Hydroboration. VIII. Bis-3-methyl-2-butylborane as a Selective Reagent for the Hydroboration of Alkenes and Dienes

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Under the usual hydroboration conditions diborane reacts rapidly with 2-methyl-2-butene to form bis-3-methyl-2-butyl-borane (or its dimer), and the latter reacts only slowly with excess 2-methyl-2-butene to form the fully alkylated borane. The large steric requirements of bis-3-methyl-2-butylborane provide a measure of steric control over the addition of the boron–hydrogen bond to the carbon–carbon double bond. Thus hydroboration of simple 1-alkenes with diborane yields 93–94% of the primary derivative, 6–7% of the secondary. Similarly, styrene yields 80% of the primary and 20% of the secondary. In these cases the use of bis-3-methyl-2-butylborane results in the formation of 98–99% of the primary derivative. Similarly, the hydroboration of *cis*- and *trans*-4-methyl-2-pentene with diborane does not distinguish significantly between the two carbon atoms of the double bond, whereas bis-3-methyl-2-butylborane results in the predominant addition of the boron atom to the carbon atom holding the least bulky substituent. Bis-3-methyl-2-butylborane exhibits major differences in its rates of reaction with various olefins: 1-hexene ≥ 3-methyl-1-butene > 2-methyl-1-butene > 3,3-dimethyl-1-butene > cyclopentene ≥ *cis*-2-hexene > *trans*-2-hexene > *trans*-4-methyl-2-pentene > cyclohexene ≥ 1-methylcyclopentene > 2-methyl-2-butene ≥ 1-methylcyclohexene ≥ 2,3-dimethyl-2-butene. The differences are large, permitting the selective hydroboration of 1-pentene in the presence of 2-pentene, the selective reaction of 1-pentene in the presence of 2-methyl-1-pentene, the selective reaction of cyclopentene in the presence of cyclohexene, the removal of 2,4,4-trimethyl-1-pentene from 2,4,4-trimethyl-2-pentene, and the removal of *cis*-2-pentene from *trans*-2-pentene. The reagent permits the selective hydroboration of the exocyclic double bond in both *d*-limonene and 4-vinylcyclohexene. Consequently, bis-3-methyl-2-butylborane is a very promising reagent for steric control of the direction of hydroboration of double bonds and for the selective hydroboration of alkenes and dienes.

The hydroboration of olefins, followed by oxidation with alkaline hydrogen peroxide of the intermediate organoborane, provides a highly convenient synthetic route for the conversion of terminal olefins into the corresponding primary alcohols.[1] A detailed study of directive effects in the hydroboration of olefins revealed that simple 1-alkenes, $RCH{=}CH_2$, undergo reaction to form predominantly the primary alcohol, 93–94%, accompanied by minor amounts, 6–7%, of the corresponding secondary alcohol. However, conjugation of the double bond with an aromatic ring results in an increase in the yield of the secondary alcohol, amounting to 20% in the case of styrene.[2]

In many instances the formation of a small quantity of the secondary alcohol offers no problem, since it can be readily separated from the major product by fractional distillation or crystallization. However, in some cases the separation can offer difficulties, and it appeared desirable to be able to circumvent the formation of the by-product. Consequently, we explored the possibility that the use of a hydroborating agent of large steric requirements might favor the desired addition of the boron atom to the terminal position and thereby minimize the formation of the secondary product.

We had previously observed that the hydroboration of 2-methyl-2-butene, in contrast to the behavior of less hindered olefins, proceeds readily only to the dialkylborane stage, R_2BH, with further reaction to the trialkylborane stage, R_3B, either slow or negligible under the reaction conditions.[1] We had found the large steric requirements of the product, bis-3-methyl-2-butylborane, (disiamylborane)[3] quite valuable in accomplishing the

monohydroboration of terminal acetylenes.[4] Accordingly, we undertook a study of the hydroboration of both terminal and internal olefins with this reagent in order to ascertain whether we could achieve some steric control over the direction of hydroboration of unsymmetrically substituted olefins.

In the course of this study, we observed some remarkable differences in the relative reactivities of olefins of different structures toward this reagent. Accordingly, we extended the study to an examination of the relative rates of reaction of disiamylborane with various olefins, its utility for the selective hydroboration of one olefin in the presence of a second olefin of larger steric requirements, and its utility for the selective hydroboration of the less hindered of two double bonds in dienes.

Results and Discussion

The Hydroboration of 3-Methyl-2-butene.—In order to establish convenient experimental conditions for the preparation of disiamylborane, a quantitative study was made of the hydroboration of 2-methyl-2-butene in diglyme[5] solution at 0 and 25°. The olefin was treated with sufficient sodium borohydride and boron trifluoride to convert it completely to the trialkylborane stage. At suitable intervals of time, aliquots of the reaction mixture were removed, quenched in wet diglyme to destroy residual hydride, and analyzed for residual 2-methyl-2-butene by gas chromatography, utilizing cyclohexane as an internal standard to facilitate the analysis.

At 0° there is a rapid conversion of the olefin to disiamylborane (1)[6] with further reaction to form

(1) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956); *J. Org. Chem.*, **22**, 1136 (1957); *J. Am. Chem. Soc.*, **81**, 6423, 6428 (1959).

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

(3) The marked versatility of bis-3-methyl-2-butylborane indicates that it will be widely utilized for selective hydroboration and suggests the desirability of a simple, convenient, name for this reagent. Unfortunately, the alkyl group, $(CH_3)_2CHCH(CH_3)$, has not received a

common name. It is suggested that this group, *sec.*-isoamyl, be termed "siamyl." Thus we would have siamyl alcohol, $(CH_3)_2CHCH(CH_3)OH$, siamyl bromide, $(CH_3)_2CHCH(CH_3)Br$, and disiamylborane, $[(CH_3)_2CHCH(CH_3)]_2BH$.

(4) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 1512 (1959).

(5) Dimethyl ether of diethylene glycol.

(6) It is convenient to refer to the product in its monomeric form, although it is probable that it exists as the dimer, $R_2BH_2BR_2$. A de-
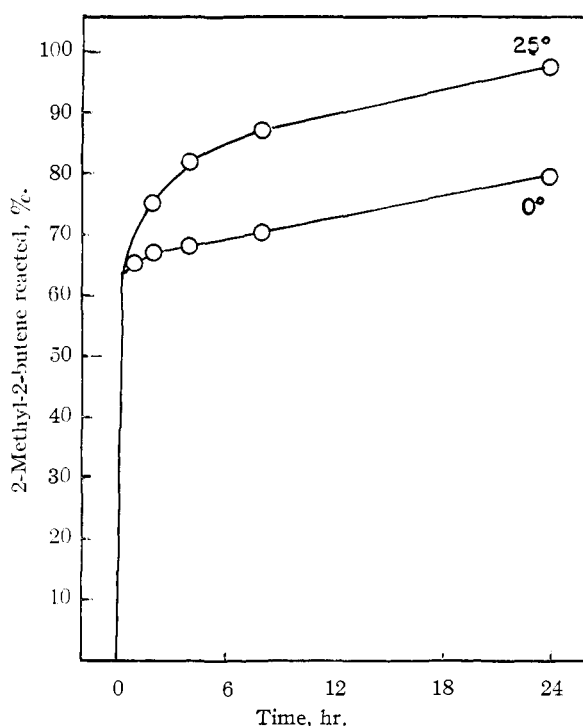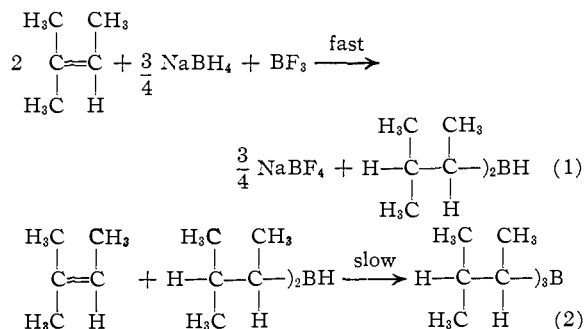
Fig. 1.—Hydroboration of 2-methyl-2-butene in diglyme solution at 0° and 25°.

the trialkylborane being very slow (2) (Fig. 1). At 25°, the second stage (2) becomes appreciable, and in 24 hours the reaction proceeds to practical completion (Fig. 1). Oxidation of the resulting trialkylborane with alkaline hydrogen peroxide yielded only 3-methyl-2-butanol in significant quantities. Consequently, the reaction is not accompanied by significant isomerization of the disiamylborane.

$$2 \begin{array}{cc} H_3C & CH_3 \\ | & | \\ C{=}C \\ | & | \\ H_3C & H \end{array} + \frac{3}{4}\ NaBH_4 + BF_3 \xrightarrow{\text{fast}}$$

$$\frac{3}{4}\ NaBF_4 + H{-}\begin{array}{cc} H_3C & CH_3 \\ | & | \\ C{-}C \\ | & | \\ H_3C & H \end{array}{-})_2BH \quad (1)$$

$$\begin{array}{cc} H_3C & CH_3 \\ | & | \\ C{=}C \\ | & | \\ H_3C & H \end{array} + H{-}\begin{array}{cc} H_3C & CH_3 \\ | & | \\ C{-}C \\ | & | \\ H_3C & H \end{array}{-})_2BH \xrightarrow{\text{slow}} H{-}\begin{array}{cc} H_3C & CH_3 \\ | & | \\ C{-}C \\ | & | \\ H_3C & H \end{array}{-})_3B \quad (2)$$
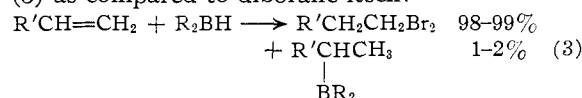
Disiamylborane was also synthesized readily by treating a solution of diborane in tetrahydrofuran with the theoretical quantity of 2-methyl-2-butene. Removal of the solvent under reduced pressure yielded the dialkylborane as a white, crystalline compound, m.p. 35–40°, unstable to air. The compound was maintained at 25° for 48 hours without change in the active hydrogen content. Oxidation of the product yielded only 3-methyl-2-butanol. Consequently, it appears that the reagent is quite stable under these conditions.

Directive Effects in the Hydroboration of Unsymmetrical Alkenes.—In order to test the possible

tailed study of the molecular state of a number of these borane containing bulky alkyl groups is under way with Mr. Gerald Klender.
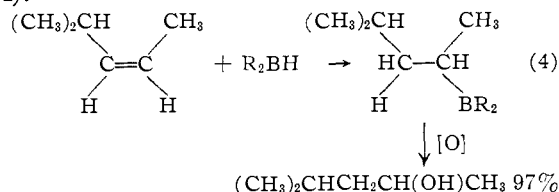
influence of the large steric requirements of disiamylborane on the direction of hydroboration of unsymmetrical olefins, solutions of the reagent in diglyme were prepared by treating the 2-methyl-2-butene with the calculated quantity of sodium borohydride and boron trifluoride at 0°, and the olefin under investigation was added to the solution. The reaction mixture was allowed to come to room temperature and to remain there until test of the solution (gas chromatography) indicated that the added olefin had reacted. The reaction mixture was then oxidized with alkaline hydrogen peroxide and the composition of the product established by gas chromatographic examination.

In this way it was observed that 1-hexene was converted into 1-hexanol, with 1% of 2-hexanol present. Similarly, styrene and p-methoxystyrene yielded the primary alcohols with a maximum of 2% of the secondary alcohols indicated. This compares with 6–20% of the secondary alcohols formed in the corresponding hydroboration of these alcohols with diborane. Consequently, disiamylborane does exhibit an enhanced tendency to add to the terminal position of a double-bond (3) as compared to diborane itself.

$$R'CH{=}CH_2 + R_2BH \longrightarrow R'CH_2CH_2Br_2 \quad 98{-}99\%$$
$$+ R'CHCH_3 \quad\quad 1{-}2\% \quad (3)$$
$$\qquad\quad | \\ \qquad\quad BR_2$$

Unsymmetrical olefins, such as $R_2C{=}CH_2$ and $R_2C{=}CHR$, undergo hydroboration to yield essentially a single product. Consequently, in these cases the use of disiamylborane would offer no advantages. However, the hydroboration of unsymmetrical internal olefins of the type $RCH{=}CHR'$ is less satisfactory, with nearly equivalent quantities of the two isomeric alcohols being realized. Thus, the usual hydroboration of trans-4-methyl-2-pentene yields 57% of 4-methyl-2-pentanol and 43% of 2-methyl-3-pentanol.[4]

The reaction of disiamylborane with cis- and trans-4-methyl-2-pentene proved to be quite slow, requiring approximately 12 hours to proceed to completion. Oxidation of the reaction product revealed that the addition had indeed occurred predominantly in one direction—placing the boron atom on the less hindered of the two carbon atoms (4).

$$\begin{array}{cc} (CH_3)_2CH & CH_3 \\ \diagdown & \diagup \\ C{=}C \\ \diagup & \diagdown \\ H & H \end{array} + R_2BH \rightarrow \begin{array}{cc} (CH_3)_2CH & CH_3 \\ \diagdown & \diagup \\ HC{-}CH \\ \diagup & \diagdown \\ H & BR_2 \end{array} \quad (4)$$

$$\downarrow [O]$$

$$(CH_3)_2CHCH_2CH(OH)CH_3 \quad 97\%$$

The experimental results are summarized in Table I.

Earlier studies had revealed that the usual hydroboration of 3-methylcyclopentene is not selective, yielding 2- and 3-methylcyclopentanol in approximately equivalent amounts (5).
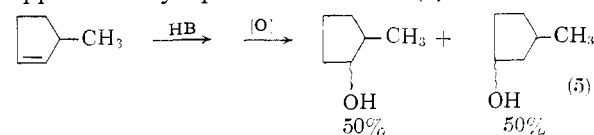
TABLE I

DIRECTIVE EFFECTS IN THE HYDROBORATION OF UNSYM-
METRICAL OLEFINS WITH DIBORANE AND DISIAMYLBORANE
(R_2BH)

Olefin	Hydro-borating agent	Temp., °C.	Time, hr.	Alcohol distribution[a,b] 1-ol	2-ol	3-ol
1-Hexene	Dibor.[c]	25	1	94	6	
	R_2BH	0	1	99	1	
Styrene	Dibor.[c]	25	1	80	20	
	R_2BH	25	2	98	2	
p-Methoxystyrene	Dibor.[c]	25	1	91	9	
	R_2BH	25	2	98[d]	2	
trans-4-Methyl-2-pentene	Dibor.[c]	25	1		57	43
	R_2BH	25	12		95	5
cis-4-Methyl-2-pentene	R_2BH	25	12		97	3

[a] The total yields, indicated by the gas chromatographic analysis, were 85–90%. [b] See ref. 2 for the specific column used for the alcohol analyses. [c] Ref. 2. [d] The product, 2-(p-anisyl)-ethanol, was isolated in 80% yield.

The similarity in the structures of 3-methyl-cyclopentene and cis-4-methyl-2-pentene suggested that disiamylborane might likewise serve to achieve the preferential conversion of the cyclic olefin to 3-methylcyclopentanol. Indeed, a 48:52 mixture of 3- and 4-methylcyclopentene was converted in this manner into 82% 3-methylcyclopentanol with only 18% of the more hindered isomer, 2-methylcyclopentanol, present. It is evident that such a directed hydroboration of cyclic olefins should be exceedingly valuable in the terpene and steroid field.

Selectivity in the Hydroboration of Alkenes.— Early attempts to study the rates of reaction of diborane with simple olefins in ether solvents had revealed the reaction to be too fast to measure, proceeding to completion in a matter of seconds.[7] The slow reaction of disiamylborane with 2-methyl-2-butene suggested a study of the ease of reaction of a number of representative olefins with this reagent.

The olefin under investigation was added to an equimolar quantity of disiamylborane in diglyme at 0°, and the rate of disappearance of the olefin followed by gas chromatography.

Terminal olefins, such as 1-hexene, 3-methyl-1-butene, 2-methyl-1-butene and 3,3-dimethyl-1-butene, reacted rapidly, with more than 90% utilization of the olefin within 0.5 hour.

Disubstituted internal olefins reacted much more slowly and exhibited remarkable differences. Thus cyclohexene reacted at a considerably lower rate than cyclopentene. The latter reacted at a slightly greater rate than cis-2-hexene. Quite remarkably, trans-2-hexene reacted at a rate considerably slower than that of the cis-isomer. A bulky group on the double bond, as in trans-4-methyl-2-pentene and trans-4,4-dimethyl-2-pentene, led to further reductions in rate.

Trisubstituted olefins, such as 2-methyl-2-butene, 1-methylcyclopentene and 1-methylcyclohexene, reacted very slowly, as did the tetrasubstituted olefin, 2,3-dimethyl-2-butene.

Consequently, this study establishes the order of reactivity of olefins toward disiamylborane to

(7) Unpublished research with Dr. Laura Case.

be: 1-hexene ≥ 3-methyl-1-butene > 2-methyl-1-butene > 3,3-dimethyl-1-butene > cyclopentene ≥ cis-2-hexene > trans-2-hexene > trans-4-methyl-2-pentene > cyclohexene ≥ 1-methylcyclopentene > 2-methyl-2-butene > 1-methylcyclohexene ≥ 2,3-dimethyl-2-butene.

The experimental results are summarized in Table II.

TABLE II

REACTION OF VARIOUS OLEFINS WITH DISIAMYLBORANE IN
DIGLYME AT 0°

Olefin[a]	Olefin reacted, % 0.5 hr.	1.0 hr.	2 hr.	4 hr.	24 hr.
1-Hexene	100				
3-Methyl-1-butene	99				
2-Methyl-1-butene	98				
3,3-Dimethyl-1-butene	93	98			
Cyclopentene	76	85	90		
cis-2-Hexene	62	79	93		
trans-2-Hexene	39	50	64	84	97
trans-4-Methyl-2-pentene	21	32	46	64	91
Cyclohexene	15	25	31	38	
1-Methylcyclopentene	12	19	25	34	
trans-4,4-Dimethyl-2-pentene	7	10	13	20	30
2-Methyl-2-butene	5	8	11		
2,3-Dimethyl-2-butene	4	6	7		
1-Methylcyclohexene	4	6	7		

[a] Olefin concentration was 0.5 M. An equivalent quantity of disiamylborane was used, partially in suspension.

The major differences in the relative reactivity of various olefin structures should permit a wide variety of selective hydroboration reactions. Consequently, a number of competitive hydroborations were carried out to test the utility of the reagent for such selective reactions.

Thus, treatment of an equimolar mixture of 1-pentene and 2-pentene with a controlled quantity of disiamylborane resulted in the preferential reaction of the 1-pentene, leaving the 2-pentene in a purity of at least 99%. Similarly, the reagent reacted preferentially with the 1-hexene in an equimolar mixture of 1-hexene and cyclohexene.

Treatment of 2,4,4-trimethyl-2-pentene containing 15% of 2,4,4-trimethyl-1-pentene as an impurity resulted in the complete removal of the latter, producing 2,4,4-trimethyl-2-pentene containing no detectable trace of the isomeric olefin.

An equimolar mixture of cyclopentene and cyclohexene (43 mmoles each), after treatment with the reagent (50 mmoles) for 10 hours at 0°, yielded a product which contained 36.1 mmoles of cyclohexene and only 2.2 mmoles of cyclopentene.

Finally, it was observed that the reagent can distinguish between simple terminal olefins and those containing a methyl branch, such as 4-methyl-1-pentene and 2-methyl-1-pentene.

The experimental data and results are summarized in Table III.

The remarkable difference in the relative reactivity of cis- and trans-2-hexene was of special interest. It suggested the possibility that disiamylborane might provide a means of removing the trans isomer from an isomeric mixture to produce the pure cis compound. Accordingly, 50

TABLE III

COMPETITIVE REACTIONS OF OLEFIN MIXTURES WITH DI-
SIAMYLBORANE (R₂BH) IN DIGLYME AT 0°

Olefin mixture	Olefin, mmoles	R₂BH mmoles	Residual olefin, mmoles[a]			
			0.5 hr.	1 hr.	3 hr.	10 hr.
1-Pentene	43	50[b]	0.4			
2-Pentene	43		38.2			
1-Hexene	43	50[b]	0			
Cyclohexene	43		36.5			
Cyclopentene	43	50[b]	17.6	11.2		2.2
Cyclohexene	43		38.7	37.8		36.1
2,4,4-Trimethyl-1-pentene	15	50[b]	4.8	3.0	0	
2,4,4-Trimethyl-2-pentene	85		85	82.5	79	
1-Pentene	50	55[c]	6.5			
2-Methyl-1-pentene	50		45			
4-Methyl-1-pentene	50	55[c]	10.5	10.5		
2-Methyl-1-pentene	50		39.0	39.0		

[a] The olefins were analyzed on an adiponitrile column.
For the separation of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, a Ucon Polar column was utilized.
[b] The olefin mixture was added rapidly to the reagent.
[c] The reagent was added to the olefin mixture.

mmoles of commercial 2-pentene, analyzing 18%
cis- and 82% trans-2-pentene, was treated with
50 mmoles of the reagent at 0°. The change in
the composition of the residual olefin with time was
followed in the usual manner. The results are
summarized in Table IV.

TABLE IV

REACTION OF DISIAMYLBORANE WITH cis- AND trans-2-
PENTENE IN DIGLYME AT 0°

Time, hr.	Residual olefin, %		Yield of trans-2-pentene, %
	cis	trans	
0	18	82	
0.25	10	90	83
0.50	4	96	66
0.75	3	97	62
1.0	2	98	55

To our knowledge, no reagent has been avail-
able previously to distinguish as cleanly between
the cis and trans isomeric olefins.[8] This selective
reaction of disiamylborane with this cis isomer
should provide a convenient means of obtaining
the trans isomers in a state of high purity. Since
the hydroboration of acetylenes provides a con-
venient synthetic route to the pure cis-olefins,[8]
it is now possible to utilize hydroboration to achieve
the synthesis of either cis- or trans-olefins in a state
of high purity.

Selectivity in the Hydroboration of Dienes.—
The observation that the rate of reaction of disi-
amylborane with olefins is very sensitive to the struc-
ture of the olefins makes possible the selective
hydroboration of a more reactive olefin in the pres-
ence of a less reactive. However, the synthetic
chemist is more frequently faced with the problem
of two or more reactive sites within a single mole-
cule. The question arises whether the information
developed on the effect of structure on reactivity

(8) A detailed study of the reaction of the reagent and related
dialkylboranes with cis, trans isomers is underway with Dr. A. Moeri-
kofer.

can be utilized to predict the point of attack in
a molecule containing two or more double bonds.

To test this point, we examined the hydroboration
of 4-vinylcyclohexene and d-limonene.

The greater reactivity of 1-hexene over cyclo-
hexene (Table I) and the preferential hydrobora-
tion of 1-hexene in the presence of cyclohexene
(Table II) suggest that 4-vinylcyclohexene should
undergo preferential reaction with the reagent at
the exocyclic double bond.

CH=CH₂   CH₂CH₂B⟨   CH₂CH₂OH

            R₂BH   [O]
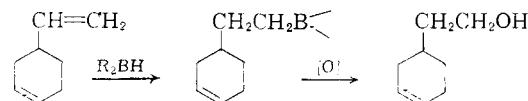
Indeed, treatment of 4-vinylcyclohexene with
disiamylborane, followed by oxidation with alka-
line hydrogen peroxide, produced 2-(4-cyclohex-
enyl)-ethanol in 72% yield. Hydrogenation of
this unsaturated alcohol gave the known 2-cyclo-
hexylethanol.

Similarly, the exocyclic double bond in d-
limonene is predicted to be the preferred point of
attack, and d-limonene was converted into the
primary terpineol in 79% yield.[9]

          R₂BH   [O]

          CH₂   CH₂BR₂   CH₂OH
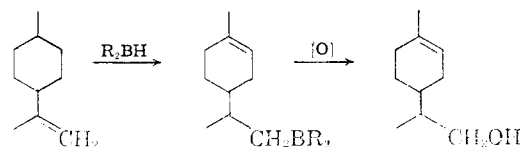
These results support the conclusion that one
can utilize the reactivities observed with simple
olefins to predict the point of attack of disiamyl-
borane in more complex molecules with multiple
reaction centers. It is apparent that this reagent
should develop into a highly useful tool for syn-
thetic work in the terpene, steroid and related
fields. We are extending the study of its full
utility for the selective hydroboration of selected
dienes and terpenes.

Experimental Part

Materials.—Diglyme (Ansul Chemical Co.) was distilled
under vacuum from a small quantity of lithium aluminum
hydride. Boron trifluoride etherate (Distillation Products,
Inc.) was distilled over calcium hydride (Metal Hydrides
Inc.) under reduced pressure. Sodium borohydride (Metal
Hydrides Inc.) was used without purification (purity: 98%).
2-Methyl-2-butene (Phillips Petroleum Co.) was likewise
used without purification (purity: 99%).

The olefins used, their physical constants and sources
were reported in an earlier paper. A mixture of 3- and 4-
methylcyclopentene was obtained from the Standard Oil
Co., Indiana.

Preparation of Boron Trifluoride in Diglyme.—In order
to avoid interference of diethyl ether with some of the
olefins in the gas chromatographic analysis, the ether in the
boron trifluoride ether was displaced with diglyme. Di-
glyme, 50 ml., was cooled in an ice-bath, 25 cc. of boron
trifluoride ethyl etherate added, and the ether removed
by applying a vacuum (~5 mm.) for 20 minutes, main-
taining the flask at 20–25°. The resulting boron trifluoride
diglymate was approximately 3.65 M. The material

(9) We had earlier attempted to achieve the monohydroboration
of d-limonene with diborane, but had not realized a simple reaction
product. Similar unsuccessful results have been described by R.
Dulou and Chrétien-Dessière, Bull. soc. chim. France, 9, 1362 (1959).
It should be mentioned here that K. Ziegler and his co-workers (ref. 12)
have recently achieved a similar selective attack on the exocyclic bond
of both 4-vinylcyclohexene and limonene with triisobutylaluminum.

darkened relatively rapidly, so that it was prepared in relatively small quantities and utilized soon after preparation.

Hydroboration of 2-Methyl-2-butene. (a). 0°.—In a dry three-neck flask equipped with a condenser, a thermometer and a pressure-equilibrated dropping funnel were placed 30 cc. of a 5 M solution of 2-methyl-2-butene (10.5 g.) in diglyme and 41 cc. of a 1 M solution of sodium borohydride (1.54 g.) in diglyme. The reaction mixture was diluted with 50 mmoles of cyclohexane (4.29) as internal standard. The reaction flask was immersed in an ice-bath. From the dropping funnel 15 cc. of a 3.65 M solution of boron trifluoride (7.8 g., 55 mmoles) in diglyme was added dropwise to the well-stirred reaction mixture over a period of 30 minutes. The apparatus was kept under a static pressure of nitrogen.

The semi-solid reaction mixture was kept at 0–5°, samples were withdrawn at appropriate time intervals and quenched in wet diglyme to destroy residual hydride. The upper phase formed was analyzed for unreacted 2-methyl-2-butene on an adiponitrile column.

(b) 25°.—Under the identical conditions described above, 2-methyl-2-butene was hydroborated at 25°. The reaction mixture was analyzed at different time intervals for unreacted olefin.

After standing for 24 hours at 25°, the reaction mixture was hydrolyzed. When hydrogen was no longer evolved, 15 cc. of 3 N sodium hydroxide was added, followed by the dropwise addition of 15 cc. of 30% hydrogen peroxide. The alcohols formed were extracted with ether. An aliquot of the dried ether extract was analyzed for alcohol on a glycerol column. The chromatogram indicated that the product was 3-methyl-2-butanol; none of the primary alcohols was observed.

Preparation of Bis-3-methyl-2-butylborane.—In a 500-cc. flask (described above) were placed 80 cc. of diglyme, 23.1 g. of 2-methyl-2-butene (0.33 mole) in 20 cc. of diglyme and 4.7 g. of sodium borohydride (0.125 mole). The flask was immersed in an ice-bath and 23.5 g. of boron trifluoride etherate (0.165 mole) was added dropwise to the well-stirred reaction mixture over a period of 30 minutes. The semi-solid reaction mixture containing 0.165 mole of disiamylborane was permitted to remain an additional 15 hours at 0–5°, then used for the hydroboration of p-methoxystyrene, *trans*- and *cis*-4-methyl-2-pentene and a mixture of 3- and 4-methylcyclopentene in order to establish the directive effects in the hydroboration of these olefins.

Preparation of 2-(p-Anisyl)-ethanol.—To 0.165 mole of disiamylborane in diglyme at 0–5° was added 20.1 g. of p-methoxystyrene (0.15 mole, n^{20}D 1.5601) over a period of 5 minutes. The reaction mixture was allowed to warm up to room temperature (approx. 2 hours) and then oxidized with alkaline hydrogen peroxide, 50 cc. of 3 N sodium hydroxide, followed by 50 cc. of hydrogen peroxide (30% solution). The temperature of the reaction mixture was kept below 50°. The reaction mixture was extracted with ether, the ether extract was washed four times with cold water to remove diglyme, dried over anhydrous magnesium sulfate and distilled. There was obtained 18.2 g. of 2-(p-anisyl)-ethanol (80% yield), b.p. 138–140 at 10 mm., m.p. 27–28° (reported[10] b.p. 148–149° at 19 mm., m.p. 27.5–28°); v.p.c. analysis indicated a purity of 98%.

Preparation of 4-methyl-2-pentanol.—To 0.110 mole of disiamylborane in diglyme at 0–5° was added 8.4 g. of *trans*-4-methyl-2-pentene (0.1 mole, n^{20}D 1.3891; Phillips, Research Grade) and 20 mmoles of n-hexane (1.72 g.) as internal standard. The reaction mixture was brought to 20–25°; v.p.c. analysis of the reaction mixture revealed that after 2 hours, 21.6 mmoles of the olefin had not reacted; after 4 hours, 12.0 mmoles; and after 6 hours, 9.0 mmoles. After standing an additional 6 hours at room temperature, the reaction mixture was oxidized by alkaline peroxide (30 ml. of 3 N sodium hydroxide and 30 ml. of hydrogen peroxide, 30% solution); v.p.c. analysis of the ether extract indicated an 83% yield of alcohol, consisting of 95% 4-methyl-2-pentanol and 5% of 2-methyl-3-pentanol.

Evaporation of the ether left a residue which was distilled in a Todd spiral column; the distillate had a b.p. 130° at 740 mm., n^{20}D 1.4117 (reported[11] for 4-methyl-2-pentanol, b.p. 133° at 760 mm., n^{20}D 1.4122.

Similarly, 0.1 mole of *cis*-4-methyl-2-pentene (n^{20}D 1.3882, Phillips Tech. Grade, 95% pure) was hydroborated with the reagent; v.p.c. analysis of the reaction mixture indicated that after 2 hours, 7 mmoles, and after 4 hours, 3.2 mmoles of the olefin had not reacted.

VPC analysis of the oxidized reaction mixture indicated a 90% yield of alcohol (by external standard) consisting of 97% of 4-methyl-2-pentanol and 3% of 2-methyl-3-pentanol.

Directive Effects in the Hydroboration of a Mixture of 3- and 4-Methylcyclopentene.—To a mixture of 0.165 mmole of disiamylborane in diglyme at 0–5° was added 12.3 g. of a mixture of 3- and 4-methylcyclopentene (0.15 mmole, b.p. 64–65°, n^{20}D 1.4226; v.p.c. analysis on a 7-m. benzyl cyanide–silver nitrate column indicated a 48:52 composition). The reaction mixture was kept for 2 hours at 0–5°, then for 2 hours at room temperature. The reaction mixture was oxidized by adding 50 cc. of 3 N sodium hydroxide followed by the addition of 50 cc. of hydrogen peroxide. The alcohol formed was extracted with ether, and the ether extract was washed four times with cold water to remove the diglyme. Evaporation of the solvent and distillation of the residue gave 12.3 g. of product (corresponding to a 82% yield of methylcyclopentanol), b.p. 147–148° (740 mm.), n^{20}D 1.4456.

Fifty mmoles of the alcohol was oxidized by sodium dichromate–sulfuric acid; v.p.c. analysis of the product on a Ucon polar column indicated 82% of 3-methylcyclopentanone and 18% of 2-methylcyclopentanone.

Rates of Reaction of Disiamylborane with Various Olefins.—In a 3-neck flask fitted with a thermometer, a pressure equalized funnel, an inlet for nitrogen and a side arm fitted with a rubber serum cap to permit removal of samples, were placed 20 cc. of a 5 M solution of 2-methyl-2-butene (7 g.) in diglyme and 41 cc. of a 1 M solution sodium borohydride (1.54 g., 10% excess) in diglyme. The flask was immersed in an ice-bath; 15 cc. of a 3.65 M solution of boron trifluoride (7.8 g.) in diglyme was added over a period of 30 minutes to the well-stirred reaction mixture. The reaction mixture was permitted to remain an additional hour at 0–5°.

To this mixture was added at once 25 cc. of a 2 M solution of the olefin (50 mmoles) and 50 mmoles of the internal standard in diglyme. In most of the cases, the reaction mixture was at this stage semi-solid.

The rate of disappearance of the olefin was determined by withdrawing samples at different time intervals and quenching them in wet diglyme. The upper phase formed was analyzed on an adiponitrile column for unreacted olefin, using the internal standard as reference. The results obtained are summarized in Table II.

Competitive Hydroboration Experiments. (a) Direct Addition.—In the flask described above were placed 20 cc. of a 5 M solution of 2-methyl-2-butene in diglyme and 38 cc. of a 1 M solution of sodium borohydride (theoretical amount to form 50 mmoles of disiamylborane). The flask was immersed in an ice-bath and 14 cc. of a 3.65 M solution of boron trifluoride (51 mmoles) in diglyme was added over 30 minutes to the well-stirred reaction mixture.

After standing for 1 hour at 0–5°, the reaction mixture was diluted with the olefin mixture (Table III) containing an internal standard. The unreacted olefin was determined by v.p.c., as described above, except for the 2,4,4-trimethyl-1-pentene and the 2,4,4-trimethyl-2-pentene, which were analyzed on a Ucon Polar column, the olefins were analyzed on an adiponitrile column.

(b) **Reverse Addition.**—In cases where the two olefins under study were both highly reactive, reverse addition was utilized. The disiamylborane (55 mmoles) was prepared at 0° in the usual way. The reaction flask was connected by means of a U-tube to a second flask, containing the olefin mixture in diglyme. By applying a slight pressure of nitrogen, the dialkylborane was passed into the cooled olefin mixture over a period of 30 minutes. During this process vigorous stirring in both flasks was maintained.

The results of these investigations are reported in Table III.

Selective Hydroboration of 4-Vinylcyclohexene.—In a three-neck flask was placed 16.2 g. of 4-vinylcyclohexene (0.15 mole, Phillips, 99% pure) in 30 cc. of diglyme. The flask was immersed in an ice-bath. This flask was connected to the flask containing 0.165 mole of disiamylborane by a U-tube as described above. During the addition of

(10) G. M. Bennett and M. M. Hafez, *J. Chem. Soc.*, **652** (1941).

(11) A. L. Henne and A. H. Matuszak, *J. Am. Chem. Soc.*, **66**, 1649 (1944).

the reagent over approximately 1 hour, the contents of the flasks were well stirred. After standing an additional hour at 0°, 10 cc. of water was added to destroy residual hydride, followed by addition of 50 cc. of 3 N sodium hydroxide and 50 cc. of hydrogen peroxide (30% solution). The temperature of the reaction mixture was kept below 50°. The reaction mixture was worked up in the usual way. After distillation there was obtained 13.7 g. (72% yield) of 2-(4-cyclohexenyl)-ethanol, b.p. 86–87° at 6 mm., $n^{20}D$ 1.4834; reported[12] b.p. 104.5° at 16 mm., $n^{20}D$ 1.4832.

The 3,5-dinitrobenzoate had m.p. 66–67°. *Anal.* Calcd. for $C_{15}H_{16}N_2O_6$: C, 56.24; H, 5.03; N, 8.79. Found: C, 56.57; H, 4.96; N, 8.80.

The unsaturated alcohol (30 mmoles) was hydrogenated in the presence of platinum oxide. The 2-cyclohexylethanol obtained (79% yield) had b.p. 77–78° at 4 mm., $n^{20}D$ 1.4651 (reported[13] b.p. 87–89 at 6 mm., $n^{20}D$ 1.4636). The 3,5-dinitrobenzoate had m.p. 71–72°, reported[14] m.p. 70–70.5°.

Selective Hydroboration of d-Limonene.—To 0.165 mole of disiamylborane in diglyme at 0° was added 20.4 g. of d-limonene (0.15 mole, b.p. 174° at 742 mm., $n^{20}D$ 1.4730,

(12) K. Ziegler, F. Krupp and K. Zosel, *Ann.*, **629**, 241 (1960).

(13) G. S. Hiers and R. Adams, *J. Am. Chem. Soc.*, **48**, 2385 (1926).

(14) J. J. Bost, R. E. Kepner and A. D. Webb, *J. Org. Chem.*, **22**, 51 (1957).

$[\alpha]^{25}D$ + 125°; reported[15] $n^{20}D$ 1.4725, $[\alpha]^{20}D$ +123°) over a period of 5 minutes. The reaction mixture was allowed to remain for ~3 hours at room temperature. The reaction mixture was oxidized by alkaline peroxide: 50 cc. of 3 N sodium hydroxide followed by 50 cc. of hydrogen peroxide (30%). The alcohol was worked up in the usual manner. By distillation, there was obtained 18.3 g. of primary terpineol (79% yield), b.p. 115–116° at 10 mm., $n^{20}D$ 1.4855, $[\alpha]^{20}D$ +99° (c in benzene 4.2); reported[12] b.p. 67–69° at 0.6 mm. $n^{20}D$ 1.4853–1.4866.

The 3,5-dinitrobenzoate had m.p. 91–93° (sintered at 85°). *Anal.* Calcd. for $C_{17}H_{20}N_2O_6$: C, 58.61; H, 5.78; N, 8.04. Found: C, 58.60; H, 5.89; N, 8.13.

(15) G. Widmark, *Acta Chem. Scand.*, **9**, 938 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE, DURHAM, N. H.]

Reduction of Some Aldehydes and Ketones with Organotin Hydrides[1,2]

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Reductions of aldehydes and ketones with tri-*n*-butyltin hydride, triphenyltin hydride, di-*n*-butyldin dihydride, diphenyltin dihydride, *n*-butyltin trihydride and phenyltin trihydride have been investigated. In each case reduction can be achieved with certain compounds. The exclusive pathway for reduction involves transfer of hydrogen to the substrate; metal-oxygen bonds are not formed. The tin-containing products from the mono-, di- and trihydrides have the compositions R_3SnSnR_3, R_2Sn and RSn, respectively. The double bond in α,β-unsaturated aldehydes and ketones is unaffected in the course of reduction. Stereoselectivity in the reduction of simple cyclohexanones is very similar to that exhibited by sodium borohydride. Nitrophenyl ketones suffer preferential reduction of the nitro group by diphenyltin dihydride.

We were interested in the preparation of tin compounds containing appropriate functional groups in two side chains so that cyclization could be effected in a subsequent step.[3] One reaction which offered such a possibility was the newly-observed addition of organotin monohydrides to double bonds.[4] If the reaction were undergone by dihydrides it might be possible to carry out the reaction between diphenyltin dihydride and methyl vinyl ketone (eq. 1). Cyclization of the resulting diketone could then lead to a tin heterocycle.

$(C_6H_5)_2SnH_2 + 2CH_2{=}CHCOCH_3 \longrightarrow$

$\qquad (C_6H_5)_2Sn(CH_2CH_2COCH_3)_2$ (1)
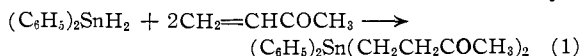
When the reactants were allowed to stand in ether solution, a reaction did occur, but as shown in eq. 2.

$(C_6H_5)_2SnH_2 + CH_2{=}CHCOCH_3 \longrightarrow$

$\qquad ((C_6H_5)_2Sn) + CH_2{=}CHCHOHCH_3$ (2)
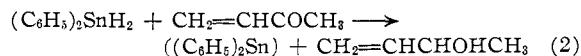
The products were easily separated by virtue of the fact that the diphenyltin was insoluble in ether.

Pure methylvinylcarbinol was isolated in 59% yield.[5]

This reaction is apparently unique among metal hydride reductions in the fact that *two hydrogens are transferred to the substrate directly;* the formation of an intermediate metal alkoxide is avoided. Consequently a hydrolysis step is not needed, and acidic or basic conditions need not exist in the reaction medium at any time. This might be of importance in the reduction of certain types of sensitive compounds. A practical disadvantage lies in the fact that one mole of dihydride reduces only one mole of ketone, whereas the alkoxide mechanism would lead to the reduction of two moles. Because of its unusual character we began a study of the scope and mechanism of the reaction. In this paper, we report the results obtained in a survey of the reactions of organotin mono-, di- and trihydrides, one aromatic and one aliphatic in each case, with several aldehydes and ketones with particular emphasis on the stereochemistry whenever it was pertinent.