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, λ_{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, λ_{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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(1) (a) This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund; (b) research supported in part by the National Science Foundation.

(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).

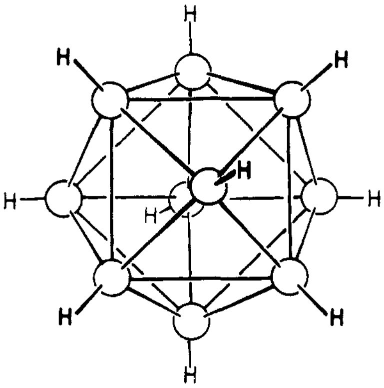

Fig. 1.—Proposed structure of the $B_{10}H_{10}^{-2}$ ion viewed approximately along the $\bar{8}$ axis.

The molecular structure (Fig. 1) has only two kinds of boron atoms in the ratio of 2 (apex) to 8 (approximately equatorial) in a polyhedron of symmetry D_{4d}. The valence orbitals of the apical boron atoms are slightly less symmetrical than those of the equatorial boron atoms, and hence the temperature-independent paramagnetism should be slightly greater for the apical boron atoms. This explanation, based upon a choice of origin at the boron nucleus, forms a more satisfactory basis for understanding B^{11} resonance shifts than that based strictly on formal charge and diamagnetism. Thus the n.m.r. results are well satisfied.

The valence orbitals can best be described by recognition of the two B_5H_5 groups, like those in B_5H_9 molecules, with almost equatorial boron atoms replacing bridge hydrogens. Of the twenty-one electron pairs, ten are used for BH single bonds, and three for each of the framework B_5 groups like those[3] in B_5H_9, and five for bonding among the sixteen remaining sp^3 orbitals of the eight almost equatorial B atoms. In D_{4d} these sixteen orbitals have the representation $A_1 + A_2 + B_1 + B_2 + 2E_1 + 2E_2 + 2E_3$. Assuming all close interactions as the same, we find[3] A_1 at $H_0 + 2\beta$, E_3 at $H_0 + (2 + 2^{1/2})^{1/2}\beta$ and E_1 at $H_0 + 2^{1/2}\beta$ as strongly bonding orbitals to be occupied by these five electron pairs. The very weakly bonding E_2 at $H_0 + (2 - 2^{1/2})^{1/2}\beta$ and non-bonding B_1 and B_2, as well as all of the antibonding orbitals are unfilled. Thus MO theory in its simplest form leads to a closed shell electronic structure for $B_{10}H_{10}^{-2}$.

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[3] W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

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RECEIVED OCTOBER 3, 1959

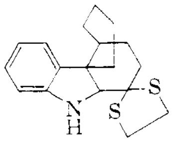
A NEW CHEMICAL DESULFURIZATION METHOD

Sir:

Hydrogenolytic desulfurization employing Raney nickel has proved to be a most useful tool in structural and small scale synthetic transformational work.[1] Other methods, catalytic and chemical, of reductive C–S cleavage have had limited utility.[2]

Hydrazine with or without alkali has been found to desulfurize cyclic or acylic dithioketals. Although the full scope and mechanism of this reaction has not as yet been established, preliminary results indicate satisfactory yields (60–95%), facility of manipulation, application to large or small scale, and freedom from the common disadvantages of the Raney nickel procedure. The substrate, 1 part by weight, in 8–20 parts by volume diethylenegycol or triethylene glycol, 3–5 parts by volume hydrazine hydrate, and 1.5–2.5 parts by weight potassium hydroxide is heated in a simple distillation apparatus. Provision may be made to collect the evolved gas over water, as the progress of reduction may be followed conveniently by this means. When the internal reaction temperature reaches the range 90–135°, depending on the nature of the substance being desulfurized, evolution of gas commences. Heating is continued at the same temperature or at gradually increasing temperatures so as to maintain a steady gas evolution and ultimately may be raised to the range 155–190° for a final completion. Times required varied from thirty minutes to three hours.

Although alkali was found not to be necessary in some cases, it lowered the effective temperature of reaction considerably. Thus, these dithioketals were desulfurized to the parent substances: 4-phenylcyclohexanone ethylenedithioketal, fluorenenone ethylenedithioketal, fluoreneone di-β-hydroxyethylthioketal, compounds I and II,[3] and *p*-menth-4-enone ethylenedithioketal, the 3-p-menthene being produced as the sole product as discerned by vapor phase chromatography.[4]



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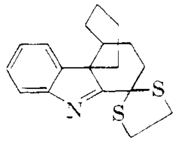

II

The gaseous by-products, collected over water, were shown to be combustible and to reduce permanganate. The sulfur was reduced completely to sulfide, no mercaptan being regenerated in the reaction. This fact plus the recognized stability of thioketals to alkali and the significantly lower reaction temperatures than those required in the Wolff–Kishner reduction vitiate an apparent relationship to the latter reaction.

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[1] R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, THIS JOURNAL, **65**, 1013 (1943).

[2] A. C. Cope and E. Farkas, *J. Org. Chem.*, **19**, 285 (1954); P. Charpentier, *Compt. rend.*, **225**, 306 (1947); H. Gilman and J. J. Dietrich, THIS JOURNAL, **80**, 381 (1958); E. Lieber and S. Somasekhara, *Chem. and Ind.*, 1367 (1958); Truce and Tate, abs. 132, Amer. Chem. Soc. Mtg., Sept. (1957) 43-P; R. Ireland, T. Wrigley and W. G. Young, THIS JOURNAL, **80**, 4604 (1958); M. S. de Winter, C. M. Siegmann and S. A. Szpilfogel, *Chem. and Ind.*, 905 (1959); F. W. Hoffmann, R. J. Ess, T. C. Simmons and R. S. Hanzel, THIS JOURNAL, **78**, 6414 (1956).

[3] The preparation of compounds I and II and the corresponding desulfurized bases will be described fully in a forthcoming publication under the authorship of V. Georgian, R. Harrisson and L. Skaletzky. Satisfactory elemental analyses were obtained for all new substances dealt with herein.

[4] This experiment was performed by Mr. James-Frederick Sauvage.