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Preparation of Mono(*B*-hydroxy) Derivatives of 1,8-Dimethyl-*closo*-dicarbaundecaborane(11). Their Properties and Derivative Chemistry[1]

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Received October 1, 1973 AIC30715*

The reaction of 1,8-$(CH_3C)_2B_9H_9$ with sodium periodate in a solution of 2 *M* hydrochloric acid and benzene at 25° gives the 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$, but in acetic acid and benzene at 0° the only *B*-hydroxycarborane isolated is 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$. On pyrolysis the mono(hydroxy)carborane dimerizes with the loss of 2 equiv of hydrogen to give two "B_9C_2" polyhedra linked *via* two bridging oxygen atoms at the B(3,3′) and B(7,7′) positions. The dimer [1,8-$(CH_3C)_2B_9H_8]_2O$, in which two "B_9C_2" polyhedra are linked *via* one bridging oxygen atom, is prepared in a manner analogous to the preparation of the 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$. Pyrolysis of the 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ in the presence of phenol yields the phenoxy-substituted carborane series $(CH_3C)_2B_nH_{n-1}(OC_6H_5)$, $n = 8$–6, where the major products formed are isomers of the $(CH_3C)_2B_8H_7OC_6H_5$ polyhedron. The 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ reacts with Na–naphthalene, $NaBH_4$, or $LiAlH_4$ to produce the 3-OH-7,9-$(CH_3)_2$-7,9-$B_9C_2H_9^-$ dicarbollide anion.

Introduction

A recent paper from our laboratory described the synthesis and properties of the bis(hydroxy)carborane 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$, which can be prepared by the reaction of 1,8-$(CH_3C)_2B_9H_9$ with sodium periodate in acetic acid and benzene at 0°.[2] The only known *B*-hydroxy derivatives reported prior to this were mono(hydroxy) derivatives of various C-substituted ortho carboranes reported by Zakharkin.[3] The chemical properties of the different types of *B*-hydroxycarboranes are in some respects remarkably different. We report here the synthesis of the mono(hydroxy)carborane 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ and a comparison of its properties with the previously reported *B*-hydroxy derivatives.[2,3]

Experimental Section

Methods and Materials. 1,8-Dimethyl-1,8-dicarba-*closo*-undecaborane(11) was prepared by literature method.[4,5] All solvents were reagent grade and the tetrahydrofuran was distilled from potassium-benzophenone before use. All reactions (except pyrolyses) were conducted under nitrogen using standard Schlenk tube techniques and subsequent product work-ups required either a nitrogen atmosphere or minimum exposure to air.

Mass spectra were measured on a MS-902 mass spectrometer or a Perkin-Elmer 270 Gas Chromatograph-Mass Spectrometer. The 32.1-MHz boron nmr spectra were recorded on a Varian Associates HA-100 spectrometer. Chemical shifts are reported relative to $(C_2H_5)_2O\cdot BF_3$ (external) and $Si(CH_3)_4$ (internal) for ^{11}B and ^1H, respectively, and TMS (external) for carbon nmr.

Preparation of 3-Hydroxy-1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11). 1,8-Dimethyl-1,8-dicarba-*closo*-undecaborane(11) (2.0 g, 12.5 mmol) was dissolved in a flask containing 75 ml of benzene. A sodium periodate solution (3.0 g, 14 mmol in 60 ml of 2 *M* HCl) was added dropwise to the stirred benzene solution over a 10-min period and stirring was continued for an additional 30 min. The aqueous and benzene layers were then separated quickly. The aqueous phase was washed twice with 15-ml portions of benzene and the combined benzene fractions were dried over magnesium sulfate. The benzene was removed *in vacuo* and the residue obtained was pumped on overnight at room temperature to remove the iodine and starting material (0.9 g recovered). Sublimation of the residue at 60° to a cold finger at 0° gave 0.48 g (2.7 mmol, 43% based on starting material recovered) of product (mp 81–86°). An analytical sample with mp 89–92° could be obtained by alternate sublimation and recrystallization from hexane. *Anal.* Calcd for $B_9C_4H_{15}O$: C, 27.27; H, 8.52. Found: 27.39; H, 8.63.

Pyrolysis of 3-Hydroxy-1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11). 3-Hydroxy-1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11) (0.1 g, 0.57 mmol) was placed in a pyrolysis tube and then sealed off under vacuum. The tube was heated at 220° in an oven for a period of 1 hr and then cooled to room temperature. Recrystallization of the residue from 10 ml of acetonitrile gave 0.03 g (0.09 mmol, 30%) of the product $[B_9C_2H_7(CH_3)_2O]_2$, which was identified by comparison to an original sample.[2]

Preparation of $[(CH_3C)_2B_9H_8]_2O$. 1,8-Dimethyl-1,8-dicarba-*closo*-undecaborane(11) (0.5 g, 3.1 mmol) was dissolved in a flask containing 20 ml of benzene. A sodium periodate solution (0.7 g, 3.3 mmol in 15 ml of 2 *M* HCl) was added dropwise to the stirred benzene solution over a 5-min period and then the reaction was stirred for an additional 2 hr or until the red color had faded. The apparatus was opened to the atmosphere, and the aqueous and benzene layers were quickly separated. The aqueous layer was washed twice with 5-ml portions of benzene and the combined benzene fractions dried over magnesium sulfate. The benzene was removed *in vacuo* and the viscous liquid residue was distilled under vacuum (0.01 mm) at 80° to give 0.14 g (0.42 mmol, 27%) of product. *Anal.* Calcd for $B_{18}C_8H_{28}O$: C, 28.74; H, 8.38. Found: C, 28.54; H, 8.44.

Pyrolysis of 3-Hydroxy-1,8-dimethyl-1,8-dicarba-*closo*-undecaborane with Phenol. 3-Hydroxy-1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11) (0.15 g, 0.85 mmol) and phenol (1.8 g, 19 mmol) were sealed under vacuum in a pyrolysis tube, heated in an oven at 220° for 70 min and then cooled to room temperature. The residue was taken up in 20 ml of water and this solution was extracted with 50 ml of pentane. The pentane solution was washed four times with 40 ml of water and then dried over magnesium sulfate. The volume of the pentane solution was reduced to 2 ml and separated on a 19 in. × $^1/_2$ in. column containing 30% Apiezon L on Chromosorb P (60–80 mesh). Five carborane products were detected and their retention times were measured relative to benzyl ether. The five peaks had parent ion envelopes at 218, 230, 242, 352, and 352 with relative retention times of 0.29, 0.48, 0.78, 3.2, and 5.5, respectively. The chromatogram peak at 0.78 was asymmetric and consisted of two compounds having the same molecular weight. The last two peaks at 3.2 and 5.5 were identified as the two isomers of the dimer $[(CH_3C)_2B_9H_7O]_2$.

Reaction of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ with Sodium Borohydride. In a flask equipped with a solids addition tube loaded with the $NaBH_4$ (0.06 g, 1.6 mmol) was dissolved 3-hydroxy-1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11) (0.29 g, 1.65 mmol) in 55 ml of freshly distilled tetrahydrofuran. The $NaBH_4$ was added directly to the THF solution and stirring at room temperature was maintained until gas evolution had ceased (~1 hr). The solution was filtered through Celite under nitrogen and the THF removed. The residue was taken up in 10 ml of water and the product precipitated with tetramethylammonium chloride. A 0.26-g amount (1.0 mmol, 61%) of the crude dry product was isolated. An analytical sample could be obtained by dissolving the product in a deoxygenated water–acetone solution and then allowing the acetone to evaporate

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[1] Presented in part at the 6th International Conference on Organometallic Chemistry, Amherst, Mass., Aug 1973.

[2] G. D. Mercer and F. R. Scholer, *Inorg. Chem.*, 12, 2102 (1973).

[3] (a) L. I. Zakharkin, V. N. Kalinin, and L. S. Podvisotskaya, *Zh. Obshch. Khim.*, 36, 1786 (1966); (b) L. I. Zakharkin, V. N. Kalinin, and V. V. Gedymin, *ibid.*, 40, 2653 (1970).

[4] M. F. Hawthorne, T. D. Andrews, P. M. Garrett, F. P. Olsen, M. Reintjes, F. N. Tebbe, L. F. Warren, P. A. Wegner, and D. C. Young, *Inorg. Syn.*, 10, 100 (1967).

[5] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 90, 869 (1968).

slowly under nitrogen. *Anal.* Calcd for $B_9C_8NOH_{27}$: C, 38.19; H, 11.22; N, 5.57. Found: C, 38.11; H, 11.22; N, 5.53.

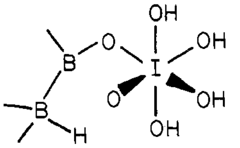
Substituting $LiAlH_4$ for sodium borohydride resulted in a much faster reaction with lower yields. The tetramethylammonium salts isolated in both cases were identical.

Reaction of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ with Sodium-Naphthalene. 3-Hydroxy-1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11) (0.1 g, 0.57 mmol) was dissolved in a flask containing 30 ml of freshly distilled tetrahydrofuran. The solution was cooled to −60° and then 12 ml (1.3 mmol) of a sodium-naphthalene solution was added dropwise over a 10-min period. The green color of the sodium-naphthalene faded immediately on contact of the two solutions. The final color of the reaction was pale yellow. After removal of the THF the residue was taken up in 8 ml of water. The naphthalene was removed by filtration and the product precipitated with tetramethylammonium chloride. Based on comparison of ir and ^{11}B nmr the product isolated is identical with the salt obtained in the reaction of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ and sodium borohydride.

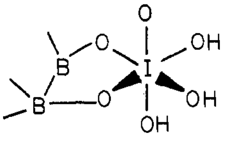
Results and Discussion

Preparation and Structure of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$. The reaction of 1,8-$(CH_3C)_2B_9H_9$ and sodium periodate in a solution of benzene and dilute hydrochloric acid gives the mono(hydroxy)carborane 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ (I), but in acetic acid and benzene only the bis(hydroxy)carborane 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$ (II) is formed (see Figure 1). The bis(hydroxy)carborane II is identical with the 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$ isolated from the reaction of sodium dichromate and 1,8-$(CH_3C)_2B_9H_9$ in a solution of benzene and sulfuric acid at 0°.[2]

In the preparation of the mono(hydroxy)carborane a slight excess of sodium periodate in 2 *M* hydrochloric acid was added dropwise to a solution of 1,8-$(CH_3C)_2B_9H_9$ in benzene under nitrogen. Within 30 min the solution developed a dark iodine color. Isolation of the carborane gave a 43% yield of a white sublimable solid, identified as 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$. In the reaction with sodium periodate, acetic acid, and benzene the iodine color is also produced, but the only carborane isolated is the 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$ (II). The two different reactions may involve the intermediates a and b, which produce the *B*-hydroxycarboranes I and II upon hydrolysis.



a



b

The selectivity of the periodate acid mixture in producing either the mono- or bis(hydroxy)carborane is dependent on the acid strength of the reaction mixture and the structure of the carborane. The stronger acid favors protonation of the periodate and therefore coordination to the carborane through only one oxygen bridge, which upon hydrolysis yields the mono(hydroxy)carborane. The weaker acid favors formation of the bidentate intermediate. Structural features of the $B_n(CCH_3)_2H_n$ series must also be considered. The reaction of the acetic acid–potassium dichromate mixture or periodate–acid mixtures with the ortho and meta carborane series did not succeed. In contrast Zakharkin[3] was successful in preparing *B*-hydroxy-*o*-carborane derivatives using 100% nitric acid as the oxidizing agent. Using similar experimental conditions the reaction of 100% nitric acid with 1,8-$(CH_3C)_2B_9H_9$ resulted in total decomposition of the carborane. The periodate–acid mixture reacts most readily with small carboranes having low symmetry. The method used by Zakharkin[3] is not applicable to these smaller carboranes and is restricted to the icosahedral carboranes.

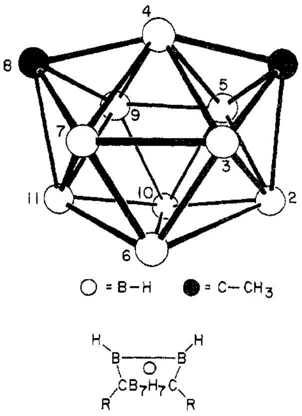


Figure 1. Numbering system for the octadecahedron. The formula below the figure has been adopted to indicate the positions of the B(3) and B(7) atoms.

The 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ is a white, sublimable solid (<0.01 Torr at 60°). The product is isolated from the organic layer of the reaction mixture and based on analysis by thin-layer chromatography and glc consists of only one geometric isomer.

The mass spectrum of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ (I) exhibits a sharp cutoff at a *m/e* 178, which is consistent with $^{11}B_9{}^{12}C_4{}^{16}O_1{}^{1}H_{15}{}^{+}$, the parent ion. The only other envelope of measurable intensity (15% of parent peak) occurred with a cutoff at P − 28, indicating loss of a B(OH) group.

The infrared spectrum has a strong band at 3600-3300 cm^{-1} indicative of an O-H stretch as well as a strong band at 1210 cm^{-1} assigned to the B-O stretch. The strong terminal B-H stretch at 2575 cm^{-1} is sharp and has no bands in the region of 2300-2500 cm^{-1} eliminating the possibility of any BH_2 groups in the molecule. KBr mull spectra do not show any broad absorption bands at 2000-1600 cm^{-1}, which would indicate the presence of a B(H)B bridging hydrogen. The assignments of the infrared spectra are consistent with prior studies on *B*-hydroxycarboranes.[2,3]

The ^{11}B nmr spectra (see Figure 2) and the ^{1}H nmr also support the proposed structure shown in Figure 1. The 32.1-MHz ^{11}B nmr spectrum of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ shown in Figure 2 indicates the presence of one B(OH) unit. There is a singlet of relative intensity 1 at −11.0 ppm relative to $(C_2H_5)_2O{\cdot}BF_3$ and an upfield multiplet with doublets of relative intensities 1:1:4:1:1. The ^{11}B nmr spectrum indicates there are at least six different boron environments and therefore favors substitution at one of the equivalent B(3,5,7,9) positions. If the hydroxyl group was located at B(4), the molecule would contain a C_2 axis and have two mirror planes perpendicular to the C_2 axis giving a total of only four different types of boron environments. If the B(OH) was located at either the B(2,11) or B(6,10), the B(OH) group would lie on a mirror plane and require only two doublets of intensity 1 in contrast to the four actually observed.

The proton nmr spectrum also supports the proposed structure. The spectrum consists of three singlets at −4.20, −2.55, and −2.12 ppm with relative intensities 1:3:3. The broad singlet at −4.20 ppm, whose chemical shift is sensitive to solvent used, is assigned to the O-H proton. Assuming the hydroxyl group is bonded to the B(3) boron atom there should be two different environments for the *C*-methyl groups. The peak at −2.55 ppm is assigned to the methyl group, C(8), furthest from the B(OH) position, while the

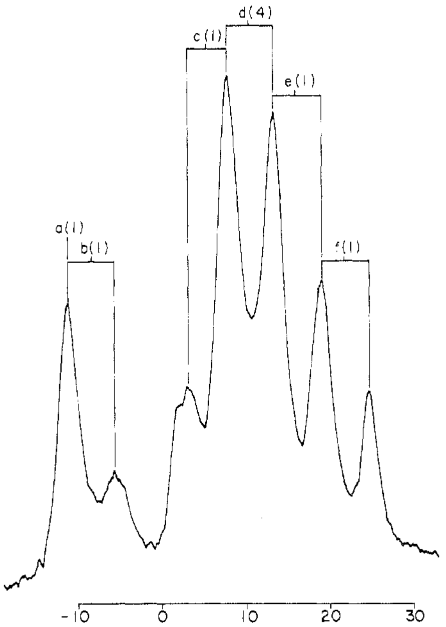
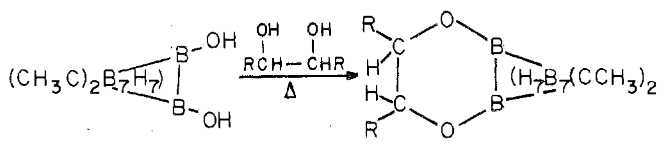


Figure 2. The 32.1-MHz ^{11}B nmr spectrum of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ in $CDCl_3$. Chemical shifts relative to boron trifluoride etherate (coupling constants, Hz): (a) −11.0 ppm, (b) −8.3 ppm (179), (c) +5.3 ppm (144), (d) +10.3 ppm (177), (e) +15.7 ppm (178), (f) +21.3 ppm (173). Intensities are given in parentheses above the respective peaks.

peak at −2.12 ppm is assigned to the methyl group, C(1), adjacent to the B(OH) group. These assignments are made on the basis that in compounds isolated to date the chemical shift for the methyl group, which is located adjacent to the B(OR) group, shifts approximately 0.3–0.5 ppm upfield relative to the chemical shift for the methyl group in the parent 1,8-$(CH_3C)_2B_9H_9$, while no apparent shift occurs for the methyl group located furthest from the B(OR) group. The peak due to the methyl groups on the parent 1,8-$(CH_3C)_2$-B_9H_9 occurs at −2.55 ppm and the peak due to the methyl groups on the 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$ occurs at −2.10 ppm. Since the ^1H nmr spectrum indicates two different environments for the *C*-CH_3 group, the hydroxy group cannot lie on the mirror plane containing the B(4,6,10) atoms and therefore favors substitution at one of the equivalent B(3,5,7,9) positions.

Although only one geometric isomer has been isolated, the possibility of producing stereoisomers of the mono(hydroxy)carborane I exists. There is an equal probability of the hydroxy group being bonded to either of the B(3,5,-7,9) atoms which will form one enantiomeric pair. The ^{11}B nmr and ^1H nmr cannot distinguish between the two stereoisomers. No attempts have been made to separate the stereoisomers.

Condensation Reactions of *B*-Hydroxycarboranes. As reported in a previous publication the reaction of 1,2-diols, such as pyrocatechol, 2,3-butanediol, or II, with 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$ results in the loss of 2 equiv of water and produces the condensation product, in which the diol is bridged to the carborane *via* two oxygen atoms at the B(3,7) positions.[2]



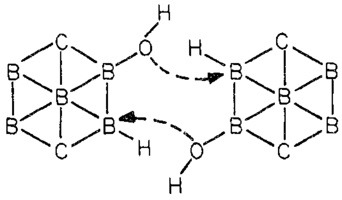
The condensation reaction of the bis(hydroxy)carborane II is quite general and occurs under comparatively mild conditions with either alkyl or aromatic bis(hydroxy) derivatives as well as with itself.

In contrast to the bis(hydroxy)carborane II the 9-hydroxy-*o*-carborane prepared by Zakharkin[3] does not dimerize under the conditions cited above and is stable at temperatures up to 400°. There was no evidence of water vapor being formed as occurs in the dimerization of II at 200°. Attempted reactions of aromatic or alkyl alcohols with the 9-hydroxy-*o*-carborane did not produce the *B*-alkoxy-*o*-carborane. Starting materials were reclaimed at temperatures up to 400°.

Comparison of the bis- and mono(hydroxy)carboranes with the *B*-hydroxy-*o*-carborane indicates other differences in chemical reactivity. Zakharkin has demonstrated that the *B*-hydroxy-*o*-carborane reacts with acetyl chloride, diazomethane, or trimethylchlorosilane to produce the corresponding acetoxy, methyl ether, or siloxane derivative. Neither the bis- or mono(hydroxy)carborane reacts with those reagents under similar conditions. The difference in behavior of the *B*-hydroxycarborane systems may be due to the difference in the inductive effect of the smaller B_9C_2 deltahedron *vs.* that of the larger and more symmetrical $B_{10}C_2$ icosahedron.

The *B*-hydroxycarboranes I and II are identical in their inability to undergo nucleophilic substitution reactions. In contrast to the *B*-hydroxy-*o*-carborane they readily undergo condensation reactions, but the results between the two are unexpectedly quite different. The pyrolysis of a neat sample of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_9$ at 200° was expected to form the carborane $[(CH_3C)_2B_9H_8]_2O$, in which two "B_9C_2" units are linked *via one* oxygen bridging atom at the B(3,3′) or B(3,7′) positions. However, pyrolysis of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ produces a white sublimable material and *hydrogen gas.* The white sublimable carborane is identical with the dimer obtained from the pyrolysis of 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$,[2] in which the B_9C_2 units are linked by *two* bridging oxygen atoms at the B(3,3′) and B(7,7′) positions. The dimer obtained from the pyrolysis of 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$ consisted of two isomers in a 2.5:1 ratio, in which the two B_9C_2 units can adopt either a trans or cis configuration about the oxygen bridges. The same ratio of isomers was obtained in the pyrolysis of the mono(hydroxy)carborane as determined by glc analysis.

The loss of hydrogen in the dimerization of the mono(hydroxy)carborane I indicates the oxygen atom at the B(3) position and the oxygen atom on a neighboring polyhedron I at the B(3′) position can attack the edge or face of the respective neighboring polyhedron, at the B(7′) or B(7) position, with subsequent loss of hydrogen gas, to form the dimer $[(CH_3C)_2B_9H_7O]_2$. This particular orientation results in the formation of the cis isomer. A similar reaction involving the oxygens at the B(3) and B(7′) on the two neighboring polyhedra would yield the trans isomer of the dimer $[(CH_3C)_2B_9H_7O]_2$. The formation of the two-oxygen-bridged species rather than the single-oxygen-bridged dimer is probably due to the tendency of boron to establish strong boron–oxygen bonds.



The dimer $[(CH_3C)_2B_9H_8]_2O$ in which two B_9C_2 polyhedra are linked *via* a single-oxygen bridge has been prepared by an alternate method. The method of preparation is identical with the procedure involved in the preparation of the mono(hydroxy)carborane I except that the reaction time is extended until the iodine color is discharged. The microanalytical data and low-resolution mass spectrum substantiate the proposed formula $[(CH_3C)_2B_9H_8]_2O$. The mass spectrum consisted of a parent ion envelope with a cutoff at *m/e* 338, which corresponds to $^{11}B_{18}{}^{12}C_8{}^{16}O_1{}^1H_{28}{}^+$. The only other envelope of measurable intensity occurred at P − 161 and represents cleavage of the dimer to form the $^{11}B_9{}^{12}C_4{}^{16}O_1{}^1H_{14}{}^+$. The P − 161 peak has an intensity only 5% of the parent peak.

The two possible stereoisomers of the mono(hydroxy)carborane I present a number of problems in determining the structure of the product. The 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ and the 7-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ are mirror images of each other, and, therefore, two diastereoisomers may form when the two polyhedra are bonded *via* the one-oxygen-bridging bond. The bridge bond may occur at the respective B(3) and B(3′) positions or at the B(3) and B(7′) positions. The ^{11}B nmr spectrum of the purified sample is nearly identical with the starting material and the resolution of the spectrum is not sufficient to indicate the existence of the two isomers. A singlet at −9.00 ppm confirms the B–O unit. The remainder of the ^{11}B nmr spectrum is an apparent 1:1:4:1:1 pattern for a ratio of eight B–H units to one B–O unit and is identical with that of I, indicating the integrity of the molecular B_9C_2 unit is maintained after the coupling reaction takes place. The ^1H nmr spectrum consists of two methyl resonances at −2.58 and −2.14 ppm indicating at least one methyl group is near the B(O) unit and at least one is far removed. The ^{13}C nmr spectrum was also taken in an attempt to confirm the presence of both isomers. Only two cage carbons and two methyl carbons were observed. All available data indicate only one isomer is produced.

The relative stabilities of the $[(CH_3C)_2B_9H_7O]_2$ and the $[(CH_3C)_2B_9H_8]_2O$ are quite different. The dimer containing the two boron–oxygen–boron bridge bonds is stable in both acid and basic media and is amenable to analysis by high-temperature glc. The single boron–oxygen–boron bridged species is far less stable and degrades rapidly in base to the 1,3-$(CH_3C)_2B_7H_{11}$ and decomposes at room temperature in the presence of air. The increased stability of the former may be attributable to the two B(O)B bonds and the steric factors involved in the structure of the $[(CH_3C)_2B_9H_7O]_2$, which inhibit the approach of either acid or basic species to the vulnerable B(O)B unit.

The second condensation reaction attempted was the pyrolysis of phenol and 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$. In the case of 3,7-$(OH)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$ pyrolysis with phenol gave the expected 3,7-$(OC_6H_5)_2$-1,8-$(CH_3)_2$-1,8-$B_9C_2H_7$.[6] Pyrolysis of 9-hydroxy-*o*-carborane with phenol at temperatures up to 400° gave no reaction.[6] The reaction of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ with phenol at 220° was attempted to determine if the chemical properties of the mono(hydroxy)carborane I were more similar to the *B*-hydroxy-*o*-carborane or to the bis(hydroxy)carborane II. Using a low-resolution mass spectrometer on line with a glc apparatus five different boron-containing products were identified by their mass spectra. The two largest peaks had retention times relative to benzyl ether of 3.2 and 5.5 and both had identical cutoffs at *m/e* 352 and were subsequently identified as the two isomers formed from the pyrolysis of 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ to give the dimer $[(CH_3C)_2B_9H_7O]_2$. The three remaining peaks had retention times of 0.78, 0.48, and 0.29. Their respective parent ion envelopes had *m/e* cutoff points at 242, 230, and 218. This corresponds to the series of phenol-substituted carboranes $(CH_3C)_2B_nH_{n-1}(OC_6H_5)$, $n = 8, 7, 6$. A comparison of these mass spectra to that of diphenyl ether[7] lends support to these assignments. The diphenyl ether mass spectrum exhibits an intense parent ion peak, $^{12}C_{12}{}^1H_{10}O^+$, and a large peak at *m/e* 77, assigned to the $C_6H_5{}^+$ ion. This same pattern is observed in the mass spectra of the $(CH_3C)_2B_nH_{n-1}(OC_6H_5)$, $n = 8, 7, 6$, series. The most intense envelope is attributed to the parent ion, while the only other major peak in each spectrum occurs at *m/e* 77. The envelope due to the $(CH_3C)_2B_nH_{n-1}O^+$ fragment is less than 10% in intensity of the parent ion envelope.

One major product produced in the reaction based on analysis by glc is $(CH_3C)_2B_8H_7OC_6H_5$ and actually consists of two definite peaks on the gas chromatogram, but the resolution was not sufficient for separation. Based on the mass spectral data we have tentatively assigned the two peaks to the 1,6 and 1,10 isomers of $(CH_3C)_2B_8H_7(OC_6H_5)$. The gas chromatogram shows only one isomer is produced for each of the remaining phenoxy-substituted carboranes in the series $(CH_3C)_2B_nH_{n-1}(OC_6H_5)$, $n = 6, 7$. Regardless of conditions employed, we have been unable to isolate any $(CH_3C)_2B_9H_8OC_6H_5$. If the pyrolysis with phenol and the mono(hydroxy)carborane is run in the presence of 1,8-$(CH_3C)_2B_9H_9$, a low yield of *m*-carborane is obtained. This may indicate the lack of any $(CH_3C)_2B_9H_8OC_6H_5$ is due to a disproportionation reaction, in which $(CH_3C)_2B_9H_8OC_6H_5$ reacts in the presence of 1,8-$(CH_3C)_2B_9H_9$ to give $(CH_3C)_2B_8H_7OC_6H_5$ and $(CH_3C)_2B_{10}H_{10}$. This reaction has a formal analogy in the pyrolysis of the parent borane anion $B_{11}H_{11}{}^{2-}$ which on heating to 250° undergoes a clean, nearly quantitative conversion to an equimolar mixture of $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ by a transfer of a BH unit.[8] In the reaction cited equimolar quantities of the $(CH_3C)_2B_8H_7OC_6H_5$ and $(CH_3C)_2B_{10}H_{10}$ are not produced indicating a number of other possible reactions are proceeding simultaneously to account for the appearance of $(CH_3C)_2B_8H_7OC_6H_5$.

Polyhedral Cage Expansion. A characteristic reaction of the *closo*-$(CH_3C)_2B_9H_9$ carborane is the reaction with a reducing agent such as Na-Hg or Na–naphthalene to produce *nido*-$(CH_3C)_2B_9H_{10}{}^-$. This formally involves the donation of an electron pair to the framework of the polyhedron to give a 26-electron system, which is characteristic of the nido 11-atom skeleton.[9] A similar system involves the reaction of *closo*-$B_9C_2H_{11}$ with electron-pair donors to form $B_9C_2H_{11}\cdot L$ molecules, which are known to be structurally similar to the *nido*-B_9C_2 carborane anion. The nido framework of these adducts and the position of the substituent L have been analyzed recently by Rudolph.[10]

The 3-OH-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$ reacts readily with Na-naphthalene, $NaBH_4$, or $LiAlH_4$ in THF to produce a proposed 3-OH-7,9-$(CH_3)_2$-7,9-$B_9C_2H_9{}^-$ dicarbollide anion.

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(6) G. Mercer and F. R. Scholer, unpublished results.

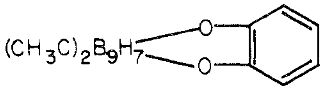
(7) E. Stenhagen, S. Abrahamson, and F. W. McLafferty, Ed., "Atlas of Mass Spectral Data," Interscience, New York, N. Y., 1969.

(8) F. Klanberg and E. Muetterties, *Inorg. Chem.*, 5, 1955 (1966).

(9) D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 91, 6002 (1969).

(10) V. Chowdry, W. R. Pretzer, D. N. Pai, and R. W. Rudolph, *J. Amer. Chem. Soc.*, 95, 4560 (1973).

Extension of the cage-opening reaction to other *B*-hydroxy derivatives is limited by the stability in base of the *B*-hydroxy derivative used. Preliminary data suggest that the dimer $[(CH_3C)_2B_9H_7O]_2$ and the catechol adduct



among others also react with Na-naphthalene in THF to yield open-cage B-substituted dicarbollide anions.

We are interested in determining the influence the B–O substituents have on the position of attack by the hydride ion and what effect the B–O substituents have on the nature of the cage-opening process. The preliminary evidence cited for the reaction involving $3\text{-OH-}1,8\text{-}(CH_3)_2\text{-}1,8\text{-}B_9C_2H_8$ and $NaBH_4$ allows us to draw some tentative answers to these questions.

Both Hawthorne and Rudolph have cited evidence for the unique boron atom B(4) as the most positive atom in the polyhedron, because of its location straddling the two electronegative carbon atoms.[9,10] Of the remaining set of boron atoms the four equivalent borons at positions 3, 7, 5, and 9 are the most positively charged, while the pairs 2, 11 and 6, 10 follow in order of decreasing positive charge. In the $3,7\text{-}(OH)_2\text{-}1,8\text{-}(CH_3)_2\text{-}1,8\text{-}B_9C_2H_7$ the positive charge will reside on the B(4,5,9) positions, which are bonded to the more electronegative carbon atoms. Hydride attack would be favored at these positions.

Unfortunately the hydride ligand, once bonded to the cage, gains anonimity and cannot be distinguished from the hydrogen bonded to the cage in the starting materials. For this reason the position of attack by the hydride ion on the $3\text{-OH-}1,8\text{-}(CH_3)_2\text{-}1,8\text{-}B_9C_2H_8$ cannot be definitely assigned.

In contrast to the problem of identifying the point of attack by H^- the nature of the cage-opening process is identified as that which involves movement of the unique seven-coordinate boron *away* from the entering ligand *toward* the B–O substituent (Figure 3). This is in direct contrast to the examples studied by Rudolph, where attack by $L = {}^-OC_2H_5$, $P(C_6H_5)_3$, or $N(CH_3)_3$ occurs so that B(4) moves *toward* the attacking nucleophile to give asymmetric lower belt substitution rather than facial substitution.[10] Rather than contradict Rudolph's work, the current study supports not only the mode of the cage-opening process but also demonstrates the cage-opening process is sensitive to the nucleophile involved and to the substituents on the polyhedron. The attack by H^- on $3\text{-OH-}1,8\text{-}(CH_3)_2\text{-}1,8\text{-}B_9C_2H_8$, which gives lower belt substitution, occurs rather easily, the reaction being completed in a matter of 30 min for 2–3 mmol. In this case, although substitution occurs so that the ligand $L = H^-$ would be a facial substitution based on the proposed mechanism, the ultimate product isolated is one in which the B–O unit is found in the lower belt.

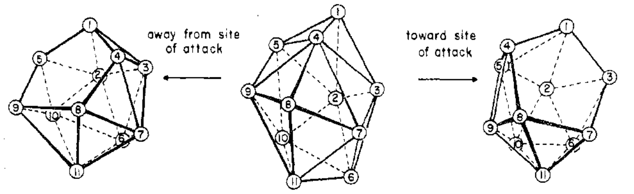
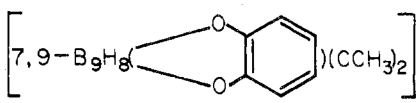


Figure 3. The two modes of cage opening where the ligand L attacks at either the B(5) or the B(9) atom. The cage can open such that the unique B(4) atom moves either toward the site of attack or away from the site of attack of the ligand.

Structure. The mechanism proposed for the cage-opening process involves attack of the H^- at either the B(5,9) or the B(4) position and movement of the unique B(4) boron to yield an asymmetrically substituted dicarbollide ion, in which the hydroxy group is located in the lower belt at the B(3) position of the $7,9\text{-}(CH_3C)_2B_9H_{10}^-$ anion. This would be isostructural to the $3\text{-}C_2H_5O\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}B_9C_2H_9^-$ isolated by Rudolph in the treatment of $1,8\text{-}(CH_3C)_2B_9H_9$ with $OC_2H_5^-$.[10] The 70.6-MHz ^{11}B nmr spectra of the proposed 3-OH- and $3\text{-}C_2H_5O\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}B_9C_2H_9^-$ are quite similar, each consisting of three sets of multiplets in a ratio of 4:3:2. However, the ethoxy derivative is more highly resolved with at least seven of the nine boron environments identified. The hydroxy derivative has only five boron environments resolved and cannot be used to assign a structure to the proposed $3\text{-OH-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}B_9C_2H_9^-$. In comparison, reaction of the catechol adduct with sodium borohydride forms



The only possible points of substitution for the catechol group are at B(3,4) or B(10,11). The 70.6-MHz spectrum shows a singlet of intensity 2 at +3.25 ppm with no fine structure due to bridge hydrogen coupling. Using a line-narrowed spectrum in the manner recently described by Clouse, Moody, Rietz, Roserry, and Schaeffer,[11] a doublet of intensity 2 appears at +25.64 ppm (132 Hz) and shows additional coupling to a bridge hydrogen (46 Hz) and is assigned to B(10,11). The catechol product is then identified as being symmetrically bonded in the lower ring at B(3,4). The complete assignment of the 7,9-dicarbollide ^{11}B nmr spectrum will be the topic of a forthcoming paper.[12] Based on comparison with the catechol adduct, the most likely position for the *B*-hydroxy group would be in the lower belt at the B(3) position. Further investigations are being conducted in this area to determine the effect of any change in the nucleophilic reagent, L, as well as changes in the nature of the B(OR) unit on the cage-opening mechanism and the structure of the final products.

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation (Grant GP-17053) and thank Professor Lee J. Todd, Indiana University, for the 70.6-MHz ^{11}B nmr spectra.

Registry No. $3\text{-OH-}1,8\text{-}(CH_3)_2\text{-}1,8\text{-}B_9C_2H_8$, 51716-75-7; $[(CH_3C)_2B_9H_8]_2O$, 51716-86-0; $1,8\text{-}(CH_3C)_2B_9H_9$, 17764-85-1; $3\text{-OH-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}B_9C_2H_9^-Me_4N^+$, 51933-25-6.

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(11) A. L. Clouse, D. C. Moody, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, 2496 (1973).

(12) G. D. Mercer, F. R. Scholer, R. Garber, and L. J. Todd, in preparation.