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# Deuterio Derivatives of 2,3-Dicarbahexaborane(8). Formation of 2,3-Dicarbaheptahydrohexaborate(1−)

*Received September 2, 1965*

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Treatment of 2,3-dicarbahexaborane(8) with sodium hydride in diglyme results in the liberation of one mole of $H_2$ and the formation of 2,3-$C_2B_4H_7^-$ ion. The ion reacts with HCl and with DCl to give 2,3-dicarbahexaborane(8) and a deuterio derivative, respectively. Bridge deuteration is indicated from $^{11}B$ and $^1H$ nmr and infrared data. An exchange between deuteriodiborane and 2,3-dicarbahexaborane(8) at 100° results in protium–deuterium exchange in the 4,5,6 terminal positions.

## Introduction

The structure of 2,3-dicarbahexaborane(8), prepared from pentaborane and acetylene either at elevated temperatures or in the presence of a Lewis base catalyst,[1-4] has been determined to be that of a pentagonal pyramid with bridge hydrogens between atoms B-(4,5) and B(5,6).[1,5-7] In the course of studies on related compounds, it became desirable to find convenient routes to deuterated derivatives of the carborane, 2,3-$C_2B_4H_8$.

## Experimental Section

**Materials.—Deuteriodiborane** was prepared by adding boron trifluoride ethyl etherate to a diglyme solution of lithium aluminum deuteride (98% D)[8] using a standard work-up and purification scheme.[9] **Deuterium chloride** was prepared from aluminum chloride and deuterium oxide (99% D).[10] **Diglyme** (Ansul) was vacuum distilled from $LiAlH_4$ at 80° directly into the reaction vessel immediately before use. **2,3-Dicarbahexaborane(8)** and **C,C′-dimethyl-2,3-dicarbahexaborane(8)** were prepared by the elevated temperature reaction between pentaborane and the appropriate alkyne (acetylene and 2-butyne, respectively).[4] Purified 2,3-$C_2B_4H_8$ exhibited infrared bands at 3050 m (CH stretch), 2620 vs (terminal B–H stretch), 1940 m (bridge hydrogen symmetric stretch), 1520 s (bridge hydrogen asymmetric stretch), 1450 m, 1340 m, 1082 ms, 1074 ms, 1040 m, 1028 m, 974 m, 961 ms, 950 m, 908 m, 900 m, 891 m, 870 m, 852 m, 840 m, 744 m, 734 ms, 725 m, and 650 m $cm^{-1}$. The mass spectrum exhibited a sharp cutoff at *m/e* 76 corresponding to the $^{12}C_2{}^{11}B_4{}^1H_8^+$ ion.

**2,3-Dicarbaheptahydrohexaborate(1−) Ion from 2,3-Dicarbahexaborane(8) and Sodium Hydride.**—A mixture of 97.2 mg of sodium hydride–mineral oil dispersion[8] (50 wt % NaH, 2.0 mmoles active hydride) and 2.0 ml of *dry* diglyme was added to a flask fitted with a reflux condenser. After evacuating and degassing the mixture, 2.0 mmoles of 2,3-dicarbahexaborane(8) was added by vacuum distillation. On warming to room temperature, hydrogen evolution commenced. After stirring for 1 hr, 1.89 mmoles of $H_2$ was collected by a Sprengel pump and measured in a gas buret. Vacuum fractionation of the diglyme solution through traps at −45 and −190° gave a trace of material in the latter trap which appeared to be mostly diglyme by infrared analysis. (In a separate control experiment 2,3-dicarbahexaborane(8) was separated quantitatively from a diglyme mixture using this fractionation method.)

When excess (2.00 mmoles) $C_2B_4H_8$ was used in the reaction with NaH (1.02 mmoles of active hydride), 0.955 mmole of $H_2$ was liberated, and 0.87 mmole of unreacted $C_2B_4H_8$ was recovered.

Aliquots of a diglyme solution of $NaC_2B_4H_7$ failed to give a precipitate either with 25% aqueous tetramethylammonium hydroxide or with a saturated CsCl solution. Instead, hydrogen was liberated, which may be indicative of extensive decomposition.

**C,C′-Dimethyl-2,3-dicarbaheptahydrohexaborate(1−).**—A mixture of 192 mg of sodium hydride–mineral oil dispersion (4.0 mmoles of active hydrogen) and 2.0 ml of *dry* diglyme was added to a flask outfitted with a reflux condenser. After evacuating and degassing the mixture, 1.7 mmoles of C,C′-$(CH_3)_2$-2,3-$C_2B_4H_6$ was added by vacuum distillation. After stirring for 1 hr at room temperature, an analysis for noncondensables by use of a Sprengel pump and attached buret gave 1.72 mmoles of $H_2$. Heating the sample at 200° for 4 hr under reflux gave only an additional 0.04 mmole of $H_2$. The $^{11}B$ nmr (12.8 Mc) spectrum of the ion solution exhibited a high-field doublet $\delta$ +48, $J$ = 156 cps, and three broad low-field peaks at $\delta$ −12.7, −1.8, +9.8 (ppm relative to $BF_3 \cdot (C_2H_5)_2O$). The over-all pattern is similar to that exhibited by $C_2H_4H_7^-$ ion (Figure 1).

Addition of decaborane(14) to an aliquot of the ion solution regenerated the starting material, C,C′-$(CH_3)_2$-2,3-$C_2B_4H_6$. Another aliquot, when treated with 25% aqueous tetramethylammonium hydroxide, did not give a precipitate; instead a considerable amount of hydrogen was liberated.

**Bridge-Deuterated 2,3-Dicarbahexaborane(8).**—Deuterium chloride (1 mmole) was added to a diglyme solution of sodium 2,3-dicarbaheptahydrohexaborate(1−) (1.0 mmole). After stirring for an overnight period, the mixture was vacuum fractionated through traps at −45, −110, and −190°. The −190° trap contained a trace quantity of an unidentified substance. The material in the −110° trap (0.83 mmole) upon glpc purification gave a fraction (0.72 mmole) with a retention volume ($R_v$ = 1.36, relative to pentaborane)[4] expected for 2,3-dicarbahexaborane(8). The infrared spectrum of this fraction exhibited a strong intensity terminal B–H stretch absorption at 2620 $cm^{-1}$, no terminal B–D absorption at 1960 $cm^{-1}$ (*vide infra*), and a significant decrease in the bridge hydrogen regions (1520 and 1940 $cm^{-1}$). The $^1H$ nmr spectrum was identical with that of $C_2B_4H_8$ except for a partial decrease of intensity of the bridge hydrogen resonance.

The partially deuterated 2,3-$C_2B_4H_8$ was further enriched by repeating the reaction sequence with sodium hydride and deuterium chloride. The infrared spectrum of the carborane

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Figure 1.—$^{11}B$ nmr (12.8 Mc) spectrum of $C_2B_4H_7^-$. Chemical shift values are given in ppm relative to $BF_3{\cdot}(C_2H_5)_2O$.

product (0.63 mmole) obtained from this second deuteration exhibited bands at 3050 m, 2620 vs, 1940 mw, 1500–1570 m, 1440 m, 1340 m, 1165 m, 1055–1070 ms (probably asymmetric bridge deuterium stretch), 990 m, 970 m, 960 m, 890–910 m, 868 m, 856 m, 746 m, 735 ms, 725 m, and 630 m $cm^{-1}$. The mass spectrum exhibited a cutoff at *m/e* 78 corresponding to the $^{12}C_2{}^{11}B_4{}^1H_6{}^2D_2^+$ ion.

**Reaction of 2,3-Dicarbaheptahydrohexaborate(1−) Ion with Hydrogen Ion Donors.**—The same procedure as described above was followed using, instead of deuterium chloride, alternately hydrogen chloride and decaborane(14). The yields of 2,3-dicarbahexaborane(8) varied from 30 to 80% depending on the dryness of the diglyme used. For high yields, direct distillation of the diglyme at 80° from a $LiAlH_4$ solution into the reaction vessel immediately before use was found to be the best procedure.

**4,5,6-Trideuterio-2,3-dicarbahexaborane(8).**—The minimum temperature at which protium–deuterium exchange occurs at a significant rate between deuteriodiborane and 2,3-dicarbahexaborane(8) was found to be *ca.* 90–100°. A 1:1 mole ratio mixture (0.2 mmole total) of the two reactants was heated for 2-hr intervals at 60, 80, and 100°. Although some exchange occurred at 80°, only at 100° did significant changes take place in the infrared spectrum of the mixture. After another 2-hr interval at 100° the infrared spectrum displayed little additional change.

A larger quantity (1.0 mmole) of the deuterated 2,3-$C_2B_4H_8$ was prepared from two 4-hr exchange reactions with equimolar quantities of $B_2D_6$. After each exchange, the deuterium-enriched carborane was separated from the partially protonated deuteriodiborane by vacuum fractionation through traps at −110 and −190°. The contents of the −110° trap from the first exchange was mixed with fresh deuteriodiborane for the second exchange period. The infrared spectrum of the carborane fraction from the final exchange exhibited bands at 3050 m, 2620 vs, 1960 vs (terminal B–D stretch), 1510 s, 1340 m, 1052 ms, 1023 m, 968 m, 956 ms, 945 m, 868 m, 820 m, 766 ms, and 680 m $cm^{-1}$. The mass specrtum exhibited a cutoff at *m/e* 79 corresponding to $^{12}C_2{}^{11}B_4{}^1H_5{}^2D_3^+$ ion. An infrared analysis[9b] of the deuteriodiborane from the last exchange indicated *ca.* 85% D enrichment of all equilibrated positions in the carborane. The $^1H$ nmr spectrum showed an intensity decrease in the quartet ($\tau$ 6.56) assigned to H–B(3,4,5).

## Results and Discussion

**Bridge Deuteration.**—A two-step sequence (eq 1, 2) which involves the formation of a stable intermediate ion, I, leads to a deuterated derivative of 2,3-dicarbahexaborane(8). The infrared spectra (*vide supra*) of the deuterated carboranes from one and two such

$$2,3\text{-}C_2B_4H_8 + NaH \xrightarrow{\text{diglyme}} Na^+C_2B_4H_7^- + H_2 \qquad (1)$$

$$Na^+C_2B_4H_7^- + DCl \longrightarrow C_2B_4H_7D + NaCl \qquad (2)$$

sequences indicate that only the bridge positions are affected during both ion formation and subsequent neutralization. This is substantiated by $^{11}B$ and $^1H$ nmr and mass spectroscopic data.

The $^{11}B$ nmr (12.8 Mc) spectrum of the parent carborane, $C_2B_4H_8$,[1,5] (Figure 2) exhibits a quartet of

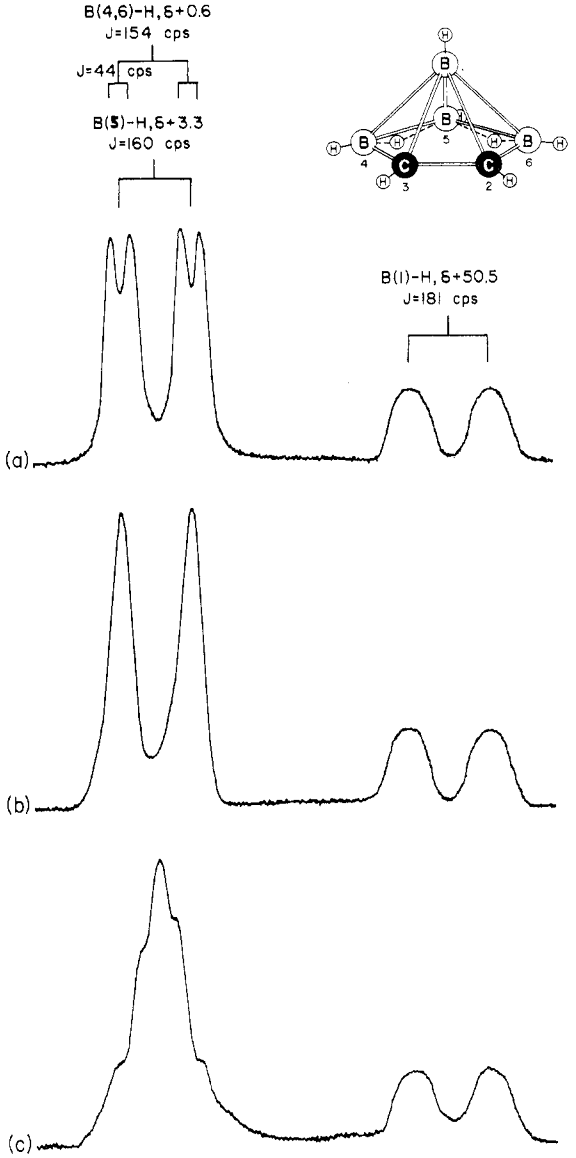

Figure 2.—$^{11}B$ nmr (12.8 Mc) spectrum of (a) $C_2B_4H_8$, (b) bridge-deuterated $C_2B_4H_8$ from $C_2B_4H_7^-$ and DCl (two exchange sequences), and (c) deuterated $C_2B_4H_8$ from 100° $B_2D_6$ exchange. Values of δ are given in ppm relative to $BF_3{\cdot}(C_2H_5)_2O$.

peaks at low field. These resonances are attributed to an overlap of the broad B(5)–H terminal doublet with the B(4,6)–H terminal doublet, the latter of which is further split by an adjacent bridge hydrogen.[11] The deuterated derivative obtained from two of the above reaction sequences (eq 1 and 2) retains the greater doublet structure ($J$ = 150–160 cps) but loses the smaller splitting pattern attributed to bridge hydrogen coupling (Figure 2b). Bridge deuterium atoms ($I$ = 1) do not exhibit *observable* coupling to the neighboring borons, which is not entirely unexpected considering the relative magnetogyric ratio of D/H = 0.154.

The $^1H$ nmr spectrum (Figure 3b) shows a decrease in the area assigned to the bridge hydrogen resonance.

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[11] An exact assignment of the low-field region has been made (ref 5). The broad doublet attributed to B(5)–H is not resolved further into a triplet expected from the two chemically identical neighboring bridge hydrogens. However, other structurally related systems exhibit a similar absence of *observable* coupling.

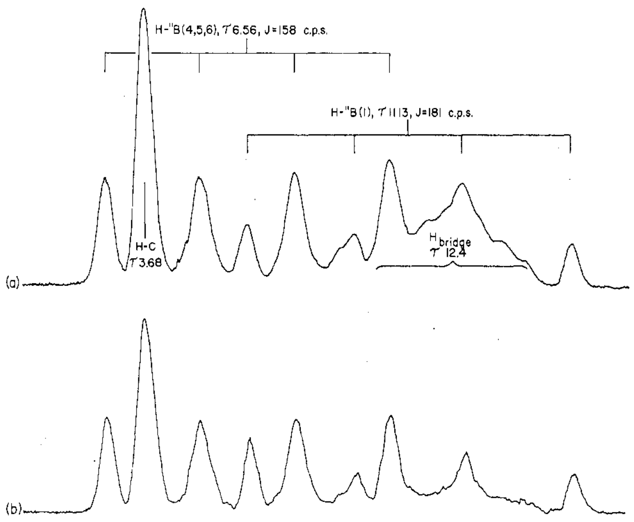

Figure 3.—$^{1}$H nmr (60 Mc) spectrum of (a) $C_2B_4H_8$ and (b) bridge-deuterated $C_2B_4H_8$ from $C_2B_4H_7^-$ and DCl (two exchange sequences).

In addition to the retention of all terminal hydrogen resonances, the intensity of the carbon-bonded hydrogen resonance has not changed during the above deuteration. This is in agreement with the absence of B–D terminal and C–D bands in the infrared spectrum.

The mass spectrum of the product from two of the above exchange sequences gives a sharp cutoff immediately above the parent peak attributed to a dideuterated 2,3-dicarbahexaborane(8). However, it is interesting to note that a small but significant amount of this same peak is found after one deuteration sequence. It is likely that during the neutralization process (eq 2) an exchange of the type described in eq 3 occurs, followed by a reaction of the deuterated ion with deuterium chloride (eq 4).

$$C_2B_4H_7D + C_2B_4H_7^- \longrightarrow C_2B_4H_6D^- + C_2B_4H_8 \qquad (3)$$

$$C_2B_4H_6D^- + DCl \longrightarrow C_2B_4H_6D_2 + Cl^- \qquad (4)$$

It is to be noted that the absence of B–D terminal bonds in the 2,3-$C_2B_4H_6D_2$ from the second exchange sequence precludes a terminal-bridge rearrangement in the ion-formation step (eq 1).

**Structure of $C_2B_4H_7^-$.**—From the above chemical and physical information the structure of $C_2B_4H_7^-$ must be closely related to its conjugate acid 2,3-dicarbahexaborane(8). Extracting a proton from a bridge position of the pentagonal pyramid makes boron atoms 4 and 6 chemically nonequivalent. The observation of a more complicated low-field region in the $^{11}$B nmr spectrum for the ion (Figure 1) than for $C_2B_4H_8$ is not then unanticipated. Unfortunately, the ion did not form insoluble salts with cations (*e.g.*, $(CH_3)_4N^+$, $Cs^+$) that are normally effective in precipitating hydroborates. Therefore, it was not possible to prepare pure salts of the ion for a more detailed study. It is clear, however, that 2,3-dicarbahexaborane(8) parallels decaborane in the behavior toward sodium hydride.[12] The carbon-bonded hydrogens are not affected, which is in opposite behavior to those of the icosahedral $C_2H_2B_{10}H_{10}$ carborane under analogous conditions.[13] In the latter compound, however, no bridge hydrogens exist.

Since it is possible to prepare a solution of the mononegative ion by removal of one bridge hydrogen, there remained the possibility that an excess of hydride might remove two such bridge hydrogens and lead to the predicted pyramidal $C_2B_4H_6^{2-}$ ion.[14] However, temperatures as high as 200° did not liberate but trace amounts of additional hydrogen from either 2,3-dicarbaheptahydrohexaborate(1−) ion or from the C,C′-dimethyl derivative.

**Terminal B–H, B–D Exchange.**—Protium–deuterium exchange between deuteriodiborane and 2,3-dicarbahexaborane(8) occurs at 100°. The growth of a strong B–D band at 1960 cm$^{-1}$ in the infrared spectrum and the collapse of the low-field doublet structure in the $^{11}$B nmr spectrum (Figure 2c) are evidence of B–H, B–D exchange between the basal terminal positions of the carborane and deuteriodiborane. Also, it is clear from the retention of the high-field doublet that the apical hydrogen is relatively unaffected. If all three of the remaining terminal hydrogens in the base of the pentagonal pyramid have undergone exchange, a cutoff at *m/e* 79 is expected in the mass spectrum. Such a cutoff is observed; however, the argument is valid only if the bridge and also carbon-attached hydrogens have not undergone exchange under these conditions. A comparison of the 1510- and 3050-cm$^{-1}$ bands (assigned to the bridge hydrogen and C–H vibrations, respectively) in the infrared both before and after exchange reveals that little change has occurred. Further, the growth of a band in the C–D region of the infrared spectrum is not observed. Unfortunately, the region expected for bridge deuterium vibrations is complicated by the possibility of other fingerprint bands. However, the $^{1}$H nmr spectrum shows no significant change in either the bridge hydrogen or the C–H regions. In these area comparisons the unchanged apical hydrogen resonance is used as a reference.

From this work and from previous studies the relative rates of exchange between deuteriodiborane and the terminal B–H hydrogens of several polyhedral compounds are summarized: 1,5-$C_2B_3H_5$;[15] 1,6-$C_2B_4H_6$;[16] 3,5,6 positions of 2,4-$C_2B_5H_7$[17] > 4,5,6 positions

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of 2,3-$C_2B_4H_8$; 1,7 positions of 2,4-$C_2B_5H_7$;[17] $B_5H_9$[18] > 1 position of 2,3-$C_2B_4H_8$. The relative unreactivity of the bridge positions in 2,3-dicarbahexaborane(8) toward an exchange of this nature is analogous to the previously reported observations for the pentaborane–deuteriodiborane exchange.[18] However, unlike pentaborane, the basal positions of 2,3-dicarbahexaborane(8) exchange much more readily than the apex.

**Acknowledgment.**—The authors wish to express their gratitude to the Office of Naval Research for financial support of this research.

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# Borazines Stable to Hydrolysis

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*Received April 5, 1965*

In order to evaluate the steric effect of increasing the stability of the borazine ring, B-tri-2,6-xylyl- and B-trimesityl-N-trimethylborazine were prepared and subjected to Friedel–Crafts acetylation, free-radical bromination, and hydrolysis experiments. The corresponding acetyl and bromo derivatives were obtained in good yields, and no hydrolysis was observed even in acidic and basic solution, indicating the remarkable enhancement of the ring stability by the *o*-methyl groups on the aryl substituents.

The lack of hydrolytic stability of covalent boron–nitrogen bonds has been an obstacle in the investigation of various reactions and application of boron–nitrogen compounds and has been referred to in many reports to show the authors' concern.[1,2] It has previously been shown in this laboratory[3] that the resonance effect in ethynylborazine derivatives can deter the hydrolysis to some extent but is not yet sufficient for thermodynamical stabilization. Attempts to stabilize the borazine ring toward hydrolysis by introduction of various substituents in aryl groups were not successful[4] until bulky substituents were placed in the *ortho* positions of B-aryl groups. The present work was undertaken to prepare borazine derivatives highly stabilized by the steric effects of substituents.

Brown, *et al.*,[5] have shown that triarylboranes are far less reactive toward oxygen and water when the vacant p orbital of the central boron atom is completely shielded by bulky substituents. Hawkins, *et al.*,[6] could enhance the hydrolytic stabilities of the arylboron compounds by introducing bulky substituents onto the *ortho* positions of the aryl groups. Such studies led us to infer that the use of the 2,6-xylyl group as a substituent would stabilize the borazine ring to hydrolysis.

B-Tri-2,6-xylyl-N-trimethylborazine (I) and B-trimesityl-N-trimethylborazine (II), shown in Figure 1, were prepared by treating B-trichloro-N-trimethylborazine with 2,6-xylyl- and mesitylmagnesium bromide, respectively, in the same way as described in the literature.[7] The yields and analytical data are summarized in Table I. In an attempt to prepare N-tri-2,6-xylylborazines, the position isomers of I, the reaction of *m*-xylidine with boron trichloride was carried out in dry toluene. The reaction mixture evolved hydrogen chloride on refluxing giving, contrary to expectation, the corresponding aminoborane instead of the borazine derivative.

Examination of molecular models of I and II suggests that the three aromatic groups on the boron atoms are forced to be perpendicular to the plane of the borazine ring by the steric effect. This was, in fact, supported by the ultraviolet and proton magnetic resonance spectra (Table II). Becher, *et al.*,[8] have shown from the ultraviolet spectra of some arylborazines that the conjugation between the phenyl groups and the borazine ring is negligible for B-triphenyl-N-trimethylborazine; *i.e.*, the phenyl groups are oriented at a right angle to the borazine ring. Compounds I and II displayed a $\pi-\pi^*$ transition band at almost the same wavelengths as did B-triphenyl-N-trimethylborazine; this indicates that the aryl groups are perpendicular to the borazine ring. The proton chemical shift data afford still further support to this structure.

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