Experimental

Preparation of 2,5-Dibromo-2,5-dinitropentanamide (IV). (a) **From Dipotassium α,α′-Dinitroadiponitrile**[2] (III).—To a solution of potassium hypobromite, prepared by the addition of 8.0 g. (0.05 mole) bromine to a solution of 7.0 g. (0.105 mole) of potassium hydroxide (85% assay) in 100 ml. of water, was added rapidly at 0° 6.0 g. (0.0218 mole) of dipotassium α,α′-dinitroadiponitrile dissolved in 30 ml. of water. The resulting solution was acidified with 5% hydrochloric acid at 0°, the precipitate filtered and washed with water to give 5.5 g. (72.5% yield) of **2,5-dibromo-2,5-dinitropentanamide** (IV), m.p. 198–203°. Recrystallization from 80% ethanol and 50% ethanol gave pure IV melting at 201–203° dec.

Anal. Calcd. for $C_5H_7N_3O_5Br$: C, 17.20; H, 2.02; N, 12.03; Br, 45.85; mol. wt., 349. Found: C, 17.32; H, 2.04; N, 12.23; Br, 46.37; mol. wt.,[12] 338.

Concentration of the filtrates of the above recrystallizations afforded a second compound, m.p. 192–193°, the infrared spectrum of which was practically identical to the spectrum of the high melting material, indicating that they were diastereisomers; Infrared: bands at 2.99, 3.20 μ (N–H st.); 5.92 μ (amide I); 6.42 μ (NO_2 asym. st.); 7.34 μ (NO_2 sym. st.).

(b) **From α,α′-Dibromo-α,α′-dinitroadiponitrile**[2] (I).—Compound I (1.5 g., 4.2 mmoles) was treated with 50 ml. of 17% potassium hydroxide solution for 30 min. at −5°. The resulting clear solution was acidified with 5% hydrochloric acid at 0° and 0.5 g. (34% yield) of 2,5-dibromo-2,5-dinitropentanamide (IV) was obtained, m.p. 190–194°. A mixed melting point determination with authentic IV was not depressed (m.p. 195–197°). The infrared spectrum of the obtained solid and authentic IV were superimposable.

Preparation of 1,1,4,4-Tetrabromo-1,4-dinitrobutane (II). (a) **From Compound** III.—To a solution of 9.6 g. (0.035 mole) of compound III in 100 ml. of water was added 21.2 g. (85% assay) of potassium hydroxide. Bromine 28.4 g. (0.18 mole) was added and the solution was heated at 70–80° until ammonia evolution ceased. The crystalline solid of 1,1,4,4-tetrabromo-1,4-dinitrobutane, m.p. 98–100° (lit. value[3] 99–100°), was obtained in 5.9 g. or 36% yield. A mixed melting point determination with authentic II was not depressed (m.p. 99–100°). The infrared spectra of the obtained solid and authentic II were superimposable.

(b) **From Compound** I.—To an aqueous solution of 20% potassium hydroxide (85% assay) was added 0.3 g. (8.4 mmoles) of α,α′-dibromo-α,α′-dinitroadiponitrile, and the suspension was heated to 70°. Complete dissolution occurred after 10 minutes and the precipitate formed was identified as 1,1,4,4-tetrabromo-1,4-dinitrobutane (II), m.p. 98–100° (lit. value[3] 99–100°). A mixed melting point determination with authentic II showed no depression (m.p. 99–100°).

(c) **From 2,5-Dibromo-2,5-dinitropentanamide** (IV).—A solution of 0.3 g. (8.6 mmoles) of 2,5-dibromo-2,5-dinitropentanamide in 20 ml. of 10% potassium hydroxide solution was stirred for two hours at 25°. The precipitate which formed in the reaction mixture was filtered, recrystallized from hexane, and identified as 1,1,4,4-tetrabromo-1,4-dinitrobutane (II), m.p. 99–100° (lit. value[3] 99–100°).

Compound II was also obtained by the addition of bromine to a solution of 2,5-dibromo-2,5-dinitropentanamide in 10% sodium hydroxide at 70°. It was identified by its melting point 98–100°, and a mixed melting point determination with authentic II, m.p. 99–100°.

Reaction of α,α′-Dibromo-α,α′-dinitroadiponitrile (I) **and Aqueous Hydrochloric Acid.**—A suspension of 5.30 g. (0.015 mole) of α,α′-dibromo-α,α′-dinitroadiponitrile (I) in 30 ml. of 12% hydrochloric acid was heated at 80° for four hours. The resulting solution was evaporated to dryness *in vacuo* and the residue was extracted with ether in a Soxhlet extraction apparatus. The extracts were evaporated *in vacuo* and 1.30 g. (73.5% yield) of succinic acid, m.p. 186–188°, was obtained. A mixed melting point determination with authentic succinic acid was not depressed (m.p. 187–189°). The infrared spectra of the obtained solid and authentic succinic acid were superimposable.

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[12] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 123.

COMMUNICATIONS TO THE EDITOR

THE HYDROBORATION OF DIENES

Sir:

The hydroboration of olefins, followed by hydrogen peroxide oxidation, provides a convenient technique for the stereospecific (*cis*, anti-Markownikoff) hydration of double bonds.[1] Likewise, hydroboration of acetylenes provides a convenient route for the synthesis of *cis* olefins and for the conversion of terminal acetylenes into aldehydes.[2] The extension of this reaction to dienes provides a new, useful means of converting such dienes into the diols or related unsaturated alcohols.

Treatment of 3 moles of 1,3-butadiene with 1 mole of diborane at −10° yields an organoborane[3] which is converted by alkaline hydrogen peroxide into butanediol (82%), predominantly the 1,4-isomer, but with small quantities of 1,3-indicated by vapor phase chromatrographical examination. Similarly, 1,5-hexadiene is readily converted into 1,6-hexanediol.

Diborane, 0.33 mole, generated from sodium borohydride and boron trifluoride etherate in diglyme,[1b] was passed into 0.1 mole of 1,5-hexadiene contained in 50 cc. of tetrahydrofuran during 1 hour. After oxidation at 0° with alkaline hydrogen peroxide,[1c] the product was distilled: b.p. 105–108° at 0.6 mm., 9.3 g., 79%, m.p. 40–43°.

Treatment of excess 1,3-butadiene with diborane results in the predominant formation of the diol accompanied by minor amounts (2–10%) of allylcarbinol (v.p.c. analysis). Competitive hydroboration of 1,3-butadiene and 1-hexene results in preferential reaction of the olefin, indicating that conjugation decreases the reactivity of the double bonds. Apparently, the first addition to 1,3-butadiene occurs predominantly 1:2, followed by a relatively fast second addition to the unconjugated double bond in the 3:4 position.

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[1] (a) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 5694 (1956); (b) *J. Org. Chem.*, **22**, 1136 (1957); (c) H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 247 (1959); (d) R. Dulou and Y. Chrétien-Bessiere, *Compt. rend.*, **248**, 416 (1959); (e) W. J. Wechter, *Chemistry and Industry*, 294 (1959); (f) S. Wolfe, M. Nussim, Y. Mazur and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

[2] H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 1512 (1959).

[3] R. Köster, Abstracts of XVIIth International Congress of Pure and Applied Chemistry, Munich, 1959, p. 8.

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., $n^{20}\text{D}$ 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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RECEIVED SEPTEMBER 24, 1959

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.), $n^{25}\text{D}$ 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.), $n^{25}\text{D}$ 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.), $n^{25}\text{D}$ 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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[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).