Organic and Biological Chemistry

Organoboranes. VI. Isomerization of Organoboranes Derived from the Hydroboration of Cyclic and Bicyclic Olefins

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Abstract: A number of representative cyclic and bicyclic olefins were converted by hydroboration into the corresponding organoboranes and subjected to isomerization conditions. In the case of simple 1-alkylcycloalkenes the boron atom moves about the ring, ultimately ending up at the primary position of the alkyl substituent. The equilibrium distribution of the boron between the ring and the side chain appears to vary with the size of the ring and the steric interactions. Thus a much larger percentage of the boron moves out of the ring into the side chain in the case of the more hindered cyclohexyl and cycloheptyl derivatives than in the case of the corresponding cyclobutyl and cyclopentyl derivatives. Consequently, hydroboration–isomerization–oxidation of 1-alkylcycloalkenes, readily available *via* the Grignard reaction from the cycloalkanones, provides a convenient synthetic route to the ω-cycloalkyl-α-alkanols. The organoboranes from norbornene, camphene, α- and β-pinene, and Δ^3-carene were also subjected to isomerization conditions, and the nature of the products was explored.

It was previously shown that the hydroboration of acyclic olefins followed by thermal isomerization at relatively mild conditions results in the migration of the boron atom along the carbon chain to appear preferentially at a terminal position.[1,2] Consequently, the hydroboration–isomerization procedure provides a convenient synthetic route from internal olefins to terminal olefins[3] or to the many primary derivatives to which organoboranes may be transformed.[4]

The objective of the present study was the examination of the possibility for extending the isomerization reaction to organoboranes obtained from cyclic and bicyclic olefins. In particular we were interested in testing the possibility that the boron atom might be isomerized from within a cycloalkyl ring out into a side chain. Demonstration of the practicality of such an isomerization would open up many interesting and useful synthetic routes.

Results and Discussion

As was pointed out earlier, the isomerization of organoboranes, under the catalytic influence of a slight excess of boron–hydrogen moieties, occurs under remarkably mild conditions (75 to 160°).[1,2] In this isomerization the boron atom moves up and down the alkyl chain, past single but not double branches, in a series of rapid 1,2-shifts, ultimately ending up predominantly in the terminal position. Analysis of such an isomerized mixture of organoboranes is difficult. Fortunately, the oxidation of organoboranes with alkaline hydrogen peroxide proceeds quantitatively to place a hydroxyl group at the precise position previously occupied by the boron atom.[5] Consequently, this oxidation, combined with glpc analysis of the isomeric alcohols, provides a powerful, highly convenient tool for the investigation of the reaction.

In view of these considerations, the following procedure was adopted for this isomerization study. The olefin was hydroborated with sodium borohydride and boron trifluoride in diglyme solution in the usual manner. The reaction mixture was then heated to the desired temperature and maintained there. At appropriate intervals of time, aliquots were withdrawn and oxidized with alkaline hydrogen peroxide. The alcohols thus produced were taken up in ether, and the dried ether extract was analyzed by glpc for the isomeric alcohols. The yield of alcohols was established by comparison with an external standard solution.

Effect of Hydride on the Rate of Isomerization. Previous studies dealing with the isomerization of organoboranes from acyclic olefins had revealed that the isomerization rate is strongly dependent upon the presence of the small excess of hydride normally used in the hydroboration reaction. The presence of a slight excess of olefin almost brings the isomerization to a halt. Consequently, our standard procedure utilized a 20% excess of hydroborating agent.

In the case of the cyclic olefins, such as 1-methylcyclohexene, we were faced with a problem. Such olefins normally undergo hydroboration only to the dialkylborane stage. This represents a "50% excess" of hydride. In some cases a large excess of hydride results in a cyclization reaction.[6] This would constitute an undesirable side reaction in the present study. Accordingly, we undertook to hydroborate 1-methylcyclohexene, utilizing various ratios of olefin to hydride, and subjected the resulting products to isomerization at 160° for various periods of time. The results are summarized in Table I.

(1) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6434 (1959).
(2) H. C. Brown and G. Zweifel, *ibid.*, **88**, 1433 (1966).
(3) H. C. Brown and M. V. Bhatt, *ibid.*, **88**, 1440 (1966).
(4) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.
(5) The results of a detailed study of this oxidation reaction will be reported shortly in a manuscript now in preparation with B. C. Subba Rao, C. H. Snyder, and G. Zweifel.
(6) H. C. Brown, K. J. Murray, H. Müller, and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1443 (1966).

Table I. Effect of Olefin : Hydride Ratio on the Isomerization of the Organoborane from 1-Methylcyclohexene[a]

1-Methylcyclohexene, mmoles	Hydride,[b] mmoles	Time, hr	Methylcyclohexanol, % *cis*-2	*trans*-2,-*trans*-3,-*cis*-4	*cis*-3,-*trans*-4	1-	Cyclohexanemethanol, %	Yield, %
100	150[c]	1	1	16	35	2	46	
		2	1	15	33	2	49	
		4	1	15	30	2	52	78
100	120[d]	1	1	16	34	2	47	
		2	1	13	31	2	54	
		4	1	13	31	2	54	83
110	100[e]	1	1	31	61	2	5	
		2	1	27	64	2	6	
		4	1	25	61	2	11	84

[a] Diglyme solution, 160 ± 5°. [b] Sodium borohydride has four "hydrides." [c] Hydroboration in a 2:1 ratio of olefin : BH_3, *i.e.*, to the R_2BH stage. [d] Hydroboration in a 3:1 ratio of olefin : BH_3, using 20% excess of "hydride." [e] Hydroboration in a 3:1 ratio of olefin : BH_3, using a 10% excess of olefin.

The results reveal that it is not necessary to use a large excess of hydride because of the tendency of the parent olefin to undergo hydroboration primarily to the R_2BH stage. Evidently, initial isomerization produces a less hindered dialkylborane so that a third equivalent of olefin can be utilized. Consequently, the usual procedure involving a 3:1 ratio of olefin : BH_3, with 20% excess hydride, is entirely satisfactory. Under these conditions the reaction appears to be essentially complete in 1 to 2 hr at 160° (refluxing diglyme).

Without excess hydride the isomerization of the boron appears to proceed with satisfactory rate within the ring. Note the formation of at least 60% of 3 and 4 derivatives within 1 hr. However, the movement of the boron atom out of the ring into the methyl group appears to be a much slower reaction and proceeds only very slowly under these conditions. We previously observed a similar phenomenon in the isomerization of the organoborane from 2-hexene.[2] With a deficiency of hydride the boron atom moves relatively rapidly between the secondary 2 and 3 positions, but only slowly out to the primary 1 position.

Effect of Temperature. The rate of isomerization of these organoboranes depends strongly on the molecular structure. This is illustrated by the following results. Isomerization of the organoborane from 1-methylcyclohexene proceeds exceedingly slowly at 100°, with only 7% of the primary organoborane realized after 8 hr, as compared to the 52 to 54% of primary groups present in the equilibrium mixture. On the other hand, the isomerization of the organoborane from α-pinene at 100° proceeds rapidly, approaching the equilibrium distribution, 80% primary, within a few hours. In practice, we have found it satisfactory to carry out the isomerization of the organoborane for 2 to 4 hr in refluxing diglyme solution (150 to 160°). With few exceptions all of the derivatives we have examined are converted into the equilibrium distributions under these conditions.

The experimental results are summarized in Table II.

Effect of Ring Size. It was previously suggested that it is the greater nonbonded interactions between the secondary hydrogen atoms of the aliphatic chain and the boron atom that cause it to prefer the less hindered primary positions. On this basis we should anticipate a significant effect of the ring size on the secondary (endocyclic) to primary (exocyclic) distribution. The larger rings, with their closer resemblence to the mobility and steric interactions of acyclic chains, should exhibit a larger preference for the boron to accumulate in the exocyclic primary position. On the other hand, the smaller, more rigid rings would be expected to exhibit a decreased tendency to shift the boron from the endocyclic secondary position. Accordingly, we undertook the hydroboration–isomerization of methylenecyclobutane, 1-methylcyclopentene, 1-methylcyclohexene, and 1-methylcycloheptene.

Table II. Effect of Temperature on the Rate of Isomerization[a]

Olefin	Temp, °C	Time, hr	Alcohol, % Primary[b]	Alcohol, % Secondary[c]	Yield, %
1-Methylcyclohexene	100	2	4	96	
		4	5	95	
		8	7	93	87
	160	1	47	53	
		2	54	46	
		4	54	46	83
α-Pinene	100	2	61	39	
		4	69	31	
		8	76	24	91
	160	1	83	17	
		2	82	18	
		4	81	19	82

[a] Diglyme solution: 3:1 ratio of olefin : BH_3, using a 20% excess of "hydride." [b] Cyclohexanemethanol or *trans*-myrtanol. [c] Also minor amounts of tertiary.

Hydroboration of methylenecyclobutane, followed by oxidation, gives cyclobutanemethanol in high yield. However, isomerization of the organoborane for 4 hr at 160°, followed by oxidation, results in a poor yield of alcohol, 22%.[7] Analysis of the alcohol fraction revealed the formation of 17% primary and 83% secondary.

1-Methylcyclopentene provided an 85% yield of alcohol, with a distribution indicated of 30% primary (cyclopentanemethanol) and 70% secondary and tertiary (only minor amounts of the latter). In the case of 1-methylcyclohexene the yield of primary increases to 54%, and 55% is realized with 1-methylcycloheptene.

The results are summarized in Table III.

(7) It is possible that the cyclobutane ring is opened at these temperatures. This would have resulted in the formation of pentanediols which would not have been extracted into the ether. The presence of 1,5-pentanediol in the aqueous phase was demonstrated. It has recently been reported that the cyclopropane ring is opened by diborane at 100°. Unfortunately, our stock of methylenecyclobutane had been exhausted and time did not permit further exploration.

Table III. Effect of Ring Size on the Isomeric Distribution[a]

Olefin	Alcohol, % Primary	Alcohol, % Secondary[b]	Yield, %	Statistical ratio[c]
Methylenecyclobutane	17	83	22	0.6
1-Methylcyclopentene	30	70	85	1.7
1-Methylcyclohexene	54	46	83	5.9
1-Methylcycloheptene	55	45	81	7.3

[a] Diglyme solution, 2 hr at 160°, using 3:1 ratio of olefin:BH_3 plus 20% excess "hydride." [b] Also minor amounts of tertiary. [c] Corrected for the varying number of methylene groups in the ring: ($-CH_2OH:CH_3$):($>CHOH:CH_2$).

In order to obtain a truer estimate of the relative tendency of the boron atom to distribute itself between the endocyclic and exocyclic positions of these ring systems, we should correct the data for the variable number of methylene groups available in the different rings. This has been done in the "statistical ratio" given in Table III. Clearly the results reveal an increasing tendency for the boron atom to prefer the exocyclic methyl group with an increase in ring size from four[8] to seven members.

Effect of the Structure of the Side Chain. The proposed interpretation of the mechanism of the isomerization reaction[2] predicts that a lengthening of the side chain should favor the accumulation of the boron atom in the exocyclic primary position. To test this prediction, 1-ethyl-, 1-propyl-, and 1-isopropylcyclohexene were subjected to the hydroboration–isomerization procedure. Four hours at 160° was utilized; it was established that the observed distribution did not alter significantly with longer reaction periods.

It was observed that the presence of an ethyl side chain resulted in the formation of 70% of the primary derivative, as compared to 54% for the methyl. Further lengthening of the chain had no significant effect. Indeed, the slight decrease to 68% primary observed with 1-propylcyclohexene is explicable in terms of the increased number of secondary positions made available by the longer chain. Finally, the decrease to 63% primary for 1-isopropylcyclohexene is explicable in terms of the larger nonbonded interactions at the primary position of the iso grouping.

The experimental data are summarized in Table IV.

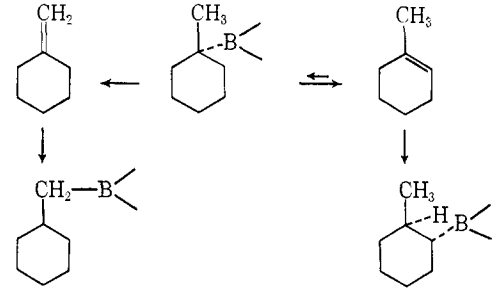
Table IV. The Effect of Alkyl Side Chains on the Isomeric Distribution[a]

Olefin	Alcohol, % Primary	Alcohol, % Secondary[b]	Yield, %
1-Methylcyclohexene	54	46	83
1-Ethylcyclohexene	70	30	95
1-Propylcyclohexene	68	32	84
1-Isopropylcyclohexene	63	37	92

[a] Diglyme solution, 4 hr at 160° using a 3:1 ratio of olefin:BH_3 plus 20% excess "hydride." [b] Also minor amounts of tertiary.

Isomeric Distribution of the Boron within the Cyclohexane Ring. Hydroboration of 1-methylcyclohexene proceeds rapidly to the dialkylborane stage. Oxidation of the product gives 98% of the *trans*-2-methylcyclohexanol, corresponding to the proposed *cis*, four-centered addition of borane to the double bond.[9] As was pointed out earlier, isomerization of a reaction mixture containing 3 moles of 1-methylcyclohexene per borane results in a relatively rapid movement of the boron atom around the ring, but with only a slow migration of the boron to the exocyclic position.

This slow isomerization of the boron to the exocyclic position is readily explicable in terms of the successive elimination–addition mechanism previously proposed for the isomerization reaction.[2] The exocyclic isomerization would require addition of the boron–hydrogen moiety to 1-methylcyclohexene to place the boron atom at the tertiary position and elimination to give methylenecyclohexene, both reactions which strongly prefer to go in the alternate direction (eq 1). Consequently, the formation of the methylenecyclohexane intermediate requires two successive unfavorable reactions, prior to the formation of the stable primary derivative.



(1)

It was of interest to explore the endocyclic phase of the isomerization. Accordingly, 1-, 3-, and 4-methylcyclohexene and methylenecyclohexane were subjected to hydroboration and isomerization under conditions conducive to examining the isomeric endocyclic derivatives. The glpc analysis was able to resolve seven of the eight isomeric alcohols. Fortunately, the *trans*-3-*cis*-4-methylcyclohexanol peak, which could not be resolved, was a minor product, and failure to resolve this peak does not handicap the interpretation.

The results (Table V) reveal that the boron atom exhibits a marked preference for the equatorial *cis*-3 and *trans*-4 positions. Slightly more than twice the amount of boron appears at the *cis*-3 than at the *trans*-4 position. Consequently, if we introduce the statistical correction of 2, the two equatorial positions are almost equally favored, with a minor residual factor in favor of the *cis*-3. The amount of *trans*-3 and *cis*-4 (axial isomers) is approximately one-sixth of the *cis*-3 and *trans*-4. Thus there is a factor of approximately 6 favoring the equatorial isomers in these positions. In the 2 position, it is the *trans*-2 that is strongly favored. The fact that this equatorial position is occupied to so much smaller an extent than the equatorial 3 or 4 positions must be the result of the steric interactions with the 1-methyl substituent.

Finally, it is of interest to call attention to the similarity in the isomeric distributions realized with the four different olefins (Table V). Clearly these must represent the equilibrium distributions.

Bicyclic Systems. The hydroboration of norbornene proceeds predominantly from the *exo* direction, with

(8) Our conclusions with regard to the cyclobutane derivative must be considered tentative until it is established that the observed isomer distribution is not seriously affected by the low yield of isolated alcohol.

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

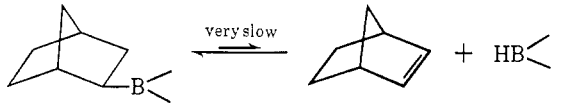
Table V. Isomerization of the Organoboranes Derived from the Hydroboration of 1-, 3-, and 4-Methylcyclohexene and Methylenecyclohexane[a]

Olefin	Time, hr	Methylcyclohexanol, %						Cyclohexanemethanol, %
		cis-2	*trans*-2	*trans*-3,-*cis*-4	*cis*-3	*trans*-4	*t*	
1-Methylcyclohexene	0	1	98				1	
	1	1	10	8	35	15	2	29
	2	1	8	7	31	10	3	40
	4	1	5	4	21	9	2	58
	8	1	6	4	21	8	2	58
3-Methylcyclohexene	4	1	8	7	25	11	1	48
	8	1	6	6	24	11	1	52
4-Methylcyclohexene	1	1	10	10	44	16	0	19
	2	1	9	8	37	12	0	33
	4	1	6	5	24	11	0	53
	8	1	5	4	22	10	0	58
Methylenecyclohexane	2	1	3	2	8	5	0	82
	4	1	6	5	20	8	0	61
	8	1	5	4	20	11	0	60
	12	1	5	4	22	10	0	59

[a] Diglyme solution, 150 ± 3°, using a 3:1 ratio of olefin: BH_3 plus 20% excess "hydride."

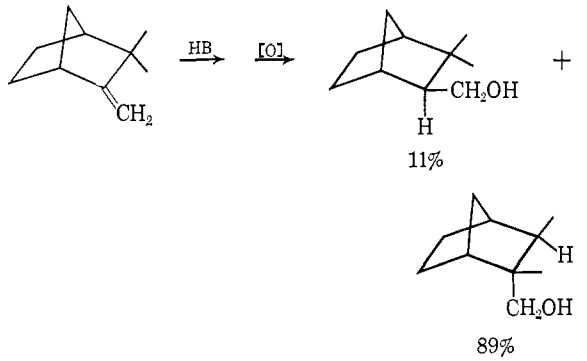
oxidation yielding essentially pure *exo*-norborneol.[9] Isomerization of the organoborane at 160° to the *endo* derivative is very slow. Thus, after 4 hr there was obtained 94% *exo* and 6% *endo* isomer. Although 4 hr at 160° had proven adequate to achieve equilibrium in all previous cases, it was not sufficient here. Thus, after 48 hr there was realized 76% *exo* and 24% *endo* isomer. We did not establish whether this represents the equilibrium distribution. However, it is quite clear that this isomerization is unusually slow.

It has been shown that displacement of norbornene from its organoborane is an also unusually slow reaction.[10] Since both the isomerization reaction and the displacement reaction involve a prior dissociation of the organoborane into norbornene and a less alkylated organoborane, the slowness of these reactions is presumably an indication of the resistance offered by the norbornyl boron intermediate to dissociate into an olefin with such a highly strained double bond (eq 2).



(2)

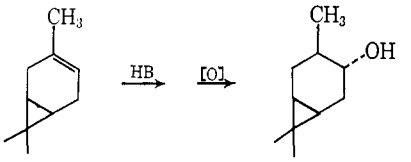
Hydroboration of camphene yields 11% *exo* and 89% *endo* isomer (eq 3).[11] Isomerization for 4 hr produces 50% *exo* and 50% *endo* isomer. This is essentially



(3)

unchanged in 8 hr: 52% *exo*, 48% *endo*. The presence of some side reactions was indicated by the presence in the glpc analysis of some minor peaks which were not identified.

Hydroboration–oxidation of Δ^3-carene gives a single isomer,[12] now identified as 4-isocaranol[13] (eq 4). It has been reported that isomerization of the organoborane yields 10-hydroxycarane, with the cyclopropane ring surviving the isomerization procedure.[14] However, in our hands, utilization of the standard isomerization conditions provided only a 35% yield of alcohol, not characterized. Evidently the cyclopropyl ring is sensitive to the isomerization conditions, and it will require careful control of reaction conditions to achieve isomerization in the presence of this reactive structure.



(4)

A detailed study was made of the isomerization of the organoborane from α- and β-pinene.[9,15,16] Simple hydroboration–oxidation of α-pinene results in the hydration of the double bond from the less hindered side, producing isopinocampheol. Isomerization of the organoborane under mild conditions (125°), prior to the oxidation, results in a fast migration of the boron to the exocyclic position. Oxidation and glpc analysis of the product revealed 76% of *trans*-myrtanol, 2% of *cis*- myrtanol, and 22% of secondary alcohols. The *cis*-myrtanol is evidently the initial isomerization product but is rapidly converted to the *trans* isomer. At lower temperatures, 75°, a high yield of the *cis*-myrtanol can be realized.

Hydroboration of β-pinene produces the *cis*-myrtanyl derivative in high purity. This is rapidly isomerized

(10) H. C. Brown, M. V. Bhatt, T. Munekata, and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 567 (1966).
(11) Compare R. Dulou and Y. Chrétien-Bessière, *Bull. Soc. Chim. France*, 1362 (1959).
(12) H. Kuczynski and A. Andrzejak, *Roczniki Chem.*, **34**, 1189 (1960).
(13) H. C. Brown and A. Suzuki, manuscript in preparation.
(14) H. G. Arlt, E. H. Sheers, and R. J. Chamberlain, *Chem. Ind.* (London), 1409 (1961).
(15) G. Zweifel and H. C. Brown, *J. Am. Chem. Soc.*, **86**, 393 (1964).
(16) J. C. Braun and G. S. Fisher, *Tetrahedron Letters*, **No. 21**, 9 (1960).

to the *trans* isomer,[16] but isomerization of the boron into the ring is quite slow. Again this slow isomerization into the ring is consistent with the proposed mechanism, as discussed previously for the methylcyclohexyl system (1).

Again, the data at 160° reveal essentially the same isomer distribution from both α- and β-pinene, confirming an approach to the true equilibrium distribution.

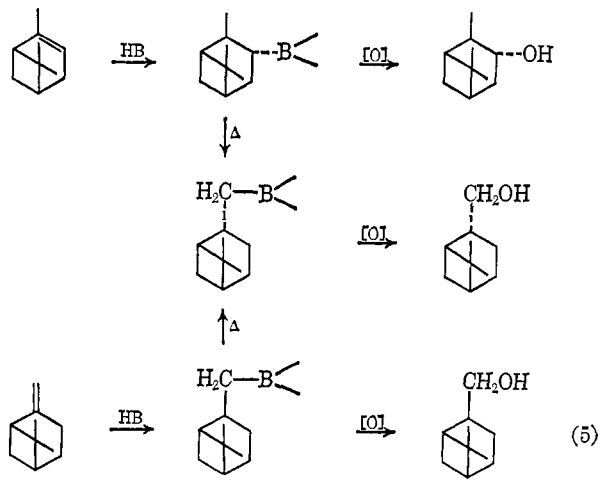
The data are summarized in Table VI.

Table VI. Isomerization of the Organoboranes Derived from the Hydroboration of α- and β-Pinene[a]

Olefin	Temp, °C	Time, hr	Alcohols, % Primary	Alcohols, % Secondary	Ratio, % *cis*-Myrtanol	Ratio, % *trans*-Myrtanol
α-Pinene	75	1	10	90	84	16
		2	14	86	77	23
		4	22	78	67	33
		8	30	70	34	66
	100	1	32	68	33	67
		2	48	52	17	83
		4	64	36	6	94
		8	72	28	3	97
	125	1	66	34	3	97
		2	76	24	3	97
		4	78	22	3	97
	160	1	83	17	2	98
			80	20	3	97
β-Pinene	100	1	97	3	25	75
		2	97	3	5	95
		4	97	3	3	97
		8	97	3	3	97
	125	1	98	2	3	97
		2	97	3	3	97
		4	96	4	3	97
		8	94	6	3	97
	160	4	84	16	3	97

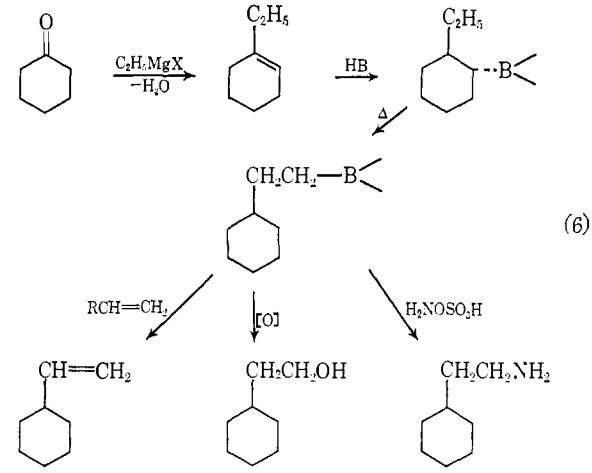
[a] Diglyme solution, using a 3:1 olefin:BH_3 plus 20% excess "hydride." [b] Also minor amounts of tertiary.

Synthetic Possibilities. It is evident that the hydroboration reaction coupled with the ready isomerization of the organoborane possesses many interesting synthetic possibilities in the synthesis of cyclic and bicyclic derivatives. Some of the rich potentialities are indicated by the following transformations which have been demonstrated in the pinane derivatives (eq 5).



(5)

More generally, it is possible to take advantage of the ready isomerization of the boron atom from within the ring to a side chain to achieve the convenient synthesis of a wide range of alicyclic derivatives. Some of the possibilities are suggested by the following reactions (6). It is fortunate that even though the isomeri-



(6)

zation generally produces an equilibrium mixture of isomers, the primary product generally possesses a distinctive boiling point which permits its ready separation from the other isomers by a simple fractionation.

Although rich possibilities are already evident, further exploration will be required to define more precisely the full scope of this reaction in cyclic and bicyclic systems.

Experimental Section

Materials. Diglyme was purified by distillation under reduced pressure from a small quantity of lithium aluminum hydride (a slight excess over that required to react with active hydrogen impurities). In order to avoid the presence of volatile ethyl ether in the isomerization reaction mixture, boron trifluoride etherate was converted into the diglymate by displacement, as described earlier.[2] Commercial sodium borohydride (98%, Metal Hydrides Inc.) was used directly.

General Procedure for the Hydroboration–Isomerization Experiments. All reactions were carried out under a nitrogen atmosphere. The apparatus consisted of a dry three-necked flask, equipped with a thermometer, condenser, pressure-equalizing funnel, and a side arm, capped with a rubber septum to permit removal of samples. In the flask was placed 50 mmoles of the olefin in 10 ml of diglyme and 15 ml of a 1.00 *M* solution of sodium borohydride in diglyme. The flask was immersed in a water bath. Hydroboration was accomplished by the addition of 5.48 ml of a 3.65 *M* solution of boron trifluoride in diglyme to the well-stirred reaction mixture over a period of 15 min. The mixture was maintained at room temperature for an additional hour.

The organoborane thus formed was brought to the desired temperature by means of a heating mantle. After an appropriate reaction time, the reaction mixture was treated with alkaline hydrogen peroxide to convert the organoborane into the corresponding alcohols. The mixture was poured into water, the alcohols were taken up in ether, and the dried ether extracts were analyzed for isomeric alcohols by glpc.

In the majority of cases the reference alcohols were available from earlier hydroboration studies. In some cases we assigned a given peak on the basis of the expected structure and the relative retention time, confirming the assignment of major products by isolation and identification. In making the analyses we assumed that the thermal conductivities of the isomeric alcohols were the same. This introduces a small uncertainty into the absolute values of the isomeric distributions, but this approximation should not affect the major conclusions indicated by the data.

For studies of the variation in isomer distribution with time, a larger quantity of the organoborane was prepared following the above procedure. At appropriate time intervals, samples were withdrawn by means of a syringe, quenched in water, and then oxidized with alkaline hydrogen peroxide. The total yield of the

alcohols obtained was established by comparison with external standards.

Hydroboration–Isomerization of Organoboranes. 1-Methylcyclopentene. To 15 ml of a 1.00 *M* solution of sodium borohydride in diglyme was added 4.1 g of 1-methylcyclopentene (50 mmoles, bp 75–76°, n^{20}D 1.4326) in 10 ml of diglyme. Hydroboration was achieved by adding 5.48 ml of 3.65 *M* boron trifluoride diglymate. The mixture was maintained for 1 hr at room temperature, then heated for 4 hr at 160° (reflux). The reaction mixture was cooled and water added to destroy residual hydride. The organoborane was oxidized at 40 to 50° by adding 10 ml of 3 *M* sodium hydroxide, followed by 6 ml of 30% hydrogen peroxide. The alcohols formed were extracted with ether. The ether extract was washed with ice–water to remove diglyme. The dried ether extract was analyzed by glpc, revealing 30% of cyclopentanemethanol and 70% of secondary and tertiary alcohols, with a total yield of 85%. The ether was removed and the residual alcohol product separated on a Carbowax 20M column. The cyclopentanemethanol isolated exhibited n^{20}D 1.4573 (lit.[17] n^{20}D 1.4577).

Methylenecyclobutane. Hydroboration–oxidation of methylenecyclobutane (n^{20}D 1.4221) in tetrahydrofuran yielded cyclobutanemethanol, n^{20}D 1.4458 (lit.[18] 1.4450). Isomerization of the organoborane in diglyme for 4 hr at 160° gave, after oxidation, a 22% yield of alcohol. Analysis indicated 17% of cyclobutanemethanol and 83% of secondary alcohols. The aqueous phase was diluted with tetrahydrofuran, then saturated with solid potassium carbonate. Analysis of the upper layer revealed a peak with the same retention time as 1,5-pentanediol.

1-Methylcyclohexene. The olefin, 4.8 g (50 mmoles, bp 108°, n^{20}D 1.4508), was hydroborated in diglyme in the usual manner. After 4 hr at 160°, oxidation revealed 54% of cyclohexanemethanol and 46% of secondary and tertiary isomers. Isolation of the primary alcohol with a Carbowax 20M column yielded cyclohexanemethanol, n^{20}D 1.4640 (lit.[17] n^{25}D 1.4621).

For the study of the alcohol distribution realized after isomerization–oxidation of the organoborane derived from 1-, 3-, and 4-methylcyclohexene and methylenecyclohexane, the analysis was carried out on a 150-ft capillary column coated with silicone–nitrile fluid (12% cyanoethyl content).

1-Methylcycloheptene. From 5.5 g of 1-methylcycloheptene (50 mmoles, n^{20}D 1.4592) there was obtained an 87% yield of alcohol: 55% primary and 45% secondary and tertiary. The cycloheptanemethanol peak was isolated, n^{20}D 1.4757 (lit.[19] n^{28}D 1.4748).

1-Ethylcyclohexene. From 5.5 g of 1-ethylcyclohexene there was obtained a 95% yield of alcohol, 70% primary and 30% secondary and tertiary. Isolation of the primary fraction, 2-cyclohexylethanol, revealed n^{20}D 1.4646 (lit.[20] n^{20}D 1.4651).

1-Propylcyclohexene. The olefin (bp 152–153°, n^{20}D 1.4578), prepared *via* the Grignard route, yielded 84% alcohol, 68% primary, and 32% other isomeric alcohols. The isolated 3-cyclohexyl-1-propanol exhibited n^{20}D 1.4660 (lit.[21] n^{25}D 1.4601).

1-Isopropylcyclohexene. The olefin (bp 150–151°, n^{20}D 1.4585), also synthesized *via* the Grignard route, provided a 92% yield of alcohol, 63% primary and 37% other isomers. The 2-cyclohexyl-1-propanol exhibited n^{20}D 1.4715.

Norbornene. The olefin, bp 96–98°, mp 46–47°, yielded 99% *exo*-norborneol on hydroboration–oxidation, 94% *exo* after 4 hr of isomerization at 160°, and 76% *exo* after 48 hr.

Camphene. Analysis of the *exo* and *endo* isomers was difficult, but was achieved on a 150-ft capillary column coated with silicone–nitrile fluid.

Δ^3-Carene. The olefin, n^{20}D 1.4735, $[\alpha]^{25}$D +14°, was hydroborated in the usual manner and then isomerized for 4 hr at 160°. Examination of the oxidized product indicated a 36% yield of alcohol with many other peaks on the chromatogram.

α- and β-Pinene. The synthesis and properties of isopinocampheol and *cis*- and *trans*-myrtanol have been previously described.[9,15,16]

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