenylurethane 172-174°. Gas chromatographic analysis indicated 97% of *trans-* and 3% *cis-*1,3-cyclopentanediol. Nature of the Organobarane from the Hydroboration of Dienes

Nature of the Organoborane from the Hydroboration of Dienes. (a) 2,3-Dimethyl-1,3-butadiene.—To 15 ml. of tetrahydrofuran at 0° were added simultaneously 15 ml. of a solution of thexylborane (18.75 mmoles) and 15 ml. of a solution of 2,3-dimethyl-1,3-butadiene (0.768 g., 9.37 mmoles) in tetrahydrofuran. The reaction mixture was maintained for 2 hr. at 0°. Infrared analysis revealed two bands, at 3.91 and 6.31  $\mu$ , assigned to the terminal >BHR and the bridge >BH<sub>2</sub>B<. Assuming that the

<sup>(18)</sup> G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, J. Am. Chem. Soc., 79, 5194 (1957).

<sup>(19)</sup> M. F. Clark and L. N. Owen, J. Chem. Soc., 2103 (1950), report: cis-, m.p. 85.5°; trans-, m.p. 115.5°.

<sup>(20)</sup> L. N. Owen and P. A. Robins, *ibid.*, 320 (1949), report: *cis-*, m.p. 108-110°; *trans-*, m.p. 141°.

remaining 50% hydride is incorporated into dithexyldiborane, the relative intensities of the two bands were similar to that observed with a solution of thexylborane having the same concentration as the reaction mixture.

The clear reaction mixture was diluted with 0.8 ml. of absolute methanol, and the hydrogen evolved was collected. There was obtained 8.8 mmoles of hydrogen after 0.5 hr., 10.0 mmoles after 1 hr., 12.5 mmoles after 4 hr. and 15.2 mmoles after 12 hr.

(b) 1,4-Cyclohexadiene.—In a 500-ml. three-necked flask was placed 100 ml. of tetrahydrofuran. The flask was immersed in an ice bath, then 100 ml. of a solution of thexylborane (0.10 mole) and 100 ml. of a solution of 1,4-cyclohexadiene (4.0 g., 50 moles) in tetrahydrofuran were added simultaneously to the tetrahydrofuran at 0° over a period of 45 min. The reaction mixture was maintained for 24 hr. at 0°.

The infrared spectra of the reaction mixture revealed two bands, at  $4.02 \mu$  and at  $6.52 \mu$ , assigned to the terminal >BHR

and to the bridge >BH<sub>2</sub>B·<. The corresponding absorption bands in thexylborane are at 3.9  $\mu$  and 6.35  $\mu$ , respectively. The relative intensities of the two bands suggest that the remaining hydride is present as dithexyldiborane.

The reaction mixture was diluted with 5 ml. of anhydrous methanol, and the rate at which the hydrogen evolved was determined. Under the same conditions a solution of thexylborane of equal concentration was subjected to methanolysis. The results obtained are summarized in Table VIII.

The organoborane obtained after methanolysis was oxidized at  $40-50^{\circ}$  by adding 21 ml. of a 3 N solution of sodium hydroxide and 21 ml. of a 30% hydrogen peroxide. The aqueous layer was saturated with solid potassium carbonate. The tetrahydrofuran extract obtained was dried over Drierite. Removal of the solvent yielded a residue which was distilled. There was obtained 4.42 g. of a distillate, b.p. 96-98° (0.3 min.). Gas chromatographic analysis indicated a mixture of diols.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

# Hydroboration. XVII. An Examination of Several Representative Dialkylboranes as Selective Hydroborating Agents

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RECEIVED DECEMBER 26, 1962

The remarkable utility of bis-(3-methyl-2-butyl)-borane prompted an examination of the characteristics of several related dialkylboranes. Dicyclohexylborane, bis-(*trans*-2-methylcyclohexyl)-borane and diisopinocampheylborane are readily synthesized by the controlled hydroboration of cyclohexene, 1-methylcyclohexene and  $\alpha$ -pinene, respectively. In contrast to the 81:19 distribution realized in the hydroboration of styrene with diborane, these reagents react to place 99% of the boron at the terminal position. Similarly, in the hydroboration of *cis*-4-methyl-2-pentene these reagents react to place 96 to 97% of the boron at the less hindered of the two carbon atoms of the double bond. Diisopinocampheylborane exhibits an unusual specificity for *cis*-2-hexene in the presence of the *trans* isomer, permitting the isolation of the pure *trans*-2-hexene from a mixture in high yield. Finally, these reagents permit the selective hydroboration of 4-methyl-1-pentene in the presentially by displacement of  $\alpha$ -pinene, even at low temperatures. These results indicate that dicyclohexylborane, bis-(*trans*-2-methylcyclohexyl)-borane and diisopinocampheylborane are useful hydroboration reagents, comparable to bis-(3-methyl-2-butyl)-borane in providing steric control over the direction of hydroboration as well as high selectivity in the competitive hydroboration of two olefins of different structures. In particular, diisopinocampheylborane in certain applications which call for high selectivity.

The reaction of diborane with olefins and acetylenes is exceedingly rapid and almost non-selective.<sup>2,3</sup> The reaction of diborane with highly hindered olefins proceeds rapidly to the formation of mono- and dialkylboranes in specific instances.<sup>4,5</sup> These substituted boranes<sup>6</sup> offer promise of providing a group of more selective hydroborating agents.

For example, the controlled hydroboration of 2,3dimethyl-2-butene produces 2,3-dimethyl-2-butylborane (thexylborane).<sup>4,5</sup> This reagent exhibits some interesting properties as a selective hydroborating agent.<sup>7</sup> Similarly, the controlled hydroboration of 2methyl-2-butene produces bis-(3-methyl-2-butyl)-borane (disiamylborane). This reagent has exhibited remarkable versatility as a reagent for the selective hydroboration of olefins,<sup>8</sup> dienes<sup>9</sup> and acetylenes.<sup>10</sup> The remarkable versatility of disiamylborane sug-

The remarkable versatility of disiamylborane suggested an examination of several related dialkylboranes. Accordingly, the utility of dicyclohexylborane, bis-

 Post-doctorate research associate, 1961-1963, on grants (G-6273 and G-19878) provided by the National Science Foundation.
 For a summary of the data and pertinent references, see H. C. Brown,

"Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(3) H. C. Brown and A. W. Moerikofer, J. Am. Chem. Soc., 86, 2063 (1963).

(4) H. C. Brown and A. W. Moerikofer, *ibid.*, 84, 1478 (1962).

(5) H. C. Brown and G. J. Klender, Inorg. Chem., 1, 204 (1962).

(6) It has been demonstrated in several cases that these derivatives exist as dimers in tetrahydrofuran solution. Consequently, these derivatives are sym-dialkyldiboranes and sym-tetraalkyldiboranes (ref. 5). However, it is convenient to refer to these derivatives in their monomeric form except where the dimeric nature of the molecule becomes a factor in the reaction under consideration.

- (7) G. Zweifel and H. C. Brown, J. Am. Chem. Soc., 85, 2066 (1963).
- (8) H. C. Brown and G. Zweifel, ibid., 83, 1241 (1961).

(9) G. Zweifel, K. Nagase and H. C. Brown, ibid., 84, 190 (1962).

(10) H. C. Brown and G. Zweifel, ibid., 83, 3834 (1961).

(trans-2-methylcyclohexyl)-borane, and diisopinocampheylborane, readily synthesized by the hydroboration of cyclohexene, 1-methylcyclohexene and  $\alpha$ -pinene, respectively, was examined in several typical selective hydroborations.

#### Results

Directive Effects in the Hydroboration of Styrene.— The hydroboration of styrene with diborane at 0° proceeds to place 81% of the boron on the terminal carbon atom and 19% on the  $\alpha$ -position.<sup>11</sup> The use of disiamylborane alters this distribution to place 98% on the terminal position.<sup>8</sup> Accordingly, styrene appeared to provide a rigorous test case in evaluating the utility of dialkylboranes in providing steric control of the direction of hydroboration.

The dialkylborane (25 mmoles), prepared in diglyme solution or suspension, was treated at  $-15^{\circ}$  with 25 mmoles of styrene in 10 ml. of diglyme. The reaction was carried out at 0° to completion, except in the case of bis-(trans-2-methylcyclohexyl)-borane. The latter derivative is exceedingly insoluble in diglyme and it was necessary to raise the temperature to 25° in order to have the reaction proceed at a reasonable rate. The organoboranes were oxidized with alkaline hydrogen peroxide and the alcohols formed analyzed by gas chromatography on a Carbowax-20M column. The results are summarized in Table I.

In one experiment styrene was added to a large excess of diborane (styrene/ $BH_3 = 1:2$ ) in tetrahydrofuran. The isomer distribution was modified only slightly, from 80:20 to 75:25.

(11) H. C. Brown and G. Zweifel, *ibid.*, 82, 4708 (1960).