Ring Opening in the Hydroboration of Vinylcyclopropane Systems. A Cyclopropylcarbinyl–Allylcarbinylborane Rearrangement[1]

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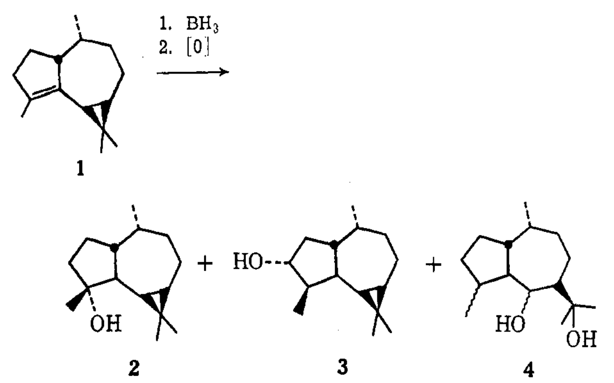
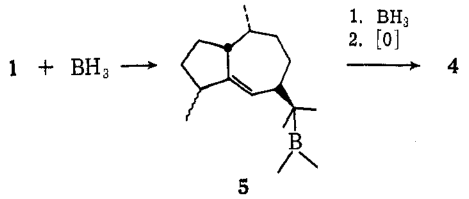
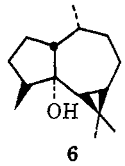
The hydroboration–oxidation of α-cyclopropyl-β,β-dimethylstyrene (**7**) at room temperature gives α-cyclopropylbenzyldimethylcarbinol (**11a**) (12%) and 5-methyl-4-phenyl-1,3-hexanediol (**12a**) (75%). From the hydroboration of **7** at −20° for 1 hr a mixture is obtained which is composed of **7** (72%), cyclopropylisopropylphenylcarbinol (**8a**) (5%), **11a** (4%), *trans*-5-methyl-4-phenyl-3-hexenol (**9a**) (6%), *cis*-5-methyl-4-phenyl-3-hexenol (**10a**) (3%), and **12a** (2%). On the basis of these results the ring opening during the hydroboration of vinylcyclopropanes is rationalized by a stepwise mechanism involving (a) normal hydroboration of the double bond; (b) homoallylic rearrangement of the α-cyclopropylcarbinylborane to an allylcarbinylborane derivative, which may undergo further hydroboration.

The cyclopropane ring does not normally react with diborane in tetrahydrofuran under the usual hydroboration conditions.[2,3] There are, however, a number of reports in the literature describing cyclopropane ring opening in the course of hydroborations of some conjugated vinylcyclopropane systems.[4-6]

Thus the hydroboration–oxidation of α-gurjunene (**1**) was reported to give the isomeric alcohols **2** and **3** in addition to the diol **4** resulting from the opening of the cyclopropane. Alcohol **2** is one of the expected, normal hydroboration products of α-gurjunene. The formation of **3** is the result of isomerization of the initially formed organoborane (precursor of **2**), while the formation of the diol **4** was interpreted in terms of conjugate addition of borane to the vinylcyclopropane system, giving first the homoallylic organoborane **5**, which is then further hydroborated and oxidized. It is worthy of note that Pesnelle and Ourisson did not mention the formation of the angular alcohol **6**, which should also arise from the hydroboration–oxidation of the tetrasubstituted double bond of **1**. The other papers in this field, dealing with the hydroboration of different vinylcyclopropane systems,[5,6] reported the formation of *unsaturated* products in addition to the normal products of hydroboration.







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The cyclopropane ring opening during the hydroboration of vinylcyclopropanes may also be rationalized by a multistage mechanism. At the initial stage the hydroboration across the double bond gives rise to the isomeric α- and β-cyclopropylorganoboron compounds, of which the β-cyclopropylorganoborane behaves normally, while the α-cyclopropylcarbinylborane undergoes a homoallylic rearrangement to give the corresponding allylcarbinylborane derivative. Analogous cyclopropylcarbinyl–allylcarbinyl rearrangements have been described involving the cyclopropylcarbinyl anion of magnesium,[7] lithium,[8] and sodium–potassium.[9]

We undertook a study of the hydroboration of a vinylcyclopropane system in an attempt to establish the mechanism of the cyclopropane ring opening during hydroboration.

As a model compound for our studies we have chosen α-cyclopropyl-β,β-dimethylstyrene (**7**) due to the following considerations: (1) it contains a tertiary carbon atom α to cyclopropane; (2) its double bond is tetrasubstituted; (3) it has a phenyl group attached to the carbon atom that bears the cyclopropane. This is desirable since the cyclopropyl group is known to have a directive effect on the hydroboration of an adjacent double bond[10] that tends to increase the placing of the boron atom on the β carbon. The phenyl group is known to have the opposite directive effect;[11] therefore its presence on the carbon atom α to the cyclo-

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[1] A preliminary account of this work was presented at the 38th Meeting of the Israel Chemical Society, Beer Sheva, Oct 8–10, 1968; E. Breuer, E. Segall, and S. Sarel, *Israel J. Chem.*, **6**, 14p (1968).

[2] See, for example, H. C. Brown and A. Suzuki, *J. Amer. Chem. Soc.*, **89**, 1933 (1967).

[3] Cyclopropanes do react, however, with diborane in the gas phase at elevated temperature: (a) W. A. G. Graham and F. G. A. Stone, *Chem. Ind. (London)*, 1096 (1957); B. Rickborn and S. E. Wood, *J. Amer. Chem. Soc.*, **93**, 3940 (1971).

[4] P. Pesnelle and G. Ourisson, *J. Org. Chem.*, **30**, 1744 (1965).

[5] W. Cocker, P. V. R. Shanon, and P. A. Staniland, *J. Chem. Soc. C*, 915 (1967).

[6] D. Dopp, *Chem. Ber.*, **102**, 1081 (1969).

[7] D. J. Patel, C. L. Hamilton, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5144 (1965).

[8] J. A. Landgrebe and J. D. Shoemaker, *ibid.*, **89**, 4465 (1967).

[9] A. Maercker, *Justus Liebigs Ann. Chem.*, **732**, 151 (1970).

[10] S. Nishida, I. Moritani, K. Ito, and K. Sakai, *J. Org. Chem.*, **32**, 939 (1967).

[11] H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, pp 113–122.

propane should counterbalance the directive effect of the latter.

Results

The addition of cyclopropyl phenyl ketone to an excess of isopropylmagnesium bromide in ether gave 1-cyclopropyl-1-phenyl-2-methyl-1-propanol (**8a**) in 66% yield.

The dehydration of the latter (**8a**) was first attempted in refluxing acetic anhydride, since this method was proven successful previously with a series of aryl cyclopropyl carbinols.[12] This reaction was found to proceed very slowly with **8a**, and only after prolonged heating it provided a mixture consisting of the desired olefin **7** (30%) and two rearranged acetates, **9b** (53%) and **10b** (18%), which was separated by preparative vapor phase chromatography.

The stereochemistry in the two geometrical isomers (**9b** and **10b**) was deduced from their uv and nmr spectra. The absence of absorption maxima around 240 mμ[13a] in the uv spectra of *both* acetates suggests that the phenyl ring cannot assume coplanarity[13b] with the double bond, probably due to nonbonded interaction between the aromatic ring and the isopropyl group. Consequently, the vinylic proton resonance of the cis isomer **10b** should appear at a higher field than in the trans isomer **9b**. Also the methylene groups of **9b** should resonate at a higher field than those of **10b**, due to a shielding effect of the aromatic ring.[14]

The relevant nmr data of the acetates **9b** and **10b** are listed in Table I.

The dehydration of **8a** could be effected more conveniently and in somewhat higher yield (50%) by the use of *p*-toluenesulfonic acid.

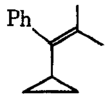
TABLE I

NMR DATA OF *cis*- AND *trans*-5-METHYL-4-PHENYL-3-HEXENYL ACETATES

Hydrogens	Chemical shift (*J*, cps) **9b**	**10b**
Aromatic	7.37–7.17 m 3 H 7.13–6.90 m 2 H	7.14 s 5 H
Vinylic	5.43 t (7) 1 H	5.20 t (7) 1 H
$CH_2\alpha$-O	3.92 t (7) 2 H	4.10 t (7) 2 H
CH allylic	2.5 m (6.5) 1 H	3.0 sept (7) 1 H
CH_2 allylic	2.12 q (7) 2 H	2.50 q (7) 2 H
CH_3 acetyl	1.93 s 3 H	2.03 s 3 H
CH_3 isopropyl	1.03 d (6.5) 6 H	1.0 d (7) 6 H

Hydroboration–oxidation of **7** was first carried out under the usual reaction conditions. Vpc analysis of the product mixture showed the presence of two products: A (with similar, but not identical retention time with that of alcohol **8a**) and B (of considerably longer retention time) in yields of 12 and 74%, respectively.

On the basis of elementary analyses and nmr spectra (see Experimental Section) the structure of A was assigned as **11a**, whereas product B is believed to constitute a diastereoisomeric mixture of 5-methyl-4-phenyl-1,3-hexanediols (**12a**). Further support for the structure of the diol **12a** can be derived from the fact that a product identical in all respects with **12a** was obtained by hydroboration–oxidation of the acetate mixture (**9b** + **10b**), followed by hydrolysis.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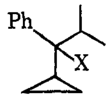
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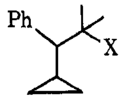
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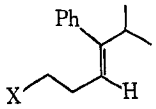
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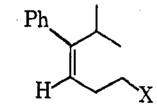
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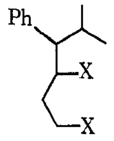
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a, X = OH
b, X = OAc
c, X = BH_2
d, X = $B(OMe)_2$

Hydroboration of **7** was then carried out at low temperatures. We found that, when **7** is hydroborated at *ca.* −20° (Dry Ice–carbon tetrachloride), and the excess hydride is decomposed at the same temperature (MeOH), followed by oxidation, a complex mixture is obtained.

The products obtained in a typical experiment (1 hr at −20°) are (1) starting material **7** (72%); (2) cyclopropylisopropylphenylcarbinol (**8a**) (5%); (3) α-cyclopropylbenzyldimethylcarbinol (**11a**) (4%); (4) *trans*-5-methyl-4-phenyl-3-hexenol (**9a**) (6%); (5) *cis*-5-methyl-4-phenyl-3-hexenol (**10a**) (3%); (6) 5-methyl-4-phenyl-1,3-hexanediol (**12a**) (~2%).

Compounds **7**, **8**, **11a**, and **12a** were identified by comparison of their retention times with those of the known compounds on several vpc columns. The homoallylic alcohols **9a** and **10a** were identified by comparison with the products of hydrolysis of the homoallylic acetates, **9b** and **10b**.

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(12) S. Sarel, E. Breuer, S. Ertag, and R. Salamon, *Israel J. Chem.*, **1**, 451 (1963).

(13) E. A. Braude in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955: (a) p 153; (b) p 169–170.

(14) Calculations based on a recent paper[15] give values of 5.41 and 5.78 ppm for the chemical shifts of the vinylic protons in **9b** and **10b**, respectively. Comparison of these values with those in Table I indicates that there is very good agreement between the calculated and observed values for the trans acetate **9b**. In contrast, the observed value for the cis acetate **10** differs by 0.58 ppm from the calculated. This difference is presumably a result of the shielding effect of the aromatic ring twisted out of the plane of the double bond.[16]

(15) U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969).

(16) On the other hand, we noted that the aromatic protons in **10b** appear as a singlet, whereas in **9b** they appear as two groups of complex multiplets in the ratio of 3:2.

The hydrogens of an aromatic ring which is conjugated to double bonds appear usually as a multiplet, whereas loss of conjugation is usually accompanied by the collapse of the multiplet into a singlet.[17,18]

On the basis of the shape of the signals of the aromatic hydrogens in the two acetates alone, one would tend to reverse the structure assignment we forwarded, since of the two structures obviously **9b** is the one in which it would be more difficult for the phenyl group to attain coplanarity with the double bond, and therefore the aromatic hydrogens of **9b** should appear as a singlet. However, since the uv spectra of both acetates indicate lack of conjugation between the phenyl ring and the double bond, we do not consider the arguments concerning the splitting of aromatic hydrogens relevant to our problem. The splitting of the aromatic hydrogens in **9b** is therefore not caused by conjugation of the ring to a double bond.

(17) (a) H. W. Whitlock and Y. N. Chuah, *Inorg. Chem.*, **4**, 424 (1965); (b) N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, **92**, 3058 (1970).

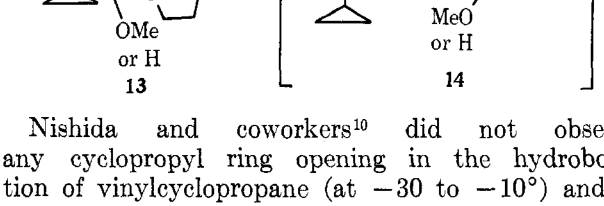
(18) Compare spectra of *cis*- and *trans*-stilbene: "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, spectrum no. 305 and 306.

Discussion

The results presented here indicate that the cyclopropane ring opening that occurs during the hydroboration of α-cyclopropyl-β,β-dimethylstyrene is a stepwise process.

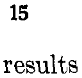
The formation of the cyclopropanic alcohol **8a** in the low-temperature experiment indicates that in the first step the reaction involves only the double bond to yield the organoboranes **8c** and **11c**. The β-cyclopropylcarbinylborane **11c** appears to be stable under these reaction conditions, whereas the α-cyclopropylcarbinylorganoborane **8c** undergoes homoallylic rearrangement to give the unsaturated organoboranes **9c** and **10c**. If this rearrangement occurs in the presence of excess hydride, the rearrangement products **9c** and **10c** undergo further hydroboration to yield a bisboron compound of type **12c**, precursor of the diol **12a**. The actual formation of **12a** was observed both in the room-temperature and in the low-temperature experiments.

The predominance of the unsaturated alcohols **9a** and **10a** over the diol **12a** in the product mixture resulting from the low-temperature reaction indicates that the rearrangement leading to the open-chain organoboranes **9c** and **10c** occurred mainly after the excess hydride was destroyed. It follows, therefore, that not only the cyclopropylcarbinylborane **8c** but also the cyclopropylcarbinlyboronate **8d** is capable of undergoing cyclopropylcarbinyl–allylcarbinyl rearrangement. This suggests that the rearrangement involves a carbanion intermediate, and that the C–B bond-breaking step is being assisted by the methoxyl groups bonded to the boron and/or by the solvent molecules as shown (**13** → **14**).



13 **14**

Nishida and coworkers[10] did not observe any cyclopropyl ring opening in the hydroboration of vinylcyclopropane (at −30 to −10°) and of spiro[2.5]oct-4-ene (**15**) (0–20°). The hydroboration of (+)-car-3-ene (**16**) was reported to give some D(−)-*cis-m*-menth-4-en-8-ol (**17**), the yield of which was found to depend on the reaction temperature (20–170°).[5]



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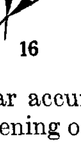

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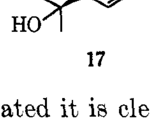

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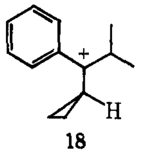
From the results so far accumulated it is clear that the cyclopropane ring opening occurs with much greater ease with *tert*-cyclopropylcarbinylboranes, in which the C–B bond breaking results in a considerable relief of steric strain, than in the *sec*-cyclopropylcarbinyl boron compounds, in which the rearrangement seems to require elevated temperatures.

Finally it is of interest to point out that the cis/trans ratio of the homoallylic alcohols **9a** and **10a** obtained in hydroboration closely resembles that of the acetates, **9b** and **10b**, resulting from the reaction of **8a** with acetic anhydride. The latter reaction may reasonably be assumed to proceed *via* a carbonium ion mechanism. The ratio of the products **9b**:**10b** indicates that conformation **18** for the carbonium ion is somewhat preferred to conformation **19**, presumably due to nonbonded interactions, which are somewhat greater between the cyclopropyl and isopropyl groups, as compared to those between the cyclopropyl and phenyl groups.[19] The isomer distribution of homoallylic alcohols obtained in the hydroboration indicates, therefore, that the conformation of the intermediate in the cyclopropylcarbinyl allylcarbinylborane rearrangement is affected by steric factors similarly to the carbonium ion intermediate.[20]



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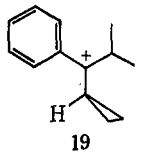

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Experimental Section[21]

Cyclopropylisopropylphenylcarbinol (8a).—Cyclopropyl phenyl ketone (8.4 g, 0.4 mol) in ether (60 ml) was added to a twofold excess of isopropylmagnesium bromide in ether. The reaction mixture was allowed to stand at room temperature overnight and decomposed by 130 ml of saturated ammonium chloride solution. After the usual work-up the carbinol was isolated by distillation: bp 95–100° (2 mm); yield 50.3 g (66%); $n^{20}\mathrm{D}$ 1.5290.

The infrared spectrum showed no absorption in the carbonyl region and the OH at 3500 cm^{-1}. The nmr spectrum showed the aromatic hydrogens as a broad multiplet at δ 7.6–7.1 (5 H), the methine CH of the isopropyl group at 2.12 (1 H) (J = 7 cps), two magnetically nonequivalent methyl groups at 0.93 d (3 H) (J = 7 cps) and 0.78 d (3 H) (J = 7 cps), and the cyclopropyl hydrogens at 1.35–0.1 m (5 H).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.10; H, 9.50. Found: C, 81.87; H, 9.22.

Reaction of Cyclopropylisopropylphenylcarbinol with Acetic Anhydride.—A mixture of 9.5 g (0.05 mol) of **8a** and 15.5 g of acetic anhydride was refluxed for 1 week. Gas chromatographic analysis revealed that after this period of time there was no starting material left in the mixture. The reaction mixture was poured into water and ether, and extracted several times with water and then several times with cold 20% sodium hydroxide solution. After drying the ether was removed and the residue was distilled, bp 70–90° (0.8 mm), yield 7.6 g. Gas chromatographic examination of the distillate on several columns revealed that it was a mixture of three compounds in the ratio of 28:54:18 in the order of their increasing retention times. Samples of these components were isolated from the mixture by preparative vpc on a 6 ft × 0.25 in. Apiezon L column at 200°.

Component I was identified as α-cyclopropyl-β,β-dimethylstyrene (**7**). The ultraviolet spectrum in ethanol showed two maxima, 226 nm (ϵ_{mol} 5980) and 241 (4150). The nmr spectrum

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(19) The estimated steric effects of the phenyl and the isopropyl groups are −1.44 and −1.71 respectively: T. C. Bruice and W. C. Bradbury, *J. Amer. Chem. Soc.*, **87**, 4838 (1965).

(20) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, **7**, 577 (1968).

(21) The purification of reagents and solvents and the preparation of borane solution in tetrahydrofuran were carried out as described by Zweifel and Brown.[22] Infrared spectra were measured on a Perkin-Elmer 237 grating spectrophotometer. Ultraviolet spectra were measured in ethanol by a Hillger-Watts Ultrascan spectrophotometer. Nmr spectra were measured by a Varian A-56-60 instrument in $CDCl_3$; all chemical shifts are given in parts per million downfield from TMS. All gas chromatographic work was carried out on a F & M Model 720 dual column programmed temperature gas chromatograph. Microanalyses were carried out by the Hebrew University microanalytical laboratory. All boiling points are uncorrected.

(22) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

showed the aromatic hydrogens at δ 7.7–6.7 (5 H), methyl hydrogens at 1.82 (3 H) s and 1.42 (3 H) s, and the cyclopropyl hydrogens at 0.7–0.1 (5 H) m.

Anal. Calcd for $C_{13}H_{16}$: C, 90.70; H, 9.30. Found: C, 90.90; H, 9.40.

Component II was identified as the trans acetate **9b**. Its infrared spectrum showed a carbonyl absorption at 1760 cm^{-1}. The ultraviolet spectrum showed one maximum at 224 nm (ϵ_{mol} 5200).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.40; H, 8.80. Found: C, 77.67; H, 8.69.

Component III was identified as the cis acetate **10b**. Its infrared spectrum showed a carbonyl absorption at 1754 cm^{-1}. The ultraviolet spectrum showed a maximum at 224 nm (ϵ_{mol} 5700).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.40; H, 8.80. Found: C, 77.57; H, 8.64.

α-Cyclopropyl-β,β-dimethylstyrene (7).—This experiment was best carried out in a vacuum distilling apparatus equipped with a short Vigreux column. *p*-Toluenesulfonic acid (4.3 g, 0.025 mol) was placed in a distilling flask of 25 ml capacity, which was heated in an oil bath to 120°, the whole apparatus being under vacuum of *ca.* 1 mm. Carbinol **8a** (8.6 g, 0.05 mol) was introduced at the fastest possible rate in order to minimize loss of material by resinification. The distillate was collected in a receiver cooled to 0°. During the course of the addition the bath temperature was raised to 180°. At the end of the experiment 4.5 g of distillate was collected in the receiver. Vpc examination revealed that it was the desired olefin in 90% purity, containing approximately 10% starting material and two impurities with retention times very close to that of the main product. Purification could not be effected by distillation; therefore, the crude product was filtered through a silica gel-silver nitrate column in petroleum ether (bp 30–60°), thus giving a gas chromatographically pure product, bp 109° (20 mm), $n^{20}D$ 1.5321. For spectral data and analysis, see previous experiment.

Hydroboration of α-Cyclopropyl-β,β-dimethylstyrene (7) at Room Temperature.—Olefin **7** (2 g, 11.4 mmol) and tetrahydrofuran (5 ml) were placed in a 50-ml hydroboration flask. To this solution 1.67 *M* borane in tetrahydrofuran (13.8 ml, 23 mmol BH_3) was added by means of a syringe. After stirring at room temperature for 24 hr, the excess hydride was decomposed by addition of water (liberation of 1200 ml of hydrogen), and the reaction mixture was oxidized by adding 3 *N* sodium hydroxide (5 ml) and 30% hydrogen peroxide (5 ml) solution. The solution was saturated with sodium hydroxide, the phases were separated, and the aqueous phase was extracted five times with ether. After drying the solution, the ether was removed, and the residue was chromatographed on basic alumina. Alcohol **11a** was eluted by 20% ether in petroleum ether, 0.25 g (∼12%). A sample was purified by preparative vpc on a GE SE-30 column at 150°. The nmr spectrum showed δ 7.22 (aromatic, broad s, 5 H), 1.28 (methyl, s, 3 H), and 1.22 (s, 3 H), and a complex multiplet at 2.1–0.1 (7H).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.10; H, 9.50. Found: C, 81.98; H, 9.68.

Diol **12a**, presumably a mixture of diastereoisomers, was eluted from the column by washing with 5% ethanol in ether, 1.75 g (∼74%). A sample was purified by preparative glc on a GE SE-30 column at 200°. The nmr spectrum of this product showed the aromatic hydrogens at δ 7.25 (broad s, 5 H), methine α to O at 4.23 (broad, 1 H), methylene α to O at 3.70 (t, *J* = 7 cps) (2 H), hydroxyl (shifted upon dilution) at 3.18 (broad, 2 H), 2.70–1.94 (complex multiplet, 2 H), 1.65–1.15 (complex multiplet, 2 H), 1.08–0.62 (complex multiplet, 6 H).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 75.00; H, 9.60. Found: C, 74.85; H, 9.62.

Products **11a** and **12a** thus isolated served as external standards for gas chromatographic determination of their yields in subsequent experiments, which, varied in reaction times and the ratios of the reactants, showed no other products.

Thin layer chromatography on silica gel in ether–chloroform (1:1) separated the product mixture to three components. Elution of the components from the plate gave alcohol **11a** and diol **12a**, whereas the least polar, nonvolatile component, which was found to contain boron by qualitative tests, was not investigated further.

Hydroboration of α-Cyclopropyl-β,β-dimethylstyrene (7) at −20°.—To olefin **7** (300 mg) placed in a small hydroboration flask immersed in a Dry Ice–carbon tetrachloride bath, 1.5 *M* borane (2.4 ml) in tetrahydrofuran was added. The solution was kept at −20° for 1 hr, then the excess hydride was decomposed by the injection of methanol (0.5 ml). It was allowed to warm up to room temperature and was oxidized as usual by alkaline hydrogen peroxide. After work-up, gas chromatographic examination (on a 6-ft GE SE-30 column with programming at the rate of 5°/min from 100 to 200°) revealed that the mixture was composed of six peaks. By comparison with the retention times of authentic samples on several gas chromatographic columns the following identifications were made: Peak 1, starting material **7** (72%); peak 2, alcohol **11a** (4%); peak 3, alcohol **8a** (5%); peak 4, trans homoallylic alcohol **9a** (6%); peak 5, cis homoallylic alcohol **10a** (3%); and peak 6, diol **12a** (2%).

Hydroboration of the Mixture of Homoallylic Acetates 9b and 10b.—The mixture of acetates (5 g, 0.021 mol) was hydroborated in tetrahydrofuran with 2 *M* borane in tetrahydrofuran (32.2 ml, 0.064 mol) at room temperature for 24 hr. The excess hydride was decomposed and the reaction mixture was oxidized by the addition of 3 *N* sodium hydroxide solution (10 ml) and 30% hydrogen peroxide (10 ml), and then refluxed for 1 hr. The crude product obtained after work-up showed no carbonyl absorption in the infrared. It was proved to be identical with diol **12a** by comparison of their gas and thin layer chromatographic behavior and of their nmr spectra.

Hydrolysis of the Mixture of Homoallylic Acetates 9b and 10b.—The acetate mixture (1 g) was refluxed with 5 *N* methanolic potassium hydroxide (1 ml) for 3 hr. The product obtained by the usual work-up showed no carbonyl absorption in the infrared. Gas chromatographic examination showed that it contained two products which were found to be identical with peaks 4 and 5 of the low-temperature hydroboration experiment (**9a** and **10a**).

Registry No.—**7**, 34564-76-6; **8a**, 34564-77-7; **9b**, 34564-97-1; **10b**, 34564-98-2; **11a**, 34608-91-8; **12a**, 34599-25-2.