Organoboranes. VII. The Displacement Reaction with Organoboranes Derived from the Hydroboration of Cyclic and Bicyclic Olefins. Conversion of Endocyclic to Exocyclic Double Bonds

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Abstract: The displacement reaction has been explored with organoboranes obtained *via* the hydroboration of representative cyclic and bicyclic olefins to establish the scope of the reaction and the utility of the procedure for the conversion of endocyclic into exocyclic olefins. Treatment of tricyclopentylborane with 1-decene in refluxing diglyme yielded 89% cyclopentene. Under similar conditions tricyclohexylborane is converted into cyclohexene and tricyclohexanemethylborane is converted into methylenecyclohexane. Di(*trans*-2-methylcyclopentyl)- and di(*trans*-2-methylcyclohexyl)borane undergo displacement to give an 80:20 mixture of the 1-methyl- and 3-methylcycloalkene. Similarly, displacement of the organoborane derived from α-pinene gives mainly the trisubstituted olefin, α-pinene, in 90% purity. *cis*-Myrtanylborane, obtained *via* hydroboration of β-pinene, is converted by displacement into β-pinene of high purity. On the other hand, trinorbornylborane does not undergo displacement, even over greatly extended periods of time. A combination of the hydroboration–isomerization–displacement reactions permits the synthesis of exocyclic from endocyclic olefins. Thus, application of this reaction sequence to 1-methylcyclohexene, 1-ethylcyclohexene, and 1-isopropylcyclohexene gave methylenecyclohexane (56% yield), vinylcyclohexane (62%), and isopropenylcyclohexane (57%). Similarly, α-pinene could be converted into β-pinene of high optical purity. It was noted that tri(*trans*-myrtanyl)borane, obtained *via* thermal isomerization, undergoes displacement at a much slower rate than tri(*cis*-myrtanyl)borane. From these results it appears that hydroboration–isomerization–displacement provides a convenient synthetic route for the isomerization of a double bond from the endocyclic to the exocyclic position.

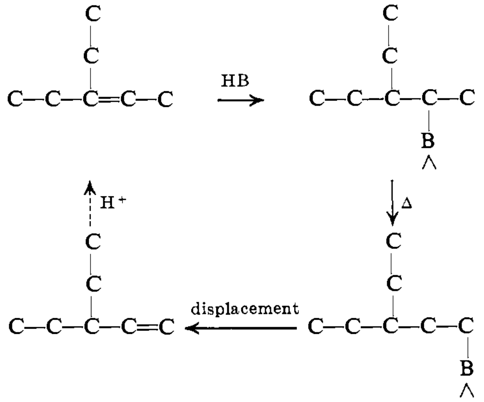
It has been established that organoboranes undergo displacement when heated in the presence of another olefin (eq 1).[3,4] A detailed study of this displacement

$$3RCH{=}CH_2 + BH_3 \longrightarrow (RCH_2CH_2)_3B$$

$$(RCH_2CH_2)_3B + 3R'CH{=}CH_2 \xrightarrow{160^\circ} 3RCH{=}CH_2\uparrow + (R'CH_2CH_2)_3B \quad (1)$$

reaction involving organoboranes derived from acyclic olefins revealed that this reversible reaction can be driven to completion by using an excess of the displacing olefin, or by removing the displaced olefin from the reaction mixture.[5]

Organoboranes undergo a facile isomerization at moderate temperatures,[4] especially so in the presence of a catalytic excess of the hydroborating agent.[6] In this isomerization the boron atom exhibits a preference for moving from a more crowded internal position to the less crowded terminal position of the chain.[6] Consequently, a combination of hydroboration, isomerization, and displacement provides a remarkably simple procedure for achieving the contrathermodynamic isomerization of acyclic olefins (eq 2).[5]



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The isomerization of organoboranes derived from the hydroboration of cyclic and bicyclic olefins has been examined.[7] It was of interest to explore the displacement reaction with these derivatives, in order to establish the scope of this reaction, and to test the applicability of the hydroboration–isomerization–displacement sequence to the conversion of endocyclic to exocyclic olefinic structures. The results of this study are reported in the present paper.

Results and Discussion

Displacement Reactions. Under the influence of heat organoboranes undergo a relatively rapid isomerization which moves the boron atom from an internal position in the chain to the terminal position It has been suggested that this isomerization reaction proceeds through a succession of elimination and readdition reactions (eq 3).[4] It is a consequence of this mechanism that an added olefin of similar reactivity should participate in these equilibrium reactions. For preparative purposes it is desirable to shift the equilibrium to essential completion, thereby obtaining one product predominantly. This desirable end can be accom-

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[1] Postdoctorate Research Associate, 1958–1959, on a program supported by the Ethyl Corporation.

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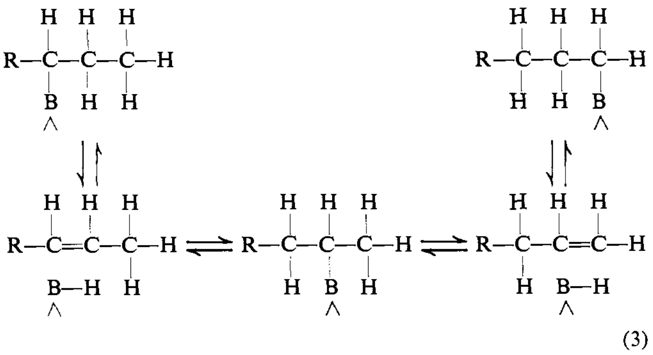
[3] R. Köster, *Angew. Chem.*, **68**, 3831 (1956); *Ann.*, **518**, 31 (1958).

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

[5] H. C. Brown and M. V. Bhatt, *ibid.*, **82**, 2074 (1960); **88**, 1440 (1966).

[6] H. C. Brown and G. Zweifel, *ibid.*, **88**, 1433 (1966).

[7] H. C. Brown and G. Zweifel, *ibid.*, **88**, 561 (1966).



(3)

Table I. Displacement of Cyclic Olefins from Their Hydroboration Products[a]

Organoborane from olefin	Time, hr	Yield, %	Olefin product (%)
Cyclopentene	4	89	Cyclopentene (100)
Cyclohexene	12	69	Cyclohexene (100)
1-Methylcyclopentene	3	72	1-Methylcyclopentene (80) 3-Methylcyclopentene (20)
1-Methylcyclohexene	6	84	1-Methylcyclohexene (77) 3-Methylcyclohexene (23)
Methylenecyclohexane	2.5	77	Methylenecyclohexane (100)
α-Pinene[b]	4	64	α-Pinene (90) β-Pinene (5) δ-Pinene (5)
β-Pinene[b]	4	71	β-Pinene (100)
Norbornene	15	0	

[a] Displacement with 1-decene in diglyme solution except where otherwise indicated. [b] Displacement with 1-dodecene in triglyme solution.

plished by using a large excess of the displacing olefin, by utilizing an unusually reactive olefin which forms a very stable organoborane, or by utilizing an olefin with a higher boiling point than the displaced product so that the latter can be removed continuously by distillation during the displacement.

It is clear that if the organoboranes were to undergo isomerization (eq 3) during the displacement reaction, there would be formed a large number of isomeric products and the reaction would have little synthetic utility. However, it has been established that the isomerization stage is fast only in the presence of a slight excess of the boron hydride hydroborating agent.[6,7] The displacing olefin destroys this catalyst for the isomerization stage and, in the case of acyclic olefins, readily permits the isolation of the product.[5]

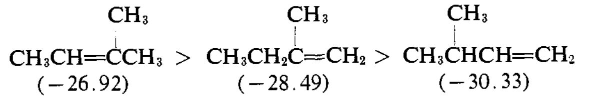
To test the feasibility of this displacement reaction in cyclic derivatives, a number of representative cyclic olefins were hydroborated and the products subjected to typical displacement conditions. The following standard procedure was utilized. A three-necked flask fitted with a dropping funnel was attached to a Todd microdistillation column. Cyclopentene, cyclohexene, methylenecyclohexane, β-pinene, and norbornene were hydroborated in a 3:1 ratio of olefin:BH_3. The trisubstituted olefins, 1-methylcyclopentene, 1-methylcyclohexene, and α-pinene, which go rapidly only to the dialkylborane stage, were hydroborated in a 2:1 ratio of olefin:BH_3. Hydroboration was carried out in diglyme solution, utilizing the action of boron trifluoride diglymate on a mixture of the olefin and sodium borohydride. Following completion of the hydroboration, a 100% excess of 1-decene was added to the organoborane. (1-Dodecene was used for the less volatile olefins, α- and β-pinene, and triglyme was utilized as the solvent in these cases.) The mixture was rapidly brought to a boil and the displaced olefin distilled through the Todd microcolumn into an ice-cooled graduated receiver. A static nitrogen atmosphere was maintained throughout the reaction.

The results are summarized in Table I.

The yields indicated in Table I represent the actual amount of olefin recovered by distillation in the time indicated. The recovery of olefin appears to follow first-order kinetics, with decreasing increments of olefin per constant interval of time. Consequently, we did not attempt to follow each reaction to its full completion, and the data in Table I should be considered to represent only the approximate rate of reaction and the approximate times required under these conditions to obtain reasonable yields of products.

The failure to realize any norbornene in 15 hr was interesting. To test the validity of this result, we placed in individual ampoules tricyclopentylborane and trinorbornylborane, in diglyme, together with an equivalent quantity of 1-octene or 1-decene. The sealed ampoules were heated at 150°. In the case of the cyclopentyl derivative there was achieved an essential equilibrium distribution of cyclopentene to 1-octene of 4:1 in 8 hr with no further change over 48 hr. On the other hand, with trinorbornylborane only traces of norbornene were detected after 100 hr.[8] Consequently, there can be no doubt that norbornene, like ethylene,[3] is not displaced from its organoborane by 1-alkenes.

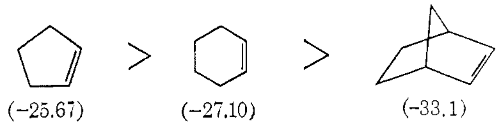
Structural Effects. In the case of the acyclic olefins it was observed that the ease of displacement appeared to parallel the relative stability of the olefin, as measured by its heat of hydrogenation.[5] Thus, the available data, qualitative though they may be, indicate the relative case of displacement from the respective organoboranes to be 2-methyl-2-butene > 2-methyl-1-butene > 3-methyl-1-butene.



$$\underset{(-26.92)}{CH_3CH{=}\overset{CH_3}{\overset{|}{C}}CH_3} > \underset{(-28.49)}{CH_3CH_2\overset{CH_3}{\overset{|}{C}}{=}CH_2} > \underset{(-30.33)}{CH_3\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2}$$

The heats of hydrogenation, given in parentheses (in kcal/mole),[9] reveal the lowest heat for the olefin that is most easily displaced.

Similarly, the relative ease of displacement of cyclopentene, cyclohexene, and norbornene parallels their respective heats of hydrogenation.[10]



It is pertinent that neither ethylene nor norbornene, with relatively high heats of hydrogenation (−32.8[11] and −33.1[10] kcal/mole, respectively), undergo significant displacement by 1-alkenes, $\Delta H = 30.1$ kcal/mole.

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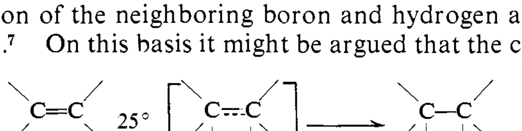
[8] We are indebted to Dr. R. K. Sharma for these experiments.

[9] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 141 (1936); M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *ibid.*, **59**, 841 (1967).

[10] R. B. Turner, "Theoretical Organic Chemistry," The Kekule Symposium, Butterworth & Co., Ltd., London, 1959, pp 76–77.

[11] G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **57**, 64 (1935).

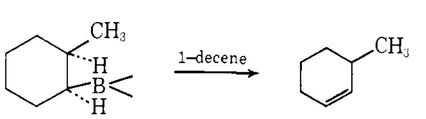
It has been suggested that the *cis* addition of the boron-hydrogen bond to cyclic olefins proceeds through a four-center transition state.[12] The principle of microscopic reversibility suggests that the elimination stage of the displacement reaction will also involve a *cis* reaction of the neighboring boron and hydrogen atoms (eq 4).[7] On this basis it might be argued that the cyclopentyl derivative, with its more nearly eclipsed conformation, would be in a better situation to undergo the elimination stage than the cyclohexyl derivative, with its eclipsed conformation. This may well be a factor in the enhanced rate exhibited by the cyclopentyl derivative. However, it cannot be the only factor, or even the major factor. The bicyclic norbornane structure possesses bonds nicely eclipsed. On this basis a rapid elimination stage might have been anticipated. The failure to achieve any significant rate of displacement suggests that the thermodynamic stability of the olefin produced is a dominant factor in the rate of the elimination stage. It was previously suggested that the hydroboration reaction is highly exothermic, so that the transition state for the addition would be expected to resemble the reactants closely. Since we are postulating that the elimination reaction proceeds through this same transition state, it is not surprising that the thermodynamic stability of the olefin produced constitutes such an important factor in the observed rate.



(4)

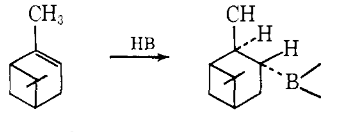
Hydroboration of 1-methylcyclopentene and 1-methylcyclohexene gives the *trans*-2-bora derivative in essentially pure isomeric form.[12] Elimination can obviously occur in two possible directions, yielding both the 1- and 3-methylcycloalkenes. Even though there are conformational arguments which suggest that elimination of 3-methylcyclohexene should be favored, the preferred formation of the 1-methylcycloalkene again argues for a dominating control over the course of the elimination by the thermodynamic stabilities of the two possible products.

In cases where elimination in two directions is not possible, the course of the reaction should be controlled entirely by the mechanism. Thus, tri(*cis*-2-methylcyclohexyl)borane would be expected to undergo elimination only to 3-methylcyclohexene.



(5)

Hydroboration of α-pinene produces diisopinocampheylborane[12,13] (eq 6). This bicyclic differs from norbornene in undergoing displacement readily. However, here also there is a marked preference for elimination toward the tertiary position; the product is 90% α-pinene and only 5% δ-pinene. (The formation of a small amount of β-pinene was also observed, but the source of this isomer is not entirely clear.)



(6)

Displacement of the boron from tri(*cis*-myrtanyl)borane, prepared *via* hydroboration of β-pinene,[13] gives pure β-pinene. It is also important for the utilization of this reaction for the synthesis of exocyclic olefins that tricyclohexanemethylborane undergoes displacement to yield pure methylenecyclohexane.

Conversion of Endocyclic to Exocyclic Olefins. As is pointed out in the accompanying publication,[7] isomerization of organoboranes derived from cyclic olefins moves the boron atom from the ring into the side chain, in structures where such side chains are available. An equilibrium distribution of the boron among all possible endocyclic and exocyclic positions is realized. Fortunately, except for the smaller ring compounds, such as cyclobutyl derivatives, the boron atom tends to prefer to accumulate at the less hindered primary position of the side chain. This is indicated by the data in Table II.

Table II. Isomerization at 160° of Organoboranes Derived from Cyclic Olefins

Olefin	Primary organoboranes, %	Secondary and tertiary organoboranes, %
1-Methylcyclohexene	54	46
1-Ethylcyclohexene	70	30
1-Isopropylcyclohexene	63	37
α-Pinene	81	19

Consequently, displacement of these isomerized products should produce the corresponding exocyclic olefins. Consequently, hydroboration–isomerization–displacement should provide a convenient synthetic route for the conversion of endocyclic olefins, readily synthesized through Grignard reactions, to the corresponding exocyclic derivatives.

In view of our previous explorations, the following experimental conditions were selected. The olefin was hydroborated in diglyme in a 3:1 ratio of olefin: BH_3, using a 20% excess of hydride. The reaction mixture was then heated under reflux (155 to 160°) for 2 to 4 hr to isomerize the organoborane. Then a 100% excess of 1-decene was added (1-dodecene in the case of α-pinene) and the reaction mixture distilled. The distillate, which contained some diglyme and 1-decene, was fractionated to obtain the pure products. The results are summarized in Table III.

The results obtained agree well with those predicted on the basis of the isomerization results (Table II). The procedure is a relatively simple one. It suffers from one significant disadvantage. The displacement yields the desired product along with appreciable quantities of endocyclic isomeric species. Consequently, to realize a pure product requires a careful fractionation or the use of preparative gas chromatography.

It was observed that the tri(*cis*-myrtanyl)borane derived from β-pinene *via* hydroboration (eq 7) underwent displacement much more readily than the *trans*

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[12] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).
[13] G. Zweifel and H. C. Brown, *ibid.*, **86**, 393 (1964).

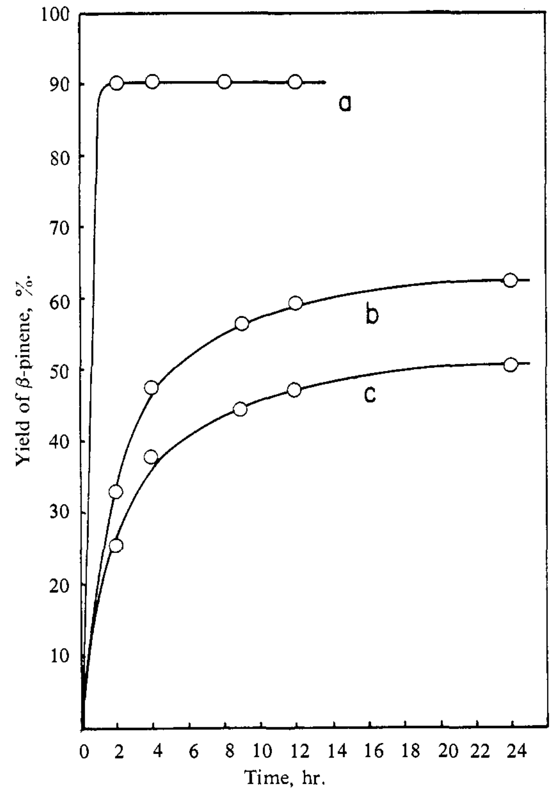
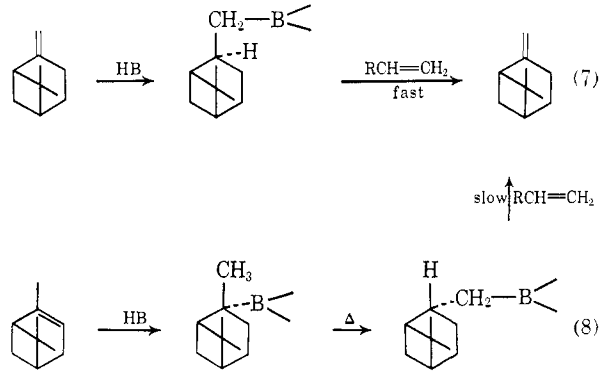


Figure 1. Rates of displacement at 145° of β-pinene from tri(*cis*-myrtanyl)borane and tri(*trans*-myrtanyl)borane: (a) displacement of the organoborane from hydroboration of β-pinene; (b) displacement of the organoborane derived from isomerization of the hydroboration product in (a); (c) displacement of the organoborane derived from hydroboration–isomerization of α-pinene.

derivative obtained *via* isomerization of the isopinocampheylborane (eq 8). It appeared this difference in the displacement rates might be the result of the fact that hydroboration of β-pinene produces the strained *cis*-myrtanyl derivative, whereas isomerization of the isopinocampheylborane, from α-pinene, produces the more stable, less strained *trans*-myrtanyl derivative. Indeed, simple thermal treatment of the initially formed *cis*-myrtanyl derivative from β-pinene converts it into the *trans* with a greatly reduced rate of displacement. The data in Figure 1 support the analysis.



The marked difference in the rate of displacement of β-pinene from the *cis*- and *trans*-myrtanyl derivatives is noteworthy. Since the same olefin is produced in the elimination stage, the rate of elimination must be greatly facilitated by the strain in tri(*cis*-myrtanyl)borane. Therefore, this represents another case of a sterically assisted reaction.

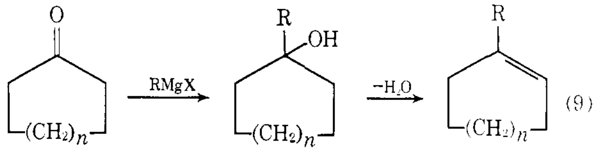
Table III. Synthesis of Exocyclic Olefins *via* Hydroboration–Isomerization–Displacement

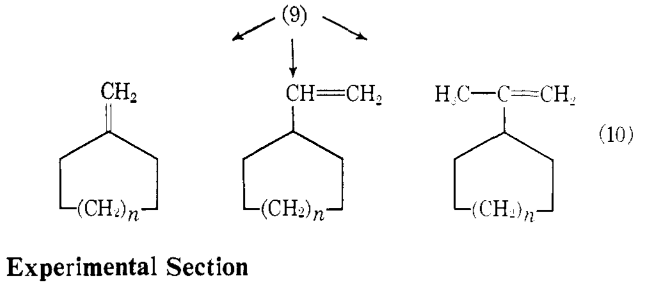
Initial olefin	Isomzn, hr	Displac, hr	Product	Yield, %
1-Methylcyclohexene	4	6	Methylenecyclohexane	56
1-Ethylcyclohexene	4	6	Vinylcyclohexane	62
1-Isopropylcyclohexene	4	6	Isopropenylcyclohexane	57
α-Pinene	2	12	β-Pinene	54
β-Pinene	2	12	β-Pinene	71

In these experiments the displaced olefin, β-pinene, was not removed from the reaction mixture. Consequently, the data must represent an approach to the distribution which can be realized under equilibrium conditions. The fact that *cis*-myrtanylborane undergoes a very fast displacement, yielding 90% of β-pinene under essentially equilibrium conditions, is quite promising. This suggests that in many cases it may not be necessary to utilize distillation of a more volatile product to achieve a good yield of the displaced olefin. If the displaced olefin is one that forms a more stable organoborane than the displaced product (1-octene > β-pinene), then this should be adequate to achieve a high yield. Since ethylene and norbornene form exceedingly stable organoboranes, their use should permit simple, essentially quantitative displacements in more complex systems where distillation would be impractical as a means of shifting the equilibrium.[14]

Conclusions

It is evident that hydroboration–isomerization–displacement provides a new, simple route to a host of exocyclic olefins. The Grignard reaction provides a convenient route to endocyclic olefins (eq 9). Application of the hydroboration–isomerization–displacement sequence converts these endocyclic derivatives into the corresponding exocyclic structures (eq 10).





Experimental Section

Materials. Diglyme and triglyme were purified by the procedure described earlier.[7] Boron trifluoride diglymate and triglymate were prepared as previously described.[15] Sodium borohydride (Metal Hydrides Inc., 98%) was used directly.

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[14] The use of squalene, with its high concentration of double bonds, would appear to provide still another solution to the problem: R. K. Sharma, B. A. Shoulder, and P. D. Gardner, *Chem. Ind.* (London), 2087 (1962).

[15] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

1-Methylcyclohexene, methylenecyclohexane, and 1-ethylcyclohexene were samples of >99 mole % purity provided by Dr. Kenneth S. Greenlee of Chemical Samples Co., Columbus, Ohio. 1-Methylcyclopentene ($n^{20}\text{D}$ 1.4320) and 1-isopropylcyclohexene ($n^{20}\text{D}$ 1.4574) were synthesized *via* the Grignard route. The latter olefin contained approximately 8% of the isomeric isopropylidenecyclohexane. α-Pinene ($n^{20}\text{D}$ 1.4660, $[\alpha]^{20}\text{D}$ +47.6°) and β-pinene ($n^{20}\text{D}$ 1.4785, $[\alpha]^{20}\text{D}$ -21.1°) were obtained from the Glidden Co.

Hydroboration–Displacement Experiments. In a typical experiment 9.6 g of 1-methylcyclohexene (100 mmoles) was placed in a three-necked flask fitted with a dropping funnel and a stirring bar, and connected to a Todd microcolumn. To the olefin was added 45 ml of a 1.00 *M* solution of sodium borohydride in diglyme. The system was flushed and then maintained under a static pressure of nitrogen throughout the hydroboration and displacement stages. Hydroboration was accomplished by adding 16.5 ml of a 3.65 *M* solution of boron trifluoride in diglyme to the well-stirred reaction mixture. The reaction flask was maintained for 30 min at room temperature.

To the reaction product was added 200 mmoles of 1-decene. The reaction mixture was heated to gentle reflux and the displaced olefin collected in an ice-cooled graduated receiver as the product reached the distillation head. In 6 hr there was collected 8.06 g, a yield of 84%. Gas chromatographic analysis of the product revealed 77% of 1-methylcyclohexene and 23% of 3-methylcyclohexene.

In the above procedure the amount of hydride used was 20% in excess of hydroboration to the dialkylborane stage. Similar amounts of hydride were used for 1-methylcyclopentene and α-pinene. For cyclopentene, cyclohexene, methylenecyclohexane, norbornene, and β-pinene, which undergo ready hydroboration to the trialkylborane stage, we utilized 30 ml of a 1.00 *M* solution of sodium borohydride and an equivalent quantity of boron trifluoride.

α- and β-pinene were hydroborated in triglyme solution, using boron trifluoride triglymate. The higher boiling solvent facilitated distillation of these less volatile olefins.

The experimental results from these hydroboration–displacement experiments are reported in Table I.

Hydroboration–Isomerization–Displacement Experiments. The following experimental procedure is typical. In a 200-ml flask fitted with a small Vigreux column was placed 11.0 g of 1-ethylcyclohexene (100 mmoles) and 30 ml of a 1.00 *M* solution of sodium borohydride in diglyme. (Since isomerization proceeds to a trialkylborane derivative, the amount of hydride utilized is based on this conversion). The flask and apparatus was flushed with nitrogen and a static nitrogen pressure was maintained throughout the reaction. Hydroboration was accomplished by adding 11.0 ml of a 3.65 *M* solution of boron trifluoride diglymate to the well-stirred reaction mixture at room temperature.

The reaction mixture was heated to reflux (155–160°) and maintained at this temperature for 4 hr. After completion of the isomerization, 200 mmoles of 1-decene was added to the reaction mixture and the heating continued. The displaced olefin was distilled out through the Vigreux column, maintaining the distillation at such a rate as to minimize the amount of diglyme and 1-decene which codistilled.

After 6 hr, the reaction was halted. Gas chromatographic analysis of the distillate indicated a 62% yield of vinylcyclohexane. The olefin mixture was distilled through a Podbielniak 8-mm Heli-grid column to obtain pure vinylcyclohexane, bp 124° at 750 mm, $n^{20}\text{D}$ 1.4455.

A slightly modified procedure was utilized for the conversion of α-pinene to β-pinene. In view of the similarity in the boiling points of β-pinene, diglyme, and 1-decene, the latter substances were substituted by the less volatile triglyme and 1-dodecene. Both the isomerization and the displacement were carried out at 160°, utilizing reduced pressure to remove the β-pinene displaced. Gas chromatographic analysis indicated a 71% yield of β-pinene. Preparative gas chromatography was utilized to separate the β-pinene from the minor amounts of α- and δ-pinene present in the product. The β-pinene thus obtained exhibited $n^{20}\text{D}$ 1.4789, $[\alpha]^{20}\text{D}$ -20.6°. Thus the β-pinene had undergone the isomerization without detectable racemization.

The results of these experiments are summarized in Table III.

Rates of Displacement of β-Pinene. In a 100-ml flask was placed 6.8 g of β-pinene (50 mmoles) and 15 ml of a 1.00 *M* solution of sodium borohydride in diglyme. After hydroboration was accomplished with 5.5 ml of 3.65 *M* boron trifluoride in diglyme, there was added 11.2 g of 1-octene (100 mmoles) and 4.08 g of *n*-nonane (internal standard). The flask was heated to 140 ± 5°. Samples were withdrawn at different time intervals and oxidized with alkaline hydrogen peroxide to destroy the organoborane. The mixture was extracted with ether; the latter was dried over anhydrous magnesium sulfate and then analyzed by glpc using the *n*-nonane as reference.

In a second experiment, β-pinene was hydroborated in an identical manner and the *cis*-myrtanyl derivative isomerized to the *trans* by heating at 160 for 2 hr. 1-Octene was then added and the displacement at 145° followed as described above.

In a third experiment, α-pinene was hydroborated and the isopinocampheylborane isomerized for 2 hr at 160°. Then 1-octene was added and the displacement with time at 145° followed as in the related two experiments.

The experimental results are shown graphically in Figure 1.

Electron Spin Resonance Spectra of Low Molecular Weight and High Molecular Weight Peroxy Radicals

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Contribution from the Research Center, Hercules Inc.,
Wilmington, Delaware 19899. *Received October 7, 1966*

Abstract: The electron spin resonance (esr) spectra of *t*-butyl, cumyl, polyethylene, polypropylene, and squalane peroxy radicals have been obtained. The temperatures at which various group and molecular averaging processes become important have been determined. The mobility of hindered phenol additivies in polypropylene is reflected by the residual dipolar coupling in the esr spectra of the phenoxy radicals.

In the kinetic study of autoxidation of polypropylene by esr,[1] there were two problems of concern: the identity and the mobility of the radicals. The esr spectra of the propagating radicals change both in line shape and line width with temperature. Three radical intermediates are often postulated in an autoxidizing system: R·, RO·, and RO_2·. Presumably, R·, which combines with O_2 with diffusion-limited rates under these conditions,[2] is not present in amounts to be detected. Though earlier reports[3] of detection of RO·

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[1] J. C. W. Chien and C. R. Boss, submitted for publication.

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