

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 mmoles) 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 μ and at 6.52 μ , assigned to the terminal >BHR

and to the bridge >BH₂B<. The corresponding absorption bands in thexylborane are at 3.9 μ and 6.35 μ , 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° 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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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 α -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 presence of 2-methyl-1-pentene. In the case of relatively hindered olefins, diisopinocampheylborane reacts preferentially by displacement of α -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 appears to be especially promising in offering significant advantages over bis-(3-methyl-2-butyl)-borane in certain applications which call for high selectivity.

The reaction of diborane with olefins and acetylenes is exceedingly rapid and almost non-selective.^{2,3} The reaction of diborane with highly hindered olefins proceeds rapidly to the formation of mono- and dialkylboranes in specific instances.^{4,5} These substituted boranes⁶ offer promise of providing a group of more selective hydroborating agents.

For example, the controlled hydroboration of 2,3-dimethyl-2-butene produces 2,3-dimethyl-2-butylborane (thexylborane).^{4,5} This reagent exhibits some interesting properties as a selective hydroborating agent.⁷ Similarly, the controlled hydroboration of 2-methyl-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,⁸ dienes⁹ and acetylenes.¹⁰

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

(*trans*-2-methylcyclohexyl)-borane, and diisopinocampheylborane, readily synthesized by the hydroboration of cyclohexene, 1-methylcyclohexene and α -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 α -position.¹¹ The use of disiamylborane alters this distribution to place 98% on the terminal position.⁸ 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° 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/BH₃ = 1:2) in tetrahydrofuran. The isomer distribution was modified only slightly, from 80:20 to 75:25.

(1) Post-doctorate research associate, 1961–1963, on grants (G-6273 and G-19878) provided by the National Science Foundation.

(2) 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.*, **85**, 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).

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

TABLE I

DIRECTIVE EFFECTS IN THE HYDROBORATION OF STYRENE WITH DIBORANE AND VARIOUS ALKYLBORANES IN DIGLYME

Borane	Reaction time, hr.	Temp., °C.	Alcohol distribution, %	
			1-Phenyl-ethanol	2-Phenyl-ethanol
Diborane ^a	1	0	19	81
Thexylborane ^b	2	0	4	96
Disiamylborane ^c	2	0	2	98
Dicyclohexylborane	12	0	1	99
Bis-(<i>trans</i> -2-methylcyclohexyl)-borane	24	25	1	99
Diisopinocampheylborane	2	0	1	99

^a Reference 11. ^b Reference 7. ^c Reference 8.

It is evident that in the hydroboration of styrene, the three dialkylboranes under examination exhibit a selectivity comparable to that shown by disiamylborane.

Directive Effects in the Hydroboration of *cis*-2-Hexene.—The hydroboration of *cis*-2-hexene with diborane proceeds to place approximately 50% of the boron on each of the two carbon atoms of the double bond.¹¹ Accordingly, this olefin was selected in order to test the ability of the dialkylborane to achieve the selective hydroboration of the less hindered 2-position. The experimental conditions and procedures were similar to those described for the corresponding experiments with styrene. The isomeric hexanols were analyzed by gas chromatography on a composite column: Theed (1 m.)-1,2,3-tris-(β -cyanoethoxy)-propane (1 m.). The results are summarized in Table II.

TABLE II

DIRECTIVE EFFECTS IN THE HYDROBORATION OF *cis*-2-HEXENE WITH DIBORANE AND VARIOUS ALKYLBORANES IN DIGLYME

Borane	Reaction time, hr.	Temp., °C.	Alcohol distribution, % ^a	
			3-Hexanol	2-Hexanol
Diborane	2	20	50	50
Thexylborane	4	0	44	56
Disiamylborane	3	0	37	63
Dicyclohexylborane	3	25	34	66
Bis-(<i>trans</i> -2-methylcyclohexyl)-borane ^b	16	25	33	67
Diisopinocampheylborane	3	0	38	62

^a The total yield of alcohols by gas chromatographic analysis was 80–90% except in the case of bis-(*trans*-2-methylcyclohexyl)-borane. ^b Reaction incomplete, with a total yield of 65% indicated by the analysis.

In view of the marked similarity of the two alkyl groups, *n*-propyl *vs.* methyl, the selectivity realized must be considered reasonable.

Directive Effects in the Hydroboration of *cis*- and *trans*-4-Methyl-2-pentene.—The hydroboration of *cis*- and *trans*-4-methyl-2-pentene with diborane results in only a moderate selectivity (60:40) for the less substituted of the two carbon atoms of the double bond. However, the larger steric requirement of the isopropyl group, as compared to that of the methyl group, provided a more reasonable test of the ability of dialkylboranes to achieve selective hydroboration of the double bond at the less hindered position.

The results are summarized in Table III. Because of the sluggishness of the reaction of bis-(*trans*-2-methylcyclohexyl)-borane with these olefins, it was not included in this study.

The results reveal a marked selectivity of the dialkylboranes for the less hindered position of the double bond, with one exception. In the case of the reaction of diisopinocampheylborane, the results revealed only 4% substitution at the more hindered position of the *cis*-4-

TABLE III

DIRECTIVE EFFECTS IN THE HYDROBORATION OF *cis*- AND *trans*-4-METHYL-2-PENTENE WITH DIBORANE AND VARIOUS ALKYLBORANES IN DIGLYME

Borane	Reaction time, hr.	Temp., °C.	Isomer	Alcohol distribution, %	
				2-Methyl-3-pentanol	4-Methyl-2-pentanol
Diborane	1	25	<i>cis</i>	38	62
	1	25	<i>trans</i>	43	57
Thexylborane ^a	4	0	<i>cis</i>	34	66
	4	0	<i>trans</i>	40	60
Disiamylborane ^b	12	25	<i>cis</i>	3	97
	12	25	<i>trans</i>	5	95
Dicyclohexylborane	12	0	<i>cis</i>	3	97
	12	0	<i>trans</i>	7	93
Diisopinocampheylborane	12	0	<i>cis</i>	4	96
	12	0	<i>trans</i>	32	68

^a Reference 7. ^b Reference 8.

methyl-2-pentene, but 32% substitution at the corresponding position of the *trans* isomer.

This difference was surprising. However, examination of the reaction mixture revealed that the reaction of the *trans* isomer with diisopinocampheylborane proceeded with displacement of α -pinene. Indeed, one mole of α -pinene was formed for every two moles of *trans*-4-methyl-2-pentene which underwent hydroboration (Table IV).

TABLE IV

DISPLACEMENT OF α -PINENE IN THE REACTION OF DIISOPINOCAMPEHYLBORANE WITH *trans*-4-METHYL-2-PENTENE AT 0°

<i>trans</i> -4-Methyl-2-pentene, ^a mmoles	Reaction time, hr.	Olefin reacted, mmoles	α -Pinene formed, mmoles
25	0	0	2.2
25	10	12.5	5.6
25	24	25	12.6
50	13	12.2	12.0
50	24	42.5	21.0

^a Diisopinocampheylborane, 25 mmoles.

In the case of *cis*-4-methyl-2-pentene, the displacement of α -pinene from the reagent is negligible. Consequently, the reaction of the two isomers with diisopinocampheylborane appears to follow different courses.

The Competitive Hydroboration of 2-Methyl-1-pentene and 4-Methyl-1-pentene.—The hydroboration-isomerization-displacement reaction of the organoborane from 2-methyl-2-pentene produces a mixture of approximately 40% 2-methyl-1-pentene and 60% 4-methyl-1-pentene.^{12,13} It appeared that the selective hydroboration of 4-methyl-1-pentene in the presence of its isomer might provide a fairly vigorous test of the relative selectivity of the different reagents.

Accordingly, an equimolar mixture of 2-methyl-1-pentene and 4-methyl-1-pentene was treated with sufficient reagent to react with one-half of the olefin used. After an appropriate time, water was added to destroy any remaining reagent. The residual olefin was determined by gas chromatography. The results are summarized in Table V.

The Competitive Hydroboration of *cis*- and *trans*-2-Hexene.—It had been demonstrated previously that disiamylborane reacts preferentially with *cis*-2-hexene, permitting the selective removal of this isomer from the *trans* derivative.⁸ Indeed, a kinetic study revealed that the *cis* isomer reacts approximately six times faster than the corresponding *trans* derivatives.¹⁴

(12) H. C. Brown and M. V. Bhatt, *J. Am. Chem. Soc.*, **82**, 2074 (1960).(13) H. C. Brown and G. Zweifel, *ibid.*, **82**, 1504 (1960).(14) H. C. Brown and A. W. Moerikofer, *ibid.*, **83**, 3417 (1961).

TABLE V

THE COMPETITIVE HYDROBORATION OF AN EQUIMOLAR MIXTURE OF 2-METHYL-1-PENTENE AND 4-METHYL-1-PENTENE IN DIGLYME AT 0°

Borane	Reaction time, hr.	—Residual olefin, mmoles—	
		2-Methyl-1-pentene	4-Methyl-1-pentene
Disiamylborane	0	25	25
	2	21	3.5
Dicyclohexylborane ^a	0	25	25
	12	19	2.5
Diisopinocampheylborane	0	25	25
	2	21	3.0

^a Reaction was not complete, even after 12 hr., since a small quantity of hydrogen was evolved on addition of water.

To test the relative effectiveness of the dialkylboranes for this separation, 25 mmoles of the 2-hexene (51% *cis*-, 49% *trans*-) was treated with 25 mmoles of the dialkylborane. The reaction mixture, in diglyme, was maintained at 0° and samples were withdrawn at appropriate time intervals, quenched and analyzed by gas chromatography for residual olefin. The experimental results are summarized in Table VI.

TABLE VI

THE COMPETITIVE HYDROBORATION OF A MIXTURE OF *cis*- AND *trans*-2-HEXENE WITH VARIOUS DIALKYLBORANES IN DIGLYME AT 0°

Borane	Reaction time, hr.	Residual olefin, %		Yield of <i>trans</i> -2-hexene, %
		<i>cis</i> -Hexene, %	<i>trans</i> -Hexene, %	
Disiamyl-	0	51	49	..
	1	21	79	70
	2	10	90	52
	4	3	97	33
Dicyclohexyl-	0	51	49	..
	2	44	56	95
	4	36	64	88
	8	17	83	66
Diisopinocampheyl-	0	51	49	..
	1	2	98	83
	1.5	1	99	79
	2	1	99	73

It is evident that diisopinocampheylborane permits a remarkably clean separation of the *cis*-2-hexene with only minor amounts of the *trans* isomer lost in the process.

Discussion

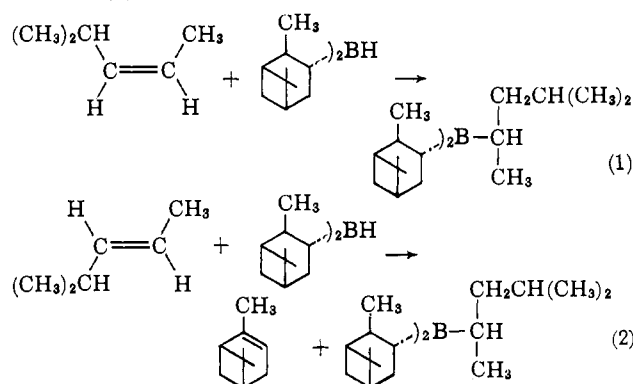
The hydroboration of styrene with diborane gives 20% of the boron on the α -carbon atom and 80% on the terminal carbon.¹¹ The use of disiamylborane greatly reduces the α -derivative with a 2:98 distribution noted.⁸ It is evident from the results realized in the present investigation that the three dialkylboranes studied, namely, dicyclohexylborane, bis-(*trans*-2-methylcyclohexyl)-borane and diisopinocampheylborane, are all equally effective in directing the addition of the boron atom to the terminal carbon atom of the double bond (Table I).

It should be pointed out that hexylborane likewise exhibits considerably greater selectivity for the terminal position (4% α),⁷ as compared to diborane itself. The reaction of styrene with diborane must proceed through three successive stages,⁸ phenylethylborane, bis-(phenylethyl)-borane and tris-(phenylethyl)-borane. Since hexylborane exhibits such a high selectivity for the terminal position, it is probable that both phenylethylborane and bis-(phenylethyl)-borane must exhibit comparable selectivity for the terminal position. This suggests that most of the 20% of the α -derivative must

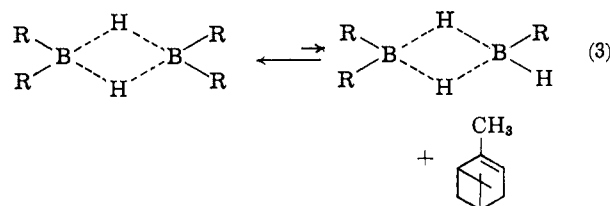
be formed in the initial stage of the reaction. On the basis of this argument, the initial reaction of borane with styrene must be essentially non-selective, placing the boron almost equally on the α and β carbon atoms.

We attempted to test this hypothesis by adding styrene to a large excess of diborane (1 styrene/2 BH₃). However, a 25:75 ratio was obtained, which is comparable to 20% α - and 80% β -derivative realized when the reaction was carried out in the stoichiometric ratio (3 styrene/1 BH₃). Therefore, it appears that the partially alkylated boranes derived from styrene are able to compete successfully with the borane (BH₃) for the remaining olefin.

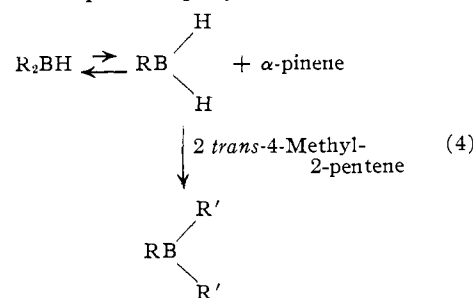
The conclusion that all of the dialkylboranes are equally effective in directing substitution to the less substituted carbon atom of the unsaturated hydrocarbon is confirmed by the results realized with *cis*-2-hexene (Table II) and *cis*- and *trans*-4-methyl-2-pentene (Table III). Only in the case of the hydroboration of *trans*-4-methyl-2-pentene by diisopinocampheylborane is the observed distribution less favorable. In this case the reaction path changes from a simple addition reaction (1), to a displacement reaction (2).



It was previously pointed out that diisopinocampheylborane, or its dimer, *sym*-tetraisopinocampheyl-diborane, appears to exist in equilibrium with α -pinene and trisopinocampheyl-diborane (3).⁵ In the case of



an olefin which reacts relatively rapidly with the reagent, such as *cis*-2-hexene and *cis*-4-methyl-2-pentene, the addition (1) occurs before very much dissociation (3) has occurred. With less reactive olefins, such as *trans*-4-methyl-2-pentene, the addition reaction is much slower. Consequently, the dissociation becomes the predominant reaction path and the hydroboration reaction proceeds through the trisopinocampheyl-diborane or monoisopinocampheylborane (4). Just as



monothexylborane exhibits much lower selectivity than the dialkylboranes, it is not surprising that hydroboration *via* this path should exhibit much lower selectivity. As a matter of fact the data indicate that the selectivity of monoisopinocampheylborane is very similar to that of the hexylborane (Table III).

In the selective hydroboration of *cis*-2-hexene in the presence of the *trans* isomer and in the selective hydroboration of 4-methyl-1-pentene in the presence of 2-methyl-1-pentene, diisopinocampheylborane exhibits a selectivity which is superior to that of the other dialkylboranes examined. Consequently, it appears that this reagent should join disiamylborane as an especially valuable selective reagent for the controlled hydroboration of olefins.

α -Pinene, used for the synthesis of diisopinocampheylborane, is readily available from natural sources in both dextro- and levorotatory form. This makes readily available an asymmetric hydroboration reagent. It was previously reported that diisopinocampheylborane exhibits a remarkable capacity for the conversion of *cis* olefins into alcohols of high optical purity.¹⁵ Moreover, its utility for the separation of racemic mixtures of olefins has been demonstrated.¹⁶ Consequently, it appears that diisopinocampheylborane has a most promising future. It is a selective hydroborating agent and has made the asymmetric synthesis of optically active organoboranes possible, thus providing a means for the assignment of absolute configurations to alcohols and olefins.¹⁷

A detailed discussion of the application of diisopinocampheylborane to asymmetric synthesis is contained in the next publication in this series.

Experimental

Materials.—Diglyme and boron trifluoride etherate were purified as described earlier. Boron trifluoride diglymate was prepared in the following way. Diglyme (50 ml.) was cooled in an ice bath, 25 ml. of boron trifluoride ethyl etherate added and the ether was removed by applying vacuum (5–10 mm.) for 20 min., maintaining the flask at 20–25°. The remaining boron trifluoride diglymate was approximately 3.65 *M*. The reagent was stored at 0°.

The olefins used, their physical constants and source were reported in earlier papers. α -Pinene ($[\alpha]^{20}_D \pm 48^\circ$, n^{20}_D 1.4660) was supplied by the Hercules Powder Co. and the Glidden Co.

Preparation of Dicyclohexylborane.—In a 100-ml. three-necked flask equipped with a thermometer, condenser, pressure equalizing funnel and a side arm, capped with a rubber septum to permit removal of samples, were placed 50 mmoles of cyclohexene (4.1 g.) in 20 ml. of diglyme and 19.7 ml. of a 1 *M* solution of sodium borohydride in diglyme. The flask was immersed in an ice bath. Diborane was generated by adding 3.3 ml. of boron trifluoride etherate (26.3 mmoles) diluted with 7 ml. of diglyme to the well stirred reaction mixture over a period of 15 min. During the boron trifluoride addition, the dialkylborane precipitated from solution. The reagent was maintained for an additional 3 hr. at 0° prior to its use.

Under similar experimental conditions optically active α -pinene ($[\alpha]^{20}_D \pm 48^\circ$) was converted into diisopinocampheylborane and 1-methylcyclohexene into bis-(*trans*-2-methylcyclohexyl)-borane.

Hydroboration of Styrene with Dicyclohexylborane.—To the dicyclohexylborane (25 mmoles) was added, at -15° a solution (10 ml.) of styrene (25 mmoles, 2.6 g.) in diglyme. The reaction

was permitted to proceed for 12 hr. at 0°. At this point the reaction mixture was nearly homogenous. Then water was added to decompose residual hydride. The organoborane formed was oxidized at 30–50° by adding 8 ml. of 3 *N* sodium hydroxide followed by dropwise addition of 8 ml. of 30% hydrogen peroxide. The reaction mixture was extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and analyzed by gas chromatography on a 1-m. Carbowax 20M column for 1-phenyl-1-ethanol and 2-phenyl-1-ethanol.

Similarly, styrene was hydroborated with diisopinocampheylborane and with bis-(*trans*-2-methylcyclohexyl)-borane. The latter reagent reacted very slowly with styrene at 0°; consequently the reaction was carried out at room temperature. The results are summarized in Table I.

Hydroboration of *cis*-4-Methyl-2-pentene with Diisopinocampheylborane.—Diisopinocampheylborane (25 mmoles) was diluted with a solution (10 ml.) of *cis*-4-methyl-2-pentene (25 mmoles, 2.1 g.) in diglyme at -15° . The reaction mixture was maintained at 0°. The excess of hydride was decomposed by adding a few ml. of water. The organoborane was oxidized in the usual way by adding 8 ml. of 3 *N* sodium hydroxide followed by 8 ml. of 30% hydrogen peroxide. The reaction mixture was worked up as described above. The dried ether extract was analyzed by gas chromatography on a 1-m. diglycerol followed by a 1-m. tris-(β -cyanoethoxy)-propane column (to retain diglyme) for 4-methyl-2-pentanol and 2-methyl-3-pentanol.

Under similar experimental conditions, *cis*-2-hexene was hydroborated with various dialkylboranes. The results of these investigations are summarized in Tables II and III.

Displacement of α -Pinene in the Reaction of *trans*-4-Methyl-2-pentene.—(a) **Preparation of Diisopinocampheylborane.**—In a 100-ml. flask were placed 19.7 ml. of a 1 *M* solution of sodium borohydride in diglyme (5% excess) and 50 mmoles of α -pinene (6.8 g., $[\alpha]^{20}_D -48^\circ$) in 10 ml. of diglyme. The flask was immersed in an ice bath. Boron trifluoride diglymate (7.2 ml. of a 3.56 *M* solution) was added to the well stirred olefin-sodium borohydride mixture (magnetic stirrer). The flask was maintained for an additional 4 hr. at 0°. The dialkylborane separated as a thick white precipitate.

The reaction mixture was hydrolyzed with water, then oxidized at 30–50° by adding 5.5 ml. of 3 *N* sodium hydroxide followed by 5.5 ml. of 30% hydrogen peroxide. Analysis of the ether extract using *m*-xylene as internal standard revealed 2.2 mmoles of unreacted α -pinene, which amounts to 4% of the α -pinene used.

(b) **Hydroboration of *trans*-4-Methyl-2-pentene.**—To 25 mmoles of diisopinocampheylborane, prepared as described above, were added 2.1 g. of *trans*-4-methyl-2-pentene (25 mmoles) and 12.5 mmoles of methylcyclohexane (1.225 g., as internal standard) at -15° . The reaction was allowed to proceed at 0°. At appropriate time intervals, 1-ml. samples were withdrawn and quenched in a saturated sodium chloride solution. The upper phase formed was analyzed by gas chromatography on an adiponitrile column for unreacted *trans*-4-methyl-2-pentene using methylcyclohexane as reference.

The reaction mixture was hydrolyzed with water and the organoborane was oxidized in the usual way. After completion of the oxidation, the reaction mixture was diluted with 20 ml. of *n*-hexane and 0.526 g. of *m*-xylene (4.96 mmoles). The latter served as internal standard for α -pinene. The reaction mixture was stirred, then a few milliliters of the upper phase formed were withdrawn, dried and analyzed by gas chromatography on an Ucon polar column for α -pinene. The results of these investigations are summarized in Table IV.

Competitive Hydroboration of a Mixture of *cis*- and *trans*-2-Hexene.—To 25 mmoles of the dialkylborane at -15° was added 25 mmoles of a 51:49 mixture of *cis*- and *trans*-2-hexene (2.1 g.) containing cyclohexane as internal standard. The reaction was permitted to proceed at 0–3°. Samples were removed at appropriate time intervals, then quenched with a saturated solution of sodium chloride. The upper phase formed was analyzed by chromatography on an adiponitrile column for remaining *cis*- and *trans*-2-hexene, using the internal standard as reference.

Similarly, an equimolar mixture of 2-methyl-1-pentene (25 mmoles) and 4-methyl-1-pentene (25 mmoles) was hydroborated with 25 mmoles of various dialkylboranes. The results of these investigations are summarized in Tables V and VI.

(15) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961).

(16) H. C. Brown, N. R. Ayyangar and G. Zweifel, *ibid.*, **84**, 4341 (1962).

(17) G. Zweifel, N. R. Ayyangar and H. C. Brown, *ibid.*, **84**, 4342 (1962).