CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, REACTION MOTORS DIVISION, THIOKOL CHEMICAL CORPORATION, DENVILLE, NEW JERSEY

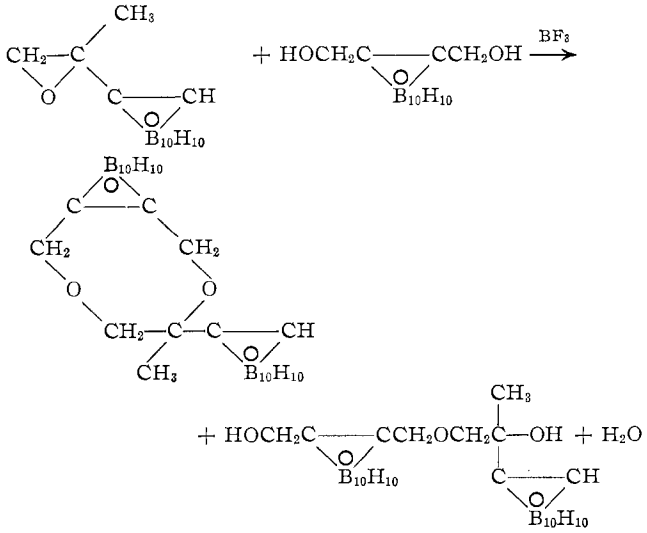
Carborane Derivatives. An Eight-Membered Exocycle of 1,2-Dicarbaclovododecaborane(12)

BY NATHAN MAYES AND JOSEPH GREEN

Received February 15, 1965

The syntheses of five- and seven-membered carborane[1] exocycles, in which one carborane participates in the ring, have been reported.[2,3] We wish to report now such an exocycle which has eight members. This compound, 1,4-dioxa-6,7-(1,2-carboranylene)-2-(1′-carboranyl)-2-methylcyclooctane, is a condensation product of 1-(epoxyisopropyl)carborane[4] and 1,2-bis(hydroxymethyl)carborane.[5] The condensation yielded, in addition to the cyclooctane, the linear ether, β-hydroxy-β-(carboran-1-yl)propyl-(1′-hydroxymethylcarboran-2′-yl)methyl ether. The linear ether is probably an intermediate of the cyclooctane; however, this was not proven by independently converting the linear compound to the cyclic compound.

The preparation and probable structures of these compounds are illustrated in the equation below.



Experimental

1-(Epoxyisopropenyl)carborane (26.0 g., 0.130 mole), 1,2-bis(hydroxymethyl)carborane (26.0 g., 0.127 mole), and 150 ml. of toluene were placed in a reaction flask fitted with a water condenser, a Dean–Stark distilling receiver, a Teflon-coated magnetic stirrer, and a gas inlet tube. The mixture was heated with stirring to reflux and became homogeneous. Boron trifluoride was bubbled into the solution several times during 48 hr. of refluxing, and 2.0 ml. of water was collected in the Dean–Stark receiver. The reaction mixture was concentrated by evaporating most of the solvent and then dissolved in methanol and precipitated by addition of water. The solid precipitate weighed 19.5 g. (40% yield); a sample twice recrystallized from hexane melted at 249–251°. Infrared analysis, molecular weight determination, and elemental analysis indicated the compound to be 1,4-dioxa-6,7-(1,2-carboranylene)-2-(1′-carboranyl)-2-methylcyclooctane. The infrared spectrum contained absorptions at 3060 cm.$^{-1}$ for CH of carborane, at 2560 cm.$^{-1}$ for BH of carborane, at 1374 cm.$^{-1}$ for CCH_3, at 1127 cm.$^{-1}$ for COC, and at 730 cm.$^{-1}$ for BH deformation of carborane. No absorption for OH was present. The molecular weight obtained cryoscopically in benzene was 378 (calculated 386). *Anal.* Calcd. for $C_9H_{30}O_2B_{20}$: C, 27.96; H, 7.82; B, 55.93. Found: C, 26.77; H, 7.92; B, 55.72.

The methanol–water mother liquor was evaporated to yield a gum from which unreacted 1,2-bis(hydroxymethyl)carborane was extracted with 5% aqueous sodium hydroxide and unreacted 1-(epoxyisopropenyl)carborane was extracted with petroleum ether. The remaining solid, weight 9.6 g. (19% yield), was identified as β-hydroxy-β-(carboran-1-yl)propyl-(1′-hydroxymethylcarboran-2′-yl)methyl ether. After three recrystallizations from heptane it melted at 196–201°. The infrared spectrum exhibited absorption bands at 3370 cm.$^{-1}$ for OH stretching and a doublet at 1170 and 1160 cm.$^{-1}$ for tertiary OH deformation. Other bands were at 3080 cm.$^{-1}$ for CH of carborane, at 2940 and 2860 cm.$^{-1}$ for aliphatic CH, at 2560 cm.$^{-1}$ for BH of carborane, at 1116 cm.$^{-1}$ for COC, and at 727 cm.$^{-1}$ for BH deformation of carborane. The molecular weight determined cryoscopically in benzene was 415 (calculated 405). The proton magnetic resonance spectrum, obtained in benzene solution with tetramethylsilane added as an internal reference, exhibited the following singlets (τ): 8.95, CH_3; 7.18, CH_2; 6.89, tertiary OH; 6.72, CH_2; and 6.26, $-CB_{10}H_{10}CH$. The CH_2OH group appeared as an AB_2 multiplet with the center of the CH_2 doublet at τ 6.56 and the center of the OH triplet at τ 8.01. The first-order coupling constant was 7.9 c.p.s. The error for all values, except the $-CB_{10}H_{10}CH$ shift, is ±0.01 p.p.m. The $-CB_{10}H_{10}CH$ shift error is greater due to its unusually broad resonance. *Anal.* Calcd. for $C_9H_{32}O_8B_{20}$: C, 26.71; H, 7.97; B, 53.44; OH, 8.40. Found: C, 26.95; H 8.09; B, 51.34; OH, 8.92.

Acknowledgment.—We wish to thank Messrs. Larry Adlum and Raymond Storey for infrared analysis and Dr. David Kates for n.m.r. analysis. This work was supported by the U. S. Air Force, Edwards Air Force Base, under contract AF 33(616)-5639.

(1) The term "carborane" is used here to denote 1,2-dicarbaclovododecaborane(12).

(2) S. Papetti, B. B. Schaefer, H. J. Troscianiec, and T. L. Heying, *Inorg. Chem.*, **3**, 1444 (1964).

(3) J. Green, N. Mayes, A. P. Kotloby, and M. S. Cohen, *J. Polymer Sci.*, **A2**, 3135 (1964).

(4) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1111 (1963).

(5) M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. S. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963).

CONTRIBUTION FROM INORGANIC MATERIALS DIVISION, NATIONAL BUREAU OF STANDARDS, WASHINGTON 25, D. C., AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND, COLLEGE PARK, MARYLAND

Additional Observations on the Electronic Spectrum of Copper(II) Acetate Monohydrate

BY CURT W. REIMANN,[1a] GERALD F. KOKOSZKA,[1a] AND GILBERT GORDON[1b]

Received February 16, 1965

Copper(II) acetate monohydrate is a binuclear complex.[2] At low temperatures it is diamagnetic and

(1) (a) National Bureau of Standards; (b) University of Maryland.

(2) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).