Monohydroboration occurs more readily with non-conjugated dienes and the conjugated dienes of cyclic systems. Thus treatment of α-terpinene and cyclohexadiene with diborane results in the utilization of nearly six moles of diene per mole of diborane. Similarly, 1,5-hexadiene is transformed readily into 5-hexen-1-ol, b.p. 78–80° at 25 mm., n^{20}_{D} 1.4355, α-naphthylurethane, m.p. 63–64°, and bicycloheptadiene into *exo*-dehydronorborneol.

Bicycloheptadiene, 18.4 g., 0.2 mole (100% excess), and 25 mmole of lithium borohydride in 25 ml. of ether at 0° was treated with 4.6 g., 33 mmoles, of boron trifluoride etherate over 30 minutes. After 1 hour at room temperature, the ether and excess diene were removed under vacuum, ether added, and the oxidation performed. Vapor phase chromatography examination indicated the formation of 63% dehydronorborneol (88% *exo*-, 12% *endo*-). The solid product was pressed on a porous plate, recrystallized and sublimed, 4.9 g., 45%, m.p. 92–93°, phenylurethane, m.p. 156–158°.

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HOMOALLYL AND HOMOBENZYL ALCOHOLS BY THE HYDROBORATION METHOD[1]

Sir:

We wish to report that H. C. Brown's elegant hydroboration-oxidation method[2] for hydrating olefins provides an especially convenient route to homoallyl and diastereomeric homobenzyl alcohols.

Hydroboration of cyclopentadiene was carried out by the general method of Brown and Zweifel,[2] except that a 70% molar excess of diene was employed in order to minimize glycol formation. Under these conditions, a 30% yield of Δ^3-cyclopentenol was isolated; b.p. 67–68° (36 mm.), n^{25}_{D} 1.4673, phenylurethan, m.p. 140.4–140.8°, mixed m.p. with authentic material[3] 140.4–141.0°, *p*-toluenesulfonate (80% yield), m.p. 53.4–54.2°, mixed m.p. with authentic material[3] 53.2–54.2°. Infrared and vapor phase chromatographic analysis showed the alcohol product to be very predominantly Δ^3-cyclopentenol, less than 1% Δ^2-cyclopentenol being present.

Treatment of *trans*-2-*p*-anisyl-2-butene,[3] b.p. 103° (10 mm.), n^{25}_{D} 1.5316, $\lambda_{\max}$ 243 mμ (ϵ 10,890), with diborane, followed by oxidation with alkaline hydrogen peroxide according to the procedure of Brown and Zweifel,[2] resulted in a 72% yield of almost pure *erythro*-3-*p*-anisyl-2-butanol, m.p. 58.5–59.5° after one recrystallization, mixed m.p. with authentic material[4] 59.5–60°. Similarly, from hydration of *cis*-2-*p*-anisyl-2-butene,[3] b.p. 117.5° (10 mm.), n^{25}_{D} 1.5495, $\lambda_{\max}$ 252 mμ (ϵ 14,540), there was obtained an alcohol product which was at least very predominantly *threo*. Reaction of the crude product with phthalic anhydride in pyridine gave a 77% yield (over-all based on olefin) of *threo*-3-*p*-anisyl-2-butyl acid phthalate, m.p. 122–123.5° after a single recrystallization, mixed m.p. with authentic material[4] 123–124°. In neither case was any benzyl alcohol detected.

As regards orientation in the over-all hydration of the double bond, the observed results with cyclopentadiene and the 2-anisyl-2-butenes were those anticipated on the basis of the reported results with unsymmetrical olefins[2] and styrene.[5] These results suggest that the hydroboration-oxidation method is a promising one for preparation of homoallyl alcohols from conjugated dienes and homobenzyl alcohols from conjugated aryl olefins.[6]

Regarding the stereochemistry of the over-all hydration of the double bond by hydroboration-oxidation, the present results illustrate for the *cis*- and *trans*-2-*p*-anisyl-2-butenes the stereospecific *cis*-addition already demonstrated in alicyclic cases.[2,7] The new method, therefore, is very convenient for the preparation of pure diastereomeric alcohols from olefins similar to the 2-*p*-anisyl-2-butenes. Especially for the *threo*-3-anisyl-2-butanol, this method is a distinct improvement over the conventional one formerly employed.[4]

These and other results will be reported in greater detail elsewhere.[3]

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[2] H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 247 (1959).

[3] E. L. Allred, J. Sonnenberg and S. Winstein, *J. Org. Chem.*, in press.

[4] S. Winstein and G. C. Robinson, THIS JOURNAL, **80**, 169 (1958).

[5] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

[6] The degree of alkyl substitution of the olefin is important. For example, hydroboration-oxidation of anethole gives a 75:25 mixture of 1-*p*-anisyl-1-propanol and 1-*p*-anisyl-2-propanol.[3]

[7] (a) W. J. Wechter, *Chemistry and Industry*, 294 (1959); (b) S. Wolfe, M. Nussim, Y. Mazur and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

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PROBABLE STRUCTURE OF THE $B_{10}H_{10}^{-2}$ ION

Sir:

The presence of $B_{10}H_{10}^{-2}$ ion[1] in "ionic $B_{10}H_{12}R_2$," where R is an electron donor such as Me_3N, has now been substantiated by the preparation of $B_{10}H_{10}(NMe_4)_2$. Infrared spectra indicated no BH_2 groups, no BHB bridges and were consistent with the presence of discrete NMe_4^+ ions. The n.m.r. B^{11} spectrum showed only a low field doublet and a high field doublet of area about four times that of the low field doublet.

No satisfactory valence structure based on semi-localized three-center bonds in the low symmetry B_{10} framework of $B_{10}H_{14}$ has been found.[2] On the other hand, a molecule of high symmetry is suggested by the n.m.r. results. A simple $B_{10}H_{10}^{-2}$ polyhedron, closely related in structure to B_5H_9 and based on satisfactory molecular orbitals, has been discovered.

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[1] M. F. Hawthorne and A. R. Pitochelli, THIS JOURNAL, to be published.

[2] J. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959).