

vigorous reaction slowed noticeably after an additional 2 min. The reaction mixture then was hydrolyzed immediately by the injection of 5 ml of water in 10 ml of tetrahydrofuran. Oxidation in the usual manner yielded a product whose gas chromatogram showed the presence of 30% residual olefin and 70% of a single peak, corresponding to the isomer B above. (Since the individual peaks were not well resolved, we cannot exclude the possibility that small quantities of the isomeric alcohols were present.) Distillation yielded 1.0 g of olefin, bp 55° (60 mm),  $n_D^{20}$  1.4690, 25%, and 1.1 g of alcohol, bp 85° (12 mm),  $n_D^{20}$  1.4807. Gas chromatographic examination of the olefin indicated the presence of 5% of an isomeric material, corresponding to the 3-methylcyclooctene indicated in the elimination.

**Product Studies.** The elimination reactions were carried out as reported earlier for the halides.<sup>5</sup> The isomeric compositions were established by gas chromatographic analysis. Authentic samples of 1- and 3-methylcyclopentene and -cyclohexene were available. In the higher members, authentic samples of 1-methylcycloheptene and 1-methylcyclooctene were available. It was assumed that the second peak in the elimination product was the 3-isomer.

**Rate Studies.** The sulfonate was weighed in a 20-ml reaction flask. Ten milliliters of pure *t*-butyl alcohol at 50° was added,

and the solution was equilibrated at 50°. The 1.0 *M* *t*-butoxide solution also was equilibrated at this temperature. The reaction was initiated by introducing 10.0 ml of the base solution into the ampoule and mixing by vigorous shaking. Thus the initial concentrations were 0.5 *M* in base and 0.15 to 0.25 *M* in the tosylate. At appropriate intervals of time, 2.00-ml aliquots were removed and quenched in 15 ml of acetone containing 1.00 ml of 1.00 *M* hydrochloric acid to neutralize the original quantity of base. The excess acid present was then titrated with saturated 0.1 *M* sodium hydroxide. Several aliquots were allowed to go to completion and the infinity titers obtained. Tests indicated that the observed rate constants were reproducible to  $\pm 3\%$ .

The rates were determined graphically, using the expression

$$k_t = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}$$

where *a* is the initial concentration of the sulfonate ester, *b* is the initial concentration of *t*-butoxide, and *x* is the amount reacted in time *t*. Representative rate data are reported in Table III.

## Organoboranes. III. Isomerization of Organoboranes Derived from the Hydroboration of Acyclic Olefins

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Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana. Received October 16, 1965

**Abstract:** Organoboranes prepared from internal acyclic olefins *via* hydroboration with the usual slight excess of reagent undergo rapid isomerization at temperatures of 100 to 160° to place the boron atom predominantly at the terminal position. It was established that the isomerization reaction is markedly catalyzed by a small excess of diborane in the reaction mixture. The scope and rate of the isomerization reaction was explored with a number of representative acyclic olefins. It was established that the boron atom readily moves down the chain past a single branch, but not past a quaternary carbon atom. Hydroboration-isomerization of the organoboranes from 2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene yields the same equilibrium mixture of organoboranes with 59% 3-methyl-1-bora- and 39% 2-methyl-1-borabutane moieties. The preference of the boron atom for the less crowded of the two primary positions is attributed to the operation of steric effects. A mechanism is proposed for the isomerization reaction involving successive *cis* eliminations of boron-hydrogen moieties from the organoborane at relatively moderate temperatures, followed by additions, rapidly achieving thermodynamic equilibrium among the possible organoboranes (except where the isomerization involves moving the boron atom past a quaternary carbon). The boron atom ends up preferentially in the least sterically crowded position of the alkyl group. Internal olefins are synthesized readily from tertiary alcohols prepared *via* the Grignard reaction. Application of the hydroboration-isomerization reaction to such olefins makes possible a number of promising syntheses of primary alcohols, amines, and related derivatives.

Organoboranes, readily accessible *via* hydroboration of olefins, are finding considerable application as useful intermediates in organic synthesis.<sup>1</sup> Thus, oxidation of organoboranes with alkaline hydrogen peroxide yields alcohols whose stereochemistry can be deduced in a predictable manner.<sup>2</sup> The noncatalytic hydrogenation of olefins *via* protonolysis of organoboranes with organic acids takes place without rearrangement, even in the case of terpenes.<sup>3</sup> Moreover, the reaction permits the introduction of one or two deuterium atoms in sterically defined positions.<sup>4</sup> Treat-

ment of organoboranes with silver nitrate under alkaline conditions provides a versatile new procedure for the formation of carbon-to-carbon bonds.<sup>5</sup> Finally, the reaction of organoboranes with hydroxylamine-O-sulfonic acid provides a convenient synthetic procedure to proceed from a particular olefin to the corresponding amine.<sup>6</sup>

It was previously observed that organoboranes undergo isomerization on heating.<sup>7,8</sup> However, isomeri-

(5) H. C. Brown and C. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1003 (1961).

(6) H. C. Brown, W. R. Heydkamp, E. Breuer, and W. S. Murphy, *ibid.*, **86**, 3565 (1964).

(7) G. F. Hennon, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *ibid.*, **79**, 5190 (1957).

(8) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6434 (1959).

(1) For a review with pertinent references, see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(2) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(3) H. C. Brown and K. Murray, *ibid.*, **81**, 4108 (1959), and unpublished observations of G. Zweifel.

(4) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961).

zation of organoboranes produced *via* hydroboration proceeded so rapidly at much lower temperatures than organoboranes synthesized through the Grignard reagent that it was considered desirable to learn the cause for the major difference in behavior. Moreover, the reaction possesses some obvious possibilities of major significance for organic syntheses. Therefore an exploration of the scope of the reaction appeared in order. Accordingly we undertook a study of the rates and products of the hydroboration-isomerization of the organoboranes produced *via* the hydroboration of a number of representative acyclic olefins.<sup>9</sup>

## Results

It has been established that organoboranes are oxidized essentially quantitatively by alkaline hydrogen peroxide to the corresponding alcohols, placing the hydroxyl group at the precise position previously occupied by the boron atom.<sup>10</sup> This procedure, together with gas chromatographic examination of the alcohols produced, was used in the present study as a convenient means of following the isomerization of the organoborane moieties.

The hydroboration of 2-hexene and its isomerization under standard conditions, 150° for 1 hr in diglyme, was selected for study of the possible effect of the hydroboration conditions on the ease of isomerization. It soon was established that no significant difference in the rate of isomerization resulted from internal hydroboration, that is, treating the olefin *in situ* with sodium borohydride and boron trifluoride, or from external hydroboration, that is, generating the diborane in a separate vessel and leading it into the diglyme solution to the olefin to achieve hydroboration. On the other hand, the amount of the hydroborating agent used in the hydroboration stage exerted an enormous effect upon the rate of isomerization. Use of the theoretical quantity, or of a deficiency (*i.e.*, excess olefin), resulted in a very slow, incomplete reaction. Use of a slight excess of the hydride brought about the usual rapid isomerization reaction we had observed previously.<sup>8</sup>

This observation provides the explanation for the remarkable difference in the rates of hydroboration observed previously.<sup>7,8</sup> The results are summarized in Table I.

**Table I.** Isomerization of the Organoboranes Derived from 2-Hexene<sup>a</sup>

2-Hexene, mmoles	Hydride, mmoles	Hydroboration procedure	Hexanol, %		
			1-	2-	3-
50	60	External	88	7	5
50	60	Internal	85	10	5
50	60	Internal <sup>c</sup>	86	8	6
50	50	Internal	20	60	20
50	40	Internal	13	64	23

<sup>a</sup> Diglyme solution, 150°, 1 hr. <sup>b</sup> Sodium borohydride has four "hydrides." <sup>c</sup> Boron trifluoride diglymate substituted for the usual boron trifluoride etherate.

(9) A preliminary report of some of our observations was published in an earlier communication: H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 1504 (1960).

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

In the usual internal generation, boron trifluoride etherate is used with sodium borohydride to achieve hydroboration. For the usual syntheses, the presence of the ethyl ether in the reaction mixture causes no difficulty. However, for study of the isomerization reaction, the presence of the ether makes it difficult to achieve the reaction temperature rapidly. This difficulty could be circumvented by substituting for the etherate the corresponding diglymate.<sup>11</sup> The latter is prepared conveniently by adding boron trifluoride etherate to diglyme and then pumping off the displaced ether.

Based on these results, the following standard procedure was adopted for a study of the scope of the reaction. In a flask was placed 30 ml of a 1.0 *M* solution of sodium borohydride (120 mmoles of hydride, 20% excess) in diglyme and 100 mmoles of the olefin in 30 ml of diglyme. Hydroboration was achieved by adding 10.8 ml of a 3.65 *M* solution of boron trifluoride in diglyme (40 mmoles of boron trifluoride) to the reaction mixture at 20 to 25°. In the cases of 2-methyl-2-butene, *trans*-4,4-dimethyl-2-pentene, and 2,4,4-trimethyl-2-pentene, where the hydroboration proceeds preferentially to the dialkylborane stage, 45 ml of the sodium borohydride solution and 60 mmoles of boron trifluoride diglymate were utilized for 100 mmoles of olefin. The reaction mixture was brought rapidly to the isomerization temperature and maintained there by means of a heating mantle. A nitrogen atmosphere was maintained. At appropriate time intervals samples were withdrawn by means of a hypodermic syringe and oxidized with alkaline hydrogen peroxide. The alcohols thus produced were subjected to gas chromatographic analysis.

In presenting the results of this study of the effects of structure on the isomerization reaction, it is convenient to consider in separate groups olefins with similar structural features. Accordingly, we shall consider four classes: (1) straight-chain olefins, (2) singly branched olefins, (3) doubly branched olefins, (4) aromatic olefins.

**Straight-Chain Olefins.** Hydroboration of terminal olefins, such as 1-pentene and 1-hexene, places 94% of the boron at the primary and 6% at the secondary position. Isomerization of these organoboranes for 4 hr at 160° gives essentially the same distribution. However, it is significant that isomerization of the organoborane from 1-hexene gives approximately 2% of the 3-hexylboron moiety, whereas this species is initially absent.

The organoboranes derived from 2-pentene and 2-hexene, with an initial boron distribution of close to 50-50 between the 2 and 3 positions, isomerize rapidly to place the boron predominantly (91-95%) at the terminal position.

The results of these experiments are summarized in Table II.

**Singly Branched Olefins.** Hydroboration of 3-methyl-1-butene gives 94% of the primary and 6% of the secondary organoborane, whereas in the case of the 2-methyl-1-butene essentially only the primary derivative is formed. 2-Methyl-2-butene undergoes hydroboration to the dialkylborane stage to place 98% of the boron at the secondary position. Isomerization

(11) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

**Table II.** Isomerization of Organoboranes Derived from the Hydroboration of Straight-Chain Olefins<sup>a</sup>

Olefin	Temp, °C	Time, hr	Alcohol, %		
			1-ol	2-ol	3-ol
1-Pentene <sup>c</sup>	25	0	94	6	0
		160	1	91	7
	160	2	93	5	2
		4	93	5	2
1-Hexene <sup>d</sup>	25	0	94	6	0
		160	1	93	5
	160	2	93	5	2
		4	94	4	2
<i>trans</i> -2-Pentene <sup>c</sup>	25	0	0	49	51
		160	1	95	4
	160	2	95	4	1
		4	95	4	1
<i>trans</i> -2-Hexene <sup>c</sup>	25	0	0	46	54
		160	1	91	6
	160	2	92	5	3
		4	91	6	3

<sup>a</sup> Diglyme solution, internal hydroboration. <sup>b</sup> *cis-trans* mixture. <sup>c</sup> Alcohols analysed on a glycerol column. <sup>d</sup> Alcohols analyzed on a tricyanoethoxypropane column.

of the organoboranes derived from these three individual olefins for 4 hr at 160° results in a nearly identical boron distribution about the chain, with 59% ending up at the less hindered primary position and 39% ending up at the more hindered such position.

A similar preference of the boron for the less hindered primary position of the 2-alkylpentyl system likewise was observed in the hydroboration-isomerization of *trans*-4-methyl-2-pentene.

The results of these experiments are summarized in Table III.

**Table III.** Isomerization of Organoboranes Derived from the Hydroboration of Singly Branched Olefins<sup>a</sup>

Olefin	Temp, °C	Time, hr	Alcohol, % <sup>b</sup>				
			1-ol	2-ol	3-ol	4-ol	5-ol
2-Methyl-1-butene <sup>c</sup>	25	0	0	0	1	99	
		160	1	27	1	Trace <sup>e</sup>	72
	160	2	46	1	Trace	53	
		4	56	1	Trace	43	
3-Methyl-1-butene <sup>c</sup>	25	0	94	6			
		160	1	73	1	Trace	26
	160	2	63	1	Trace	36	
		4	59	1	Trace	40	
2-Methyl-2-butene <sup>c</sup>	25	0	0	98	2	0	
		160	1	52	1	Trace	47
	160	2	57	2	Trace	41	
		4	58	2	Trace	40	
<i>trans</i> -4-Methyl-2-pentene <sup>d</sup>	25	0	0	57	43	0	
	160	4	59	1	1	Trace	39

<sup>a</sup> Diglyme solution, internal hydroboration. <sup>b</sup> Numbered as  $\text{C}-\text{C}-\text{C}(\text{C})-\text{C}$  and  $\text{C}-\text{C}-\text{C}-\text{C}(\text{C})-\text{C}$ . <sup>c</sup> Alcohols analyzed on a glycerol column. <sup>d</sup> Alcohols analyzed on a glycerol-tricyanoethoxypropane column. <sup>e</sup> <0.5%.

**Doubly Branched Olefins.** 3,3-Dimethyl-1-butene, with an initial boron distribution of 94% primary and 6% secondary, undergoes isomerization to essentially pure primary organoborane. The hydroboration of 2,4,4-trimethyl-1-pentene proceeds to place 99% of the boron at the terminal position, and no alteration of the distribution is realized during 4 hr at 160°.

An exceedingly fast migration of the boron from the internal to the terminal position occurs in the isomeri-

zation of the dialkylborane from 2,4,4-trimethyl-2-pentene. The evolution of hydrogen during the isomerization stage was noted. Gas chromatographic analysis of the oxidized reaction mixture revealed the presence of only the isomerized alcohol, 2,4,4-trimethyl-1-pentanol. However, the yield was only 69%, in contrast to the essentially quantitative yields realized in the other cases.<sup>12</sup>

An improved yield of the alcohol is realized by hydroboration of 2,4,4-trimethyl-2-pentene in the ratio of three olefins to one BH<sub>3</sub>, followed by isomerization. Under these conditions cyclization is avoided and the 2,4,4-trimethyl-1-pentanol is obtained in 90% or better yield.

The results of these investigations are summarized in Table IV.

**Table IV.** Isomerization of Organoboranes Derived from the Hydroboration of Doubly Branched Olefins<sup>a</sup>

Olefin	Temp, °C	Time, hr	Alcohol, %		
			1-ol	2-ol	3-ol
3,3-Dimethyl-1-butene <sup>b</sup>	25	0	94	6	
		160	4	99	1
2,4,4-Trimethyl-1-pentene <sup>b</sup>	25	0	99	1	0
		160	1	99	Trace
	160	4	99	Trace	1
		25	0	0	2
2,4,4-Trimethyl-2-pentene <sup>b</sup>	160	1	97	1	2
		2	98	Trace	2
	160	4	99	Trace	1

<sup>a</sup> Diglyme solution, internal hydroboration. <sup>b</sup> Alcohols analyzed on a Carbowax 1500 column.

**Aromatic Olefins.** Hydroboration of styrene produces 80% of the primary and 20% of the secondary organoborane. Essentially the same distribution is observed after isomerization. Hydroboration of *trans*-1-phenylpropene gives 85% of the  $\alpha$  and 15% of the  $\beta$  derivative. Isomerization moves the boron out to the primary carbon atom, but the distribution realized, 13%  $\alpha$ , 9%  $\beta$ , and 78%  $\gamma$ , is not as predominantly primary as in the aliphatic case. A similar isomer distribution was realized after isomerization of the organoborane from allylbenzene. These results are summarized in Table V.

**Table V.** Isomerization of Organoboranes Derived from the Hydroboration of Aromatic Olefins<sup>a</sup>

Olefin	Temp, °C	Time, hr	Alcohol, %		
			1-ol	2-ol	3-ol
Styrene	25	0	80	20	
		160	4	80	20
Allylbenzene <sup>b</sup>	25	0	90	10	0
		160	1	85	7
	160	2	85	8	7
		4	86	7	7
<i>trans</i> -1-Phenyl-1-propene <sup>b</sup>	25	0	0	15	85
		160	1	76	10
	160	2	76	10	14
		4	78	9	13

<sup>a</sup> Diglyme solution, internal hydroboration. <sup>b</sup> Alcohols analyzed on a Carbowax 20M column.

(12) An investigation of this peculiarity revealed that cyclization to a boron heterocycle had occurred and oxidation had produced a diol as a by-product: H. C. Brown, K. J. Murray, H. Müller, and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1443 (1966).

**Rates of Isomerization.** These experiments indicate the scope of the isomerization reaction and define the isomer distributions at equilibrium. However, it is evident that the reaction is too fast at 160° to establish the nature of the intermediates and the rates at which these are formed and transformed in the reaction. Accordingly, it was decided to prepare several representative derivatives and to follow their isomerizations at temperatures which would permit establishment of the intervening stages.

The results for the isomerization of 2-hexene at 125° in the presence of an excess and a deficiency of "hydride" are summarized in Table VI.

Table VI. Rates of Isomerization of the Organoboranes Derived from the Hydroboration of 2-Hexene<sup>a</sup>

2-Hexene, mmoles	Hydride, mmoles	Time, hr	Hexanol, %		
			1-	2-	3-
150	100	1	0	62	38
		2	Trace	73	27
		4	2	77	21
		8	11	71	18
		24	31	52	17
100	120	1	43	38	19
		2	66	23	11
		4	88	11	5
		8	90	7	3
		24	91	6	3

<sup>a</sup> Diglyme solution, 125° internal hydroboration, with boron trifluoride diglymate.

It is evident again that there is an enormous difference in the rates of isomerization in the presence and absence of the excess hydride. In the former case the reaction is essentially complete in 4 hr at 125°, whereas in the absence of the catalytic excess of the hydride there is formed only 2% of the primary derivative at this time.

Table VII. Rates of Isomerization of the Organoboranes Derived from the Hydroboration of 1-, 2-, and 3-Hexene<sup>a</sup>

Olefin	Temp, °C	Time, hr	Hexanol, %		
			1-	2-	3-
<i>cis</i> -3-Hexene	125	1	44	30	26
		2	57	25	18
		4	74	15	11
		8	82	9	9
	150	24	88	6	6
		1	89	7	4
		2	91	6	3
		16	90	6	4
<i>trans</i> -2-Hexene	125	1	43	38	19
		2	66	23	11
		4	84	11	5
		8	90	7	3
	150	24	91	6	3
		1	88	7	5
		2	90	7	3
		16	92	5	3
1-Hexene	125	1	94	4	2
		2	94	4	2
		8	93	5	2
		24	92	6	2
	150	1	90	6	4
		2	92	6	2
		8	91	6	3
		16	91	6	3

<sup>a</sup> See footnotes to Table VI.

The rates of isomerization of the organoboranes from 1-, *trans*-2-, and *cis*-3-hexene were examined at 125 and 150°, using the standard 20% excess of hydride. The results are summarized in Table VII.

The data clearly establish that the reaction proceeds rapidly even at 125° and approaches the same equilibrium distribution in the three systems.

The methylbutenes were of interest in determining whether there would be any difficulty in moving the boron atom past the single branch. However, the rate data, summarized in Table VIII, reveal no such difficulty. Again, all three systems approach the same equilibrium distribution.

Finally, 2,4,4-trimethyl-2-pentene was hydroborated to the dialkylborane stage and subjected to isomerization. The product underwent isomerization with remarkable ease. The data are summarized in Table IX.

As was pointed out earlier<sup>12</sup> this dialkylborane undergoes cyclization at the usual isomerization temperature. This side reaction can be minimized by using olefin-to-hydride ratios adequate to yield the trialkylborane. In the case of 2-hexene, such ratios resulted in a greatly reduced rate of isomerization (Table I). However, in the present case, no significant change in rate was observed accompanying the use of the stoichiometric amount of hydride (Table IX). The explanation presumably arises from the fact that the badly hindered olefin, 2,4,4-trimethyl-2-pentene, cannot react with the catalytically active species and be converted into the catalytically inactive trialkylborane until after isomerization has occurred to the less sterically demanding primary derivative.<sup>13</sup>

The versatility of the hydroboration reaction coupled with isomerization is indicated by the transformation of 3-ethyl-3-pentanol into the corresponding secondary and primary alcohols. Thus the parent alcohol, readily synthesized *via* the Grignard reaction, can be dehydrated to yield the tertiary olefin, 3-ethyl-2-pentene. Hydroboration-oxidation of this olefin affords essentially pure 3-ethyl-2-pentanol. Alternatively, isomerization of the initially formed organoborane, followed by oxidation, affords essentially pure 3-ethyl-1-pentanol. In both cases the yields and purities are excellent.

## Discussion

It was originally noted that tri-*sec*-butylborane, synthesized *via* the Grignard reaction, isomerizes into tri-*n*-butylborane when heated for 24 to 48 hr at 200 to 220°. In contrast to this report of the very slow isomerization of organoboranes, it was noted that related secondary trialkylboranes, synthesized *via* the hydroboration reaction, underwent rapid isomerization at much lower temperatures, such as 160° (refluxing diglyme).<sup>8</sup> Initially, it was thought that this enormous rate enhancement was due to the presence of the solvent diglyme, and this does appear to have a modest effect upon the isomerization rate. However, the present study clearly establishes that the primary cause of the enhanced rate in our studies is the slight excess of diborane normally used in the hydroboration reaction to ensure complete conversion of the olefin.

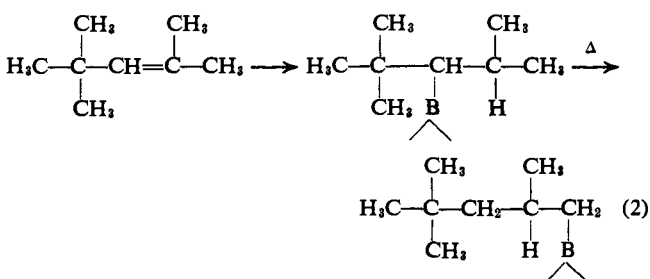
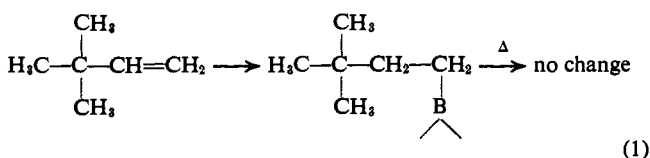
(13) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **84**, 1478 (1962).

Table VIII. Rates of Isomerization of the Organoboranes Derived from the Hydroboration of the Methylbutenes<sup>a</sup>

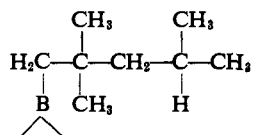
Temp, °C	Time, hr	2-Methyl-1-butene <sup>b,d</sup>				3-Methyl-1-butene <sup>b,d</sup>				2-Methyl-2-butene <sup>c,d</sup>			
		1-ol	2-ol	3-ol	4-ol	1-ol	2-ol	3-ol	4-ol	1-ol	2-ol	3-ol	4-ol
75	1									9	85	6	Trace
	2									12	81	6	Trace
	4									14	79	6	1
	8									23	66	5	6
	24									41	43	4	12
100	1	Trace	Trace	Trace	99	99	Trace	Trace	1	38	44	5	13
	2	Trace	Trace	Trace	99	99	Trace	Trace	1	46	53	3	18
	4	Trace	Trace	Trace	99	99	Trace	Trace	1	55	17	2	26
	8	Trace	Trace	Trace	99	99	Trace	Trace	1	63	5	Trace	32
	24	4	Trace	Trace	96	95	Trace	Trace	5	64	2	Trace	34
125	1	1	1	Trace	98	95	2	Trace	3	62	4	Trace	34
	2	4	1	Trace	95	95	1	Trace	4	61	3	Trace	36
	4	6	Trace	Trace	94	93	1	Trace	6	60	2	Trace	38
	8	12	1	Trace	87	88	1	Trace	11	58	2	Trace	40
	24	34	1	Trace	65					58	2	Trace	40
150	1	25	1	Trace	74	81	1	Trace	18				
	2	40	1	Trace	59	75	1	Trace	25				
	4	46	1	Trace	53	65	1	Trace	34				
	8	55	1	Trace	44	61	1	Trace	38				
	24	59	1	Trace	40	58	1	Trace	41				

<sup>a</sup> See footnotes to Table VI. <sup>b</sup> 20% excess hydride over conversion to trialkylborane. <sup>c</sup> Hydride for conversion to dialkylborane. <sup>d</sup> For numbering system, see footnote b, Table III.

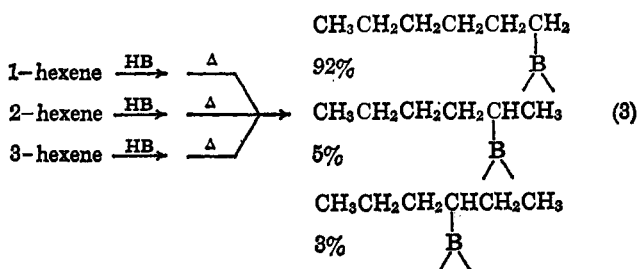
The results with 3,3-dimethyl-1-butene (eq 1) and 2,4,4-trimethyl-2-pentene (eq 2) clearly establish that the boron atom readily migrates past a single branch, but not past a double branch.



but no



In the case of 1-, 2-, and 3-hexene, isomerization moves the boron throughout the chain. Thus, it is significant that the organoborane from 1-hexene, which contains no 3-hexylboron derivative initially, produces a small quantity (2%) of this isomer under isomerization conditions. However, the boron atom

Table IX. Rates of Isomerization of the Organoboranes Derived from the Hydroboration of 2,4,4-Trimethyl-2-pentene<sup>a</sup>

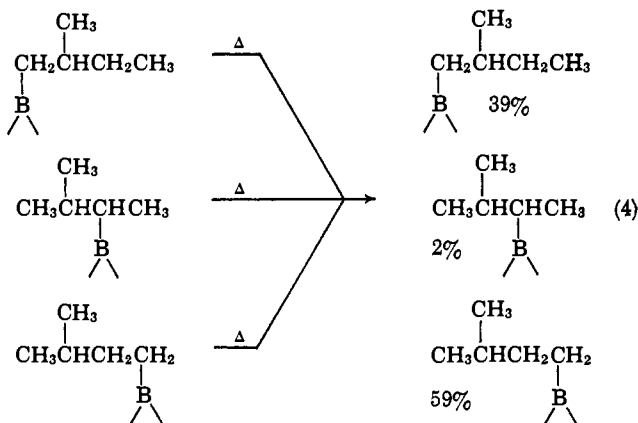
Olefin/hydride	Temp, °C	Time, hr	2,4,4-Trimethyl-x-pentanol, %		
			1-	2-	3-
2:3 <sup>b</sup>	50	2	15	40	45
		4	19	41	40
		8	22	45	33
		24	50	31	19
		2	62	21	17
2:3 <sup>b</sup>	75	2	76	9	15
		4	85	5	10
		8	96	2	2
		24	98	1	1
		1	98	Trace	1
2:3 <sup>b</sup>	100	2	99	Trace	1
		4	99	Trace	1
		2	75	20	5
		4	86	9	5
		8	96	3	1
3:3 <sup>c</sup>	75	24	98	2	Trace
		2	99	Trace	1

<sup>a</sup> See footnotes to Table VI. <sup>b</sup> Hydride for conversion to dialkylborane. <sup>c</sup> Hydride for conversion to trialkylborane.

clearly prefers the primary position. Moreover, within the limits of the experimental uncertainty, all three isomers yield the same equilibrium distribution (eq 3).

It is evident that the isomerization reaction must provide a means to achieve thermodynamic equilibrium between all of the alkylboron moieties under relatively mild conditions. On this basis the primary alkylboron structure must be considerably more stable than the corresponding secondary. It was originally suggested that the greater stability of the primary derivative must be the result of decreased steric interactions in this position between the boron atom and the three alkyl groups. This proposal is supported by the results realized for the isomerization of the organoboranes from the three methylbutenes (eq 4).

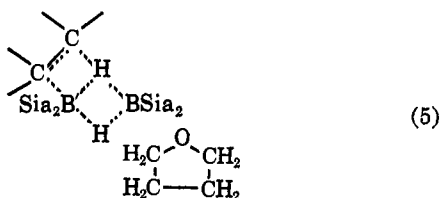
In this case the boron atom evidently finds no difficulty in moving past the single branch from either direction. Here also the same distribution is realized from the organoboranes from each of the three olefins.



However, it is highly significant that with two possible primary positions to select from, the boron atom ends up preferentially at the least hindered of the two, in spite of the statistical factor that would favor the other.

Originally, it was proposed that the isomerization reaction involved a sequence of very rapid *cis* eliminations and readditions, which shifted the boron atom up and down the chain to permit establishment of the thermodynamic equilibrium.<sup>8</sup> This mechanism predicted the facile migration of the boron atom past a single branch and its incapability of migrating past a double branch. The steric interpretation for the preference of the boron atom for the terminal carbon atom of straight-chain derivatives is consistent with the observation that in the unsymmetrical methylbutyl system the boron atom moves preferentially to that terminal carbon atom which is in the less crowded environment. However, the mechanism in its original form does not account for the catalysis by excess hydride and it must be modified to include this important characteristic.

Study of the kinetics of the reaction of disiamylborane, or rather its dimer, *sym*-tetrasiamyldiborane, with olefins has established that the reaction is second order, first order in each component.<sup>14</sup> The hydroboration reaction involves a *cis* addition of the boron-hydrogen linkage to the double bond<sup>2</sup> and the hydroboration reaction is very powerfully catalyzed by ether solvents.<sup>8</sup> Consequently, it was proposed that the hydroboration reaction involved the transition state (eq 5), in which the ether solvent serves to solvate and stabilize the leaving disiamylborane group.

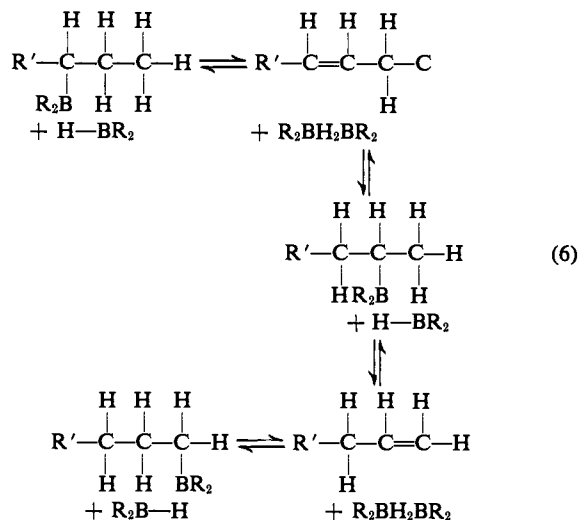


If we make the reasonable assumption that the elimination of a boron-hydrogen bond from the organoborane will involve a *cis* elimination which will be essentially the reverse of the above addition, the nature of the catalysis by excess hydride becomes clear. The excess hydride will mean that there will be present in the reaction mixture, in addition to the usual trialkyl-

(14) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **83**, 3417 (1961).

borane, a small quantity of dialkylborane, or its dimer. This dialkylborane can readily facilitate the *cis* elimination of a dialkylborane moiety from the trialkylborane, yielding the olefin and the *sym*-tetraalkyldiborane.

On this basis the modified mechanism for the isomerization becomes that shown in reaction 6.



It was pointed out that in the case of the organoborane from 2-hexene, the presence of excess olefin markedly inhibits the isomerization (Table VI). On the other hand, the presence of excess 2,4,4-trimethyl-2-pentene apparently fails to inhibit the isomerization of the dialkylborane from this olefin. Both results are consistent with the proposed mechanism.

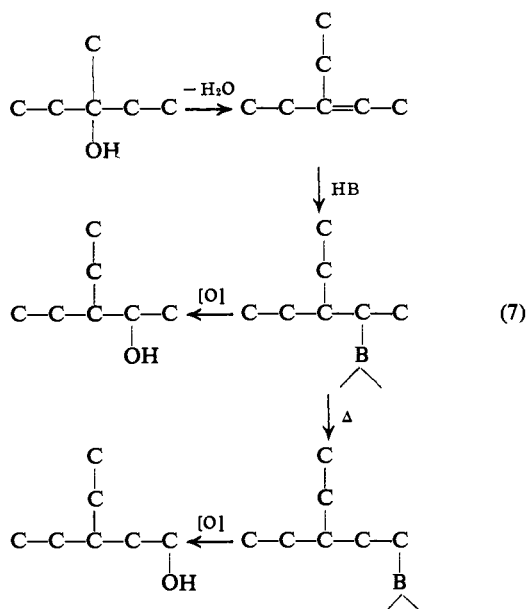
In the case of 2-hexene, hydroboration goes rapidly to the trialkylborane stage. Consequently, the excess olefin reacts rapidly with the catalytically active dialkylborane species (or its dimer) and converts it to the inactive trialkylborane. On the other hand, the reaction of 2,4,4-trimethyl-2-pentene goes rapidly to the monoalkylborane and only slowly beyond to the dialkylborane.<sup>13</sup> We have never been able to accomplish the conversion of this highly hindered olefin to the corresponding trialkylborane prior to isomerization.

Before closing we should point out that hydroboration, combined with isomerization, makes possible a number of very interesting synthetic approaches. One example is provided by the conversion of triethylcarbinol in nearly quantitative yields into essentially pure secondary and primary alcohols (eq 7).

Finally, it is of interest to point out that in all of our studies on isomerization, even with highly labile terpene structures, the boron atom appears to be capable of surprising mobility about the outer sheath of hydrogen surrounding the carbon skeleton, but at no time have we observed any rearrangement of the skeleton itself.

## Experimental Section

**Materials.** Diglyme was distilled from lithium aluminum hydride (a small excess over that required to react with active hydrogen impurities) under reduced pressure. Boron trifluoride diglymate was prepared by mixing one part (by volume) of distilled boron trifluoride etherate with two parts (by volume) of diglyme. The ether was pumped off under vacuum (5 to 10 mm) for 20 min at 20°. The resulting solution was 3.65 *M* in boron trifluoride. The sources of the olefins used and their purities and properties were reported earlier.<sup>10</sup>



**Hydroboration.** The following procedure was used to prepare the organoboranes for the isomerization experiments. In a three-neck flask, fitted with a pressure-equalized funnel, an inlet for nitrogen, and a side arm fitted with a rubber cap to permit the removal of material by means of a hyperdermic syringe, was placed 30 ml of a 1.00 *M* solution of sodium borohydride in diglyme and 100 mmoles of the olefin in 30 ml of diglyme solution. The reaction flask was immersed in a water bath at 20 to 25°. From the funnel 10.8 ml (40 mmoles) of boron trifluoride diglymate was added to the reaction mixture over a period of 30 min. The reaction flask was permitted to remain at room temperature for 1 additional hr.

2-Methyl-2-butene, *trans*-4,4-dimethyl-2-pentene, and 2,4,4-trimethyl-2-pentene were hydroborated in the ratio of two olefins per  $\text{BH}_3$ . Accordingly, 45 mmoles of sodium borohydride and 60 mmoles of boron trifluoride diglymate were used for the hydroboration of 100 mmoles of the olefin. The hydroboration of 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene, in the ratio of three olefins per  $\text{BH}_3$ , was carried out as described above.

**Isomerization.** The organoborane was heated to the desired temperature by means of a heating mantle as rapidly as possible

(5 to 10 min). The reaction mixtures were maintained at the temperatures indicated with a maximum variation in the temperature of approximately  $\pm 5^\circ$ . At the indicated time intervals, 10-ml samples were withdrawn with a syringe. Water was added to decompose residual hydride. The mixtures then were oxidized in the usual manner by adding sodium hydroxide, followed by 30% hydrogen peroxide. The alcohols formed were extracted with ether. After drying over anhydrous magnesium sulfate, the samples were analyzed by gas chromatography. The identity of the individual products was established by comparing the retention times with authentic samples. The observed yields were in the range of 90%, except for 2,4,4-trimethyl-1-pentanol, where a yield of only 69% was obtained, due to the cyclization reaction.<sup>12</sup>

**Preparation of 3-Ethyl-1-pentanol via the Hydroboration of 3-Ethyl-1-pentene.** In a three-neck flask was placed 9.8 g of 3-ethyl-1-pentene (100 mmoles) and 30 ml of a 1.00 *M* solution of sodium borohydride in diglyme. Diborane was generated by adding 10.6 ml of a 3.65 *M* solution of boron trifluoride in diglyme to the mixture over a period of 30 min at 20 to 25°. The reaction was allowed to remain for 1 additional hr at this temperature. Sufficient water then was added to decompose residual hydride. The organoborane was oxidized by adding 10 ml of a 3 *M* solution of sodium hydroxide, followed by 10.5 ml of 30% hydrogen peroxide. The alcohol was taken up in ether and the combined ether extracts were washed four times with ice-water to remove diglyme. Distillation gave 10.6 g, 91% yield of 3-ethyl-1-pentanol, bp 168–169° (740 mm),  $n_D^{20}$  1.4296.

**Preparation of 3-Ethyl-2-pentanol via Hydroboration of 3-Ethyl-2-pentene.** 3-Ethyl-2-pentene, bp 94–95°,  $n_D^{20}$  1.4148, was prepared by dehydration of 3-ethyl-3-pentanol with iodine in the customary manner. The olefin, 9.8 g 100 mmoles, was hydroborated using 45 mmoles of sodium borohydride and 60 mmoles of boron trifluoride in diglyme. The procedure then followed that described above. There was obtained 9.6 g, 83% yield, of 3-ethyl-2-pentanol, bp 150–151°,  $n_D^{20}$  1.4282.

**Preparation of 3-Ethyl-1-pentanol via Hydroboration-Isomerization of 3-Ethyl-2-pentene.** To 14.7 g of 3-ethyl-2-pentene, 150 mmoles, was added 45 ml of a 1.00 *M* solution of sodium borohydride in diglyme, followed by 45 mmoles of boron trifluoride in diglyme. This corresponds to a ratio of three olefins per  $\text{BH}_3$ . After the hydroboration stage, the reaction mixture was heated for 2 hr at 160°. The organoborane was oxidized at 40 to 50° by adding 16 ml of 3 *M* sodium hydroxide solution, followed by 16 ml of 30% hydrogen peroxide. The reaction mixture was worked up in the usual manner. There was obtained 15.4 g, 88%, of 3-ethyl-1-pentanol, bp 169–170° (740 mm),  $n_D^{20}$  1.4296.