

Organic Reactions

VOLUME 13

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PREFACE TO THE SERIES

In the course of nearly every program of research in organic chemistry the investigator finds it necessary to use several of the better-known synthetic reactions. To discover the optimum conditions for the application of even the most familiar one to a compound not previously subjected to the reaction often requires an extensive search of the literature; even then a series of experiments may be necessary. When the results of the investigation are published, the synthesis, which may have required months of work, is usually described without comment. The background of knowledge and experience gained in the literature search and experimentation is thus lost to those who subsequently have occasion to apply the general method. The student of preparative organic chemistry faces similar difficulties. The textbooks and laboratory manuals furnish numerous examples of the application of various syntheses, but only rarely do they convey an accurate conception of the scope and usefulness of the processes.

For many years American organic chemists have discussed these problems. The plan of compiling critical discussions of the more important reactions thus was evolved. The volumes of *Organic Reactions* are collections of chapters each devoted to a single reaction, or a definite phase of a reaction, of wide applicability. The authors have had experience with the processes surveyed. The subjects are presented from the pre-viewpoint, and particular attention is given to limitations, influencing influences, effects of structure, and the selection of experimental uses. Each chapter includes several detailed procedures illustrating significant modifications of the method. Most of these procedures have been found satisfactory by the author or one of the editors, but unlike those in *Organic Syntheses* they have not been subjected to careful testing in two or more laboratories. When all known examples of the reaction are not mentioned in the text, tables are given to list compounds which have been prepared by or subjected to the reaction. Every effort has been made to include in the tables all such compounds and references; however, because of the very nature of the reactions discussed and their frequent use as one of the several steps of syntheses in which not all of the intermediates have been isolated, some instances may well have been missed. Nevertheless, the investigator will be able

to use the tables and their accompanying bibliographies in place of most or all of the literature search so often required.

Because of the systematic arrangement of the material in the chapters and the entries in the tables, users of the books will be able to find information desired by reference to the table of contents of the appropriate chapter. In the interest of economy the entries in the indices have been kept to a minimum, and, in particular, the compounds listed in the tables are not repeated in the indices.

The success of this publication, which will appear periodically, depends upon the cooperation of organic chemists and their willingness to devote time and effort to the preparation of the chapters. They have manifested their interest already by the almost unanimous acceptance of invitations to contribute to the work. The editors will welcome their continued interest and their suggestions for improvements in *Organic Reactions*.

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CHAPTER 1

HYDRATION OF OLEFINS, DIENES, AND ACETYLENES VIA HYDROBORATION

GEORGE ZWEIFEL AND HERBERT C. BROWN

Purdue University

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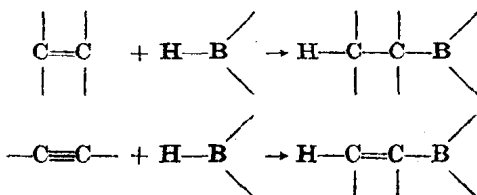
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INTRODUCTION

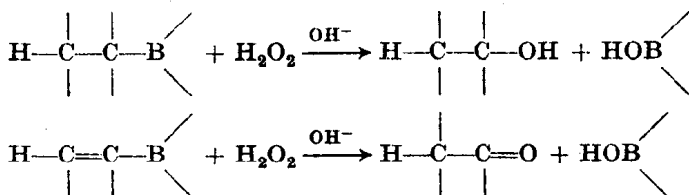
The hydroboration of olefins, dienes, and acetylenes involves the addition of a boron-hydrogen bond to the carbon-carbon multiple bond.^{1,2} This



¹ Brown and Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956); **81**, 6423, 6428 (1959); *J. Org. Chem.*, **22**, 1136 (1957).

² Brown and Zweifel, *J. Am. Chem. Soc.*, **81**, 1512 (1959); **83**, 3834 (1961).

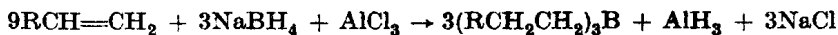
reaction provides a new convenient route to the corresponding organoboranes and makes them readily available as intermediates in organic synthesis. One of the important reactions which the organoboranes undergo is the rapid and essentially quantitative oxidation with alkaline hydrogen peroxide.



The hydroboration of olefins involves a *cis* addition of the boron-hydrogen bond, the boron atom becoming attached to the less substituted of the two olefinic carbon atoms of the double bond. Furthermore the oxidation occurs with retention of configuration, placing the hydroxyl group at the precise position occupied by the boron atom in the initial organoborane. Both the hydroboration and the oxidation reactions appear to be free of the carbon skeleton rearrangements that occasionally accompany other hydration procedures. As a result, hydroboration followed by oxidation with alkaline hydrogen peroxide has become an important new synthetic method for the anti-Markownikoff, *cis* hydration of double bonds.

This chapter surveys the available information on the hydration of olefins, dienes, acetylenes, and their derivatives by the hydroboration-oxidation procedure.*

Early observations on the reaction of diborane with olefins indicated that the reaction required elevated temperatures and long reaction periods³ and did not provide a convenient route to organoboranes. Later it was observed that anhydrous aluminum chloride enhanced the reducing power of sodium borohydride to the point where the reagent at room temperature readily reduced substances such as nitriles and esters, groups which are normally resistant to sodium borohydride itself.⁴ Even more unexpected was the observation that olefins reacted with the reagent, utilizing one B-H equivalent per molecule of olefin and forming an organoborane.⁴

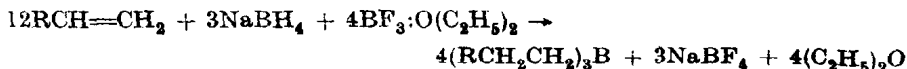


* Another survey is to be found in an article by Brown, *Tetrahedron*, **12**, 117 (1961), and a detailed treatment of the hydroboration reaction and of the synthetic applications of the resulting organoboranes is given by Brown, *Hydroboration*, W. A. Benjamin, New York, 1962.

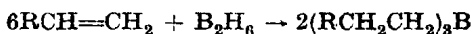
³ Hurd, *J. Am. Chem. Soc.*, **70**, 2053 (1948); Stone and Eméleus, *J. Chem. Soc.*, **1950**, 2755; Whatley and Pease, *J. Am. Chem. Soc.*, **76**, 835 (1954); Stone and Graham, *Chem. & Ind. (London)*, **1955**, 1881.

⁴ Brown and Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956); **81**, 6423 (1959).

This discovery led to the search for alternative procedures for hydroboration. It was found that hydroboration could readily be achieved by treating an olefin with sodium borohydride and boron trifluoride in an appropriate solvent.



It was also discovered that, contrary to the impression given by the earlier reports, diborane itself adds rapidly and quantitatively to olefins in ether solvents.¹



The reaction appears to be as general as the addition of hydrogen or bromine to multiple carbon-carbon bonds.

Johnson and Van Campen had noted that alkaline hydrogen peroxide effected a complete dealkylation of tri-*n*-butylborane and related organoboranes to form alcohols and boric acid.⁵ A detailed study of this reaction revealed that the oxidation is essentially quantitative at 25°, that the solvents utilized for the hydroboration do not interfere with the oxidation and hence the reaction can be performed without isolating the organoborane, and that the reaction is of very wide generality.⁶

The subject matter of this chapter is limited to hydroboration-oxidation as a specific combination for the hydration of multiple carbon-carbon bonds under mild conditions. It may be noted, however, that organoboranes undergo protonolysis in the presence of carboxylic acids, providing a non-catalytic means of hydrogenating multiple carbon-carbon bonds.⁷ Organoboranes also undergo coupling on treatment with alkaline silver nitrate, and this reaction provides a new synthesis for carbon-carbon bonds.⁸

HYDROBORATION OF OLEFINS

As a result of the developments outlined above, two convenient procedures are available for the hydroboration of olefins under mild conditions: (1) treatment of a mixture of the unsaturated compound and an alkali metal borohydride in a suitable solvent with boron trifluoride etherate (or other acid), and (2) external generation of diborane followed by its reaction with the unsaturated compound in an appropriate solvent. Each of these procedures possesses advantages that will lead to its selection for specific reactions. Both procedures are described in the section on Experimental Procedures.

⁵ Johnson and Van Campen, *J. Am. Chem. Soc.*, **60**, 121 (1938).

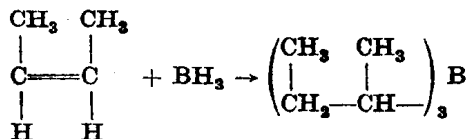
⁶ H. C. Brown, C. H. Snyder, B. C. Subba Rao, and G. Zweifel, to be published.

⁷ Brown and Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959).

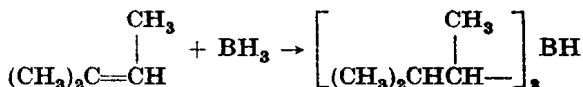
⁸ Brown, Hébert, and Snyder, *J. Am. Chem. Soc.*, **83**, 1001 (1961); Brown and Snyder, *ibid.*, **83**, 1001 (1961); Brown, Verbrugge, and Snyder, *ibid.*, **83**, 1002 (1961).

Scope and Stoichiometry

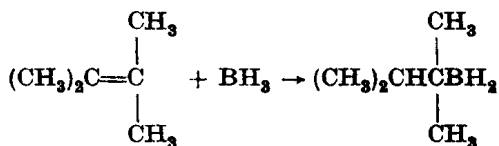
The hydroboration reaction has been applied to a large number of olefins of widely different structures. In practically all cases the reaction proceeds simply and rapidly. Only the most hindered olefins exhibit any resistance to addition. Simple olefins commonly utilize all the hydrogen atoms of diborane and form the trialkylborane.



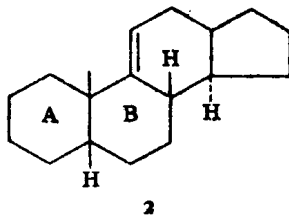
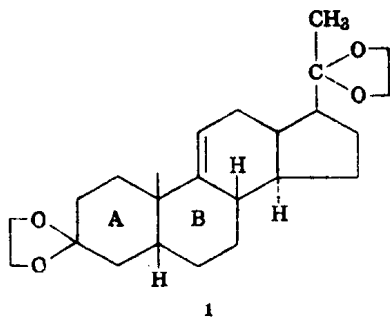
However, trisubstituted olefins, such as 2-methyl-2-butene and 1-methylcyclohexene, utilize only two of the three hydrogen atoms of the borane group forming a dialkylborane.



Further reaction to form a trialkylborane is very slow at room temperature. Finally, tetrasubstituted olefins, such as tetramethylethylene, react rapidly to utilize only one hydrogen atom of the borane group and form the monoalkylborane.



Up to the present time only two olefins, the steroids 1 and 2 (Refs. 9 and 10, respectively), have been reported not to undergo hydroboration.



⁹ Wechter, *Chem. & Ind. (London)*, 1959, 294.

¹⁰ Nussim and Sondheimer, *Chem. & Ind. (London)*, 1960, 400.

On the other hand, the analogous compounds with the A/B-*trans* junction do undergo hydroboration.

The stoichiometry of the hydroboration reaction for a number of representative olefins is summarized in Table I.

TABLE I
STOICHIOMETRY OF HYDROBORATION OF REPRESENTATIVE OLEFINS^{1,11}

	Acyclic Olefins		Cyclic Olefins
(a)	3 Olefin + BH ₃ $\xrightarrow{20^\circ}$ Trialkylborane, R ₃ B		
	2-Methyl-1-butene		Cyclopentene
	3-Methyl-1-butene		Cyclohexene
	1-Hexene		Cycloheptene
	2-Hexene		Norbornene
	3-Hexene		β -Pinene
	4-Methyl-2-pentene		
	3,3-Dimethyl-1-butene		
	2,4,4-Trimethyl-1-pentene		
	Styrene		
	α -Methylstyrene		
	1-Tetradecene		
(b)	2 Olefin + BH ₃ $\xrightarrow{20^\circ}$ Dialkylborane, R ₂ BH		
	2-Methyl-2-butene		1-Methylcyclopentene
	4,4-Dimethyl-2-pentene		1-Methylcyclohexene
	2,4,4-Trimethyl-2-pentene		α -Pinene
(c)	1 Olefin + BH ₃ $\xrightarrow{20^\circ}$ Monoalkylborane, RBH ₂		
	2,3-Dimethyl-2-butene		1,2-Dimethylcyclopentene
	2,2,5,5-Tetramethyl-3-hexene ¹²		1,2-Dimethylcyclohexene

Directive Effects¹³

The oxidation of an organoborane to an alcohol by alkaline hydrogen peroxide is essentially quantitative and proceeds without rearrangement. Consequently, the structure of the alcohol formed serves to locate the position of the boron atom in the organoborane.

Terminal olefins, RCH=CH₂, give predominantly addition of the boron atom to the terminal carbon atom (93–94%). Thus hydroboration of 1-hexene yields an organoborane which, upon oxidation with alkaline hydrogen peroxide, is converted to a mixture composed of 94% 1-hexanol and 6% 2-hexanol. Similar results are observed with 1-butene, 1-pentene,

¹¹ Brown and Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

¹² Logan and Flautt, *J. Am. Chem. Soc.*, **82**, 3446 (1960).

¹³ Brown and Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

and 1-octene, establishing the predominantly *anti*-Markownikoff direction of addition.¹ Branching of the alkyl chain as in 3-methyl-1-butene, 3,3-dimethyl-1-butene, and 4,4-dimethyl-1-pentene makes no essential difference in the direction of addition.

The presence of an alkyl substituent in the 2 position increases the directive effect. The boron atom adds to the terminal position of olefins such as 2-methyl-1-butene to the extent of 99%.

TABLE II
DIRECTIVE EFFECTS IN THE HYDROBORATION OF
TERMINAL OLEFINS AT 20°

Olefin	Distribution, ^a %	
	1-ol	2-ol
1-Butene	93	7
1-Pentene	94	6
2-Methyl-1-butene	99	1
3-Methyl-1-butene	94	6
1-Hexene	94	6
3,3-Dimethyl-1-butene	94	6
4,4-Dimethyl-1-pentene	93	7
Styrene	80	20
<i>p</i> -Chlorostyrene	65	35
2,4,4-Trimethyl-1-pentene	99	1
α -Methylstyrene	100	Trace
<i>p</i> -Methylstyrene	82	18
<i>p</i> -Methoxystyrene	91	9
Allylbenzene	90	10

^a The yields by gas-liquid partition chromatography were $90 \pm 10\%$.

The addition to styrene is less selective; 80% of the boron becomes attached to the terminal position and 20% to the secondary carbon atom. Moreover, the direction of addition is strongly modified by substituents in the *para* position of the aromatic nucleus.

The results are summarized in Table II.

The data in Table II—specifically the facts that ethylene, isopropylethylene, and *t*-butylethylene give 93%, 94%, and 94%, respectively, of primary alcohol—clearly show that an increase in the bulk of the alkyl group attached to the double bond does not influence the direction of addition. These results argue against steric control of the direction of addition. The marked influence of *para* substituents on the direction of addition to styrene supports the contention that the direction of addition is controlled primarily by electronic factors.

Dialkyl ethylenes, $RCH=CHR'$, such as 2-pentene and 2-hexene, undergo addition to place the boron atom in approximately equal

amounts on the 2- and 3-carbon atoms. This is true even for molecules such as *trans*-4-methyl-2-pentene and *trans*-4,4-dimethyl-2-pentene, where the two alkyl groups differ markedly in their steric requirements. Only in *trans*-1-phenylpropene, where the phenyl group is opposed to a methyl group, is a marked directive effect indicated; the boron atom becomes attached to the carbon atom holding the phenyl substituent to the extent of 85% (Table III).

TABLE III
DIRECTIVE EFFECTS IN THE HYDROBORATION OF
INTERNAL OLEFINS AT 20°

Olefin	Alcohol Distribution, ^a %	
	2-ol	3-ol
<i>cis</i> -2-Pentene	55	45
<i>trans</i> -2-Pentene	51	49
2-Methyl-2-butene ^b	98 ^c	2
<i>cis</i> -2-Hexene	50	50
<i>trans</i> -2-Hexene	46	54
<i>trans</i> -4-Methyl-2-pentene	57	43
<i>trans</i> -4,4-Dimethyl-2-pentene ^b	58	42
2,4,4-Trimethyl-2-pentene ^b	2	98 ^d
<i>trans</i> -1-Phenylpropene	85 ^e	15 ^f

^a The yields by gas-liquid partition chromatography were $90 \pm 10\%$.

^b The addition yields a dialkylborane.

^c The product is 3-methyl-2-butanol.

^d The product is 2,2,4-trimethyl-3-pentanol.

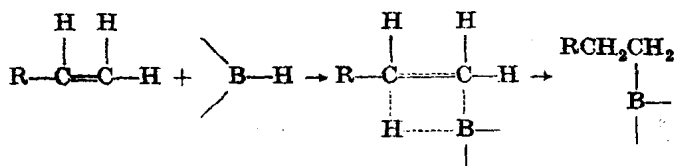
^e The product is 1-phenyl-1-propanol.

^f The product is 1-phenyl-2-propanol.

Trisubstituted olefins, $R_2C=CHR$, such as 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene, add the boron atom predominantly at the less substituted ethylenic carbon atom.

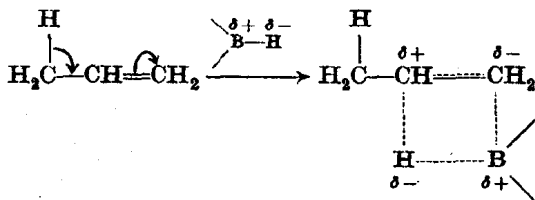
The data are summarized in Table III

Diborane undergoes *cis* addition to cyclic olefins and to acetylenes, which will be discussed later. Consequently, the addition very likely involves a four-center transition state.

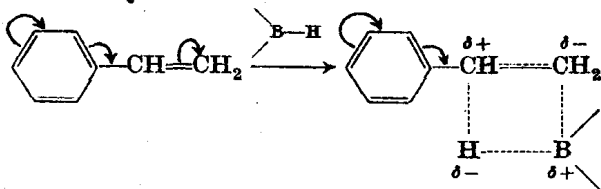


The boron-hydrogen bond is presumably polarized, the hydrogen having some hydridic character. The addition of the boron atom to the terminal position is then readily understood on the basis of the electronic shifts

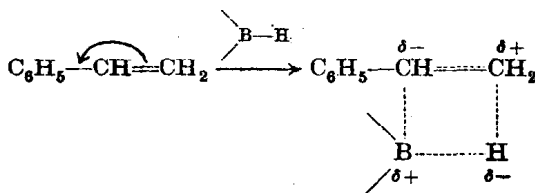
generally assumed in order to account for the normal ionic addition to propylene.



A similar rationalization explains the addition of the boron atom to the terminal position of styrene.



It is generally recognized that a phenyl group can supply electrons to an electron-deficient center or serve as an electron sink. This provides a simple explanation for the increased substitution in the α position observed in styrene.



Electron-withdrawing substituents, such as *p*-chloro, should stabilize and electron-supplying substituents, such as *p*-methoxy, should destabilize such a transition state. This conclusion is in accord with the influence of the *p*-chloro and the *p*-methoxyl group on the hydroboration of substituted styrenes (Table II).

Little quantitative information is available concerning the influence of other substituents on the direction of the addition reaction. It is evident that major effects will be encountered. Trimethylvinylsilane undergoes hydroboration to place 37% of the boron atoms at the secondary position¹⁴ as compared to 6% for 3,3-dimethyl-1-butene.¹³

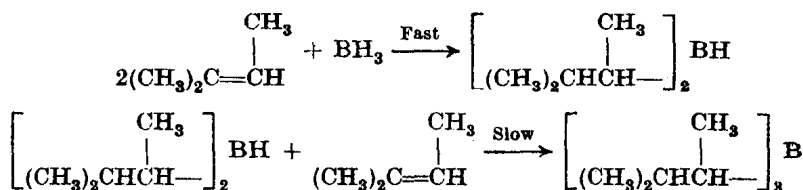
Bis-(3-methyl-2-butyl)borane as a Selective Hydroborating Agent¹⁵

It was pointed out earlier that highly substituted olefins, such as 2-methyl-2-butene, undergo hydroboration rapidly to the dialkylborane

¹⁴ Seyferth, *J. Inorg. Nucl. Chem.*, **7**, 152 (1958).

¹⁵ Brown and Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

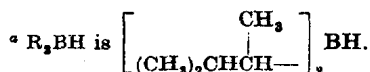
stage, further reaction to the trialkylborane stage being relatively slow.



The slowness of the last stage, in contrast to the high speed with which other olefins form the trialkylboranes, is presumably a result of the large steric requirement of the intermediate dialkylborane. It therefore

TABLE IV
DIRECTIVE EFFECTS IN THE HYDROBORATION OF UNSYMMETRICAL
OLEFINS WITH DIBORANE AND WITH BIS-(3-METHYL-2-BUTYL)BORANE

Olefin	Hydroborating Agent	Temp., °C.	Time, hr.	Alcohol Distribution, %		
				1-ol	2-ol	3-ol
1-Hexene	Diborane	25	1	94	6	
	R ₂ BH ^a	0	1	99	1	
<i>cis</i> -4-Methyl-2-pentene	R ₂ BH ^a	25	12		97	3
<i>trans</i> -4-Methyl-2-pentene	Diborane	25	1		57	43
	R ₂ BH ^a	25	12		95	5
Styrene	Diborane	25	1	80	20	
	R ₂ BH ^a	25	2	98	2	
<i>p</i> -Methoxystyrene	Diborane	25	1	91	9	
	R ₂ BH ^a	25	2	98	2	



appeared that this dialkylborane might exhibit an enhanced sensitivity to the steric requirement of the substituents on double bonds of other olefins and thereby exert a steric influence on the direction of hydroboration.

The reagent, bis-(3-methyl-2-butyl)borane, reacted rapidly with 1-hexene, and oxidation of the product yielded 1-hexanol in an isomeric purity of at least 99%, in contrast to the 94% isomeric purity realized with diborane itself. Similarly, styrene yielded less than 2% of the secondary alcohol, in contrast to 20% formed in the corresponding reaction with diborane. Finally, *cis*-4-methyl-2-pentene gave 97% of the less hindered isomer, 4-methyl-2-pentanol.

The experimental data are summarized in Table IV.

In these studies the ease with which different olefins reacted with bis-(3-methyl-2-butyl)borane was found to vary enormously. Thus the reaction with 1-hexene was complete in a matter of minutes at 0°, whereas

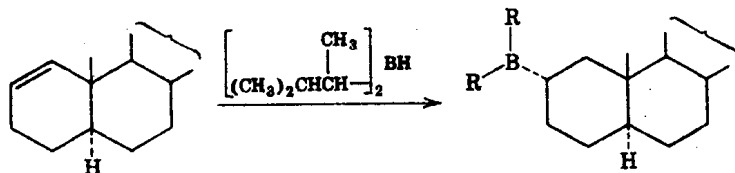
internal olefins reacted much more slowly, cyclopentene reacting faster than *cis*-2-hexene and the latter reacting considerably faster than cyclohexene. *cis*-2-Hexene also reacted considerably faster than the *trans* isomer. Trisubstituted olefins, such as 2-methyl-2-butene and 1-methylcyclohexene, reacted very slowly.

The results may be expressed in the following series of relative rates of reaction: 1-hexene \geq 3-methyl-1-butene $>$ 2-methyl-1-butene $>$ 3,3-dimethyl-1-butene $>$ *cis*-2-hexene \geq cyclopentene $>$ *trans*-2-hexene $>$ *trans*-4-methyl-2-pentene $>$ cyclohexene \geq 1-methylcyclopentene $>$ 2-methyl-2-butene \geq 1-methylcyclohexene \geq 2,3-dimethyl-2-butene.

The differences in reactivities are quite large and can be utilized for the selective hydroboration of a more reactive olefin in the presence of a less reactive one. Thus treatment of a mixture of 1-pentene and 2-pentene with a controlled quantity of bis-(3-methyl-2-butyl)borane yielded pure 2-pentene. Similar treatment of a mixture of 1-hexene and cyclohexene afforded essentially pure cyclohexene, while an equimolar mixture of cyclopentene and cyclohexene gave a product containing only minor amounts of the more reactive cyclopentene. A commercial mixture of *cis*- and *trans*-2-pentene (18% *cis* and 82% *trans*) with the reagent gave a product that contained more than 97% of the *trans* isomer.

In contrast to the results achieved with acyclic olefins, no significant directive effect was noted in the hydroboration of 3-methylcyclopentene, 3-methylcyclohexene, or 3,3-dimethylcyclohexene.¹¹

In a rigid cyclic system, selective reaction was observed. Treatment of 1-cholestene with bis-(3-methyl-2-butyl)borane resulted in the predominant formation of cholestan-2 α -ol, in contrast to the nearly 1:1 mixture of cholestan-1 α -ol and cholestan-2 α -ol obtained with diborane.¹⁶



Asymmetric Synthesis

The remarkable selectivity of a dialkylborane in hydroboration is further illustrated by the conversion of olefins to optically active alcohols.¹⁷ Hydroboration of α -pinene ($[\alpha]_D + 47^\circ$) gives diisopinocampheylborane.¹¹ This reagent was utilized for the hydroboration of *cis*-2-butene, *cis*-3-hexene, and norbornene. Oxidation of the resulting organoborane with

¹⁶ Sondheimer and Nussim, *J. Org. Chem.*, **26**, 630 (1961).

¹⁷ Brown and Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961).