2100 cm^{-1}) for germyl compounds,[12–14,25] but the lowering is perhaps to be expected.[26,27]

Nmr Spectrum of $H_3GeBH_3^-$.—The nmr spectrum provides confirmation of the $H_3GeBH_3^-$ structure. The signal of the three equivalent BH_3 protons is centered at 0.16 ppm to low field of tetramethylsilane. The signal is split into a 1:1:1:1 quartet by the ^{11}B nucleus (spin $^3/_2$, 81.2% abundance) and a weak 1:1:1:1:1:1:1 septet by the ^{10}B nucleus (spin 3, 18.8% abundance). Each member of the quartet and the septet is further split into a 1:3:3:1 quartet by the three equivalent GeH_3 protons. The coupling constants, $J_{^{11}BH} = 81$ cps and $J_{^{10}BH} = 27$ cps, are essentially the same as those found for the hydroborate ion.[28,29] The observed ratio $J_{^{11}BH}/J_{^{10}BH} = 3.00$ agrees very well with the value 2.99 predicted from the magnetogyric ratios of ^{10}B and ^{11}B. Thus we can rule out the possibility that each member of the quartet hides a member of the septet, corresponding to $J_{^{10}BH} = 40.5$ cps. The coupling constant $J_{HH'} = 4.7$ cps is very plausible for protons separated by two intervening atoms.[30–32] The signal of the three equivalent GeH_3 protons is centered at 2.30 ppm to low field of tetramethylsilane. The signal may be approximately accounted for by considering only the coupling with the BH_3 protons ($J_{HH'} = 4.7$ cps) and the coupling with the ^{11}B nucleus ($J_{^{11}BH'}$). If we assume the latter coupling constant to be of approximately the same magnitude as $J_{HH'}$, we predict an overlapping of the 16 peaks so as to form a septet, as observed.[33] However, because of the serious overlapping of the peaks and the neglect of $J_{^{10}BH'}$, it is not possible to calculate the exact value of $J_{^{11}BH'}$ from the spectrum.

Reaction of Excess B_2H_6 with $KGeH_3$.—The principal by-products in the B_2H_6–$KGeH_3$ reaction are potassium hydroborate and a species, soluble in 1,2-dimethoxyethane, which yields digermane upon acid hydrolysis. We tentatively suggest that the latter species is potassium digermanyltrihydroborate, formed in the reaction

$$2KH_3GeBH_3 \longrightarrow KBH_4 + KGe_2H_5BH_3 \qquad (6)$$

When the solvent is removed from the $KGe_2H_5BH_3$, hydrogen and germanium hydrides are evolved, and a yellow residue, having the characteristics of a mixture of polymeric germanium hydride and potassium hydroborate, is formed. This latter process may be expressed by eq 3. Both of these side reactions are promoted by the presence of excess diborane, particularly during removal of the 1,2-dimethoxyethane solvent. Possibly diborane aids in the formation of germanium dihydride, which then acts as an intermediate in the polymerization reactions

$$H_3GeBH_3^- + {}^1/_2B_2H_6 \longrightarrow GeH_2 + B_2H_7^-$$

$$GeH_2 + H_3GeBH_3^- \longrightarrow Ge_2H_5BH_3^-$$

$$GeH_2 + Ge_2H_5BH_3^- \longrightarrow Ge_3H_7BH_3^-, \text{ etc.}$$

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(25) R. C. Lord and C. M. Steese, *J. Chem. Phys.*, **22**, 542 (1954).

(26) The α-C–H stretch frequency is lowered by 76–310 cm^{-1} on going from alcohols to the corresponding alkoxide ions.[27] The CH_3O^- ion may be looked upon as an analog of the $GeH_3BH_3^-$ ion.

(27) F. H. Seubold, Jr., *J. Org. Chem.*, **21**, 156 (1956).

(28) Ogg[29] reported $J_{^{11}BH} = 82$ cps and $J_{^{10}BH} = 27$ for BH_4^-.

(29) R. A. Ogg, *J. Chem. Phys.*, **22**, 1933 (1954).

(30) $J_{HH'} = 8$ cps has been observed for H_3PBH_3;[31] $J_{HH'} = 4.8$ cps for both GeH_3PH_2 and GeH_3AsH_2.[32]

(31) R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg. Chem.*, **5**, 723 (1966).

(32) J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, **38**, 1033 (1963).

(33) The observed intensities for the GeH_3 septet are in fair agreement with those expected for the overlap of the 16 peaks.

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Deuterium Isotope Studies on 2,3-Dicarbahexaborane(8)

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Deuterium exchange at various positions on the $C_2B_4H_8$ molecule has been studied. D_2 exchanges with all boron-bonded hydrogen atoms, and B_2D_6 in the presence of diglyme exchanges only at the 4 and 6 terminal positions. The $(CH_3)_2C_2B_4H_6$ and DCl exchange, catalyzed by aluminum chloride, occurs at both apex and base terminal positions. 2,3-Dicarbahexaborane(8)-2,3-d_2, $D_2C_2B_4H_6$, has been prepared by heating B_5H_9 with C_2D_2. The infrared spectrum is given and it is shown that there is no migration of deuterium from carbon to boron during the synthesis.

Introduction

In the course of considering mechanism studies on reactions of 2,3-dicarbahexaborane, it became advantageous to prepare a number of derivatives with deuterium labeling in a variety of specific positions. Described in this report are the results of studies using variously D_2, DCl, and a diglyme solution of B_2D_6 showing the specific positions on the $C_2B_4H_8$ molecule where exchange occurs.

Experimental Section

Materials.—**Deuterium**, D_2, was Matheson CP Grade, 99.5%. A sample of Harshaw chrome catalyst CR-0102T, $^1/_8$ in., was generously donated by the Harshaw Chemical Co. **Deuterium chloride** was prepared by treating Al_2Cl_6 or PCl_3 with D_2O and purified by fractional distillation. **Deuteriodiborane** was prepared by adding boron trifluoride ethyl etherate to a diglyme solution of lithium aluminum deuteride (98% D)[1] using a standard work-up and purification scheme.[2] **Diglyme**, bis(2-methoxyethyl) ether (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 thermal reaction between pentaborane(9) and acetylene or 2-butyne, respectively,[3] and purified by glpc.

Apparatus.—Standard high-vacuum techniques were used in the handling of all materials. Proton nmr spectra were recorded using a Varian A-60 spectrometer. Boron-11 nmr were recorded both at 12.8 (Varian V-4300) and at 32 Mc. Infrared spectra were recorded on a Beckman IR-5.

$C_2B_4H_8$–D_2 Exchange.—Deuterium exchange occurs between $C_2B_4H_8$ and D_2 either on heating or in the presence of a catalyst at room temperature. $C_2B_4H_8$ (1.0 mmol) and D_2 (1.6 mmol) were sealed in a 25-ml bulb which had a 5-mm tube attached so that the nmr spectrum could be taken. There was no change in the spectrum after the mixture was heated to 200° for 18 hr, but when the temperature was increased to 245° for 18 hr, exchange was indicated by the ^{11}B nmr spectrum. Treating the same sample with fresh D_2 at 245° gave a ^{11}B nmr in which all of the multiplets due to B–H coupling collapsed. It was also apparent from the spectrum that some deuterated $C_2B_5H_7$ had formed from the pyrolysis of $C_2B_4H_8$.

For the catalyzed exchange, approximately 5 g of chromia-alumina catalyst (Harshaw Chemical Co. No. CR-0102-T1/8) were placed in a 13 × 150 mm Vycor tube fitted by a ground joint to a 1-l. bulb which could be attached to the vacuum system through a stopcock and ground joint. The tube and bulb were evacuated and the catalyst was heated to 450° for about 18 hr with continuous pumping by means of an oil diffusion pump. Then 0.91 mmol of $C_2B_4H_8$ was condensed into the bulb and 6 mmol of D_2 was added. The catalyst was dropped into the bulb from the side tube to provide efficient contact with the surface and the mixture was kept at room temperature for 17 hr. The process was repeated with fresh D_2; the catalyst could be poured back into the Vycor tube and reheated between exchanges when necessary.

The deuterium exchange in both of these experiments was followed by nmr and infrared spectra. The results were identical except for the pyrolysis of $C_2B_4H_8$ in the uncatalyzed exchange. Infrared spectrum (cm^{-1}): 3050 m (C–H stretch), 1970 vs (B–D terminal), 1440 m (B–D bridge), 1340 m, 1120 s (B–D bridge), 1050 m, 1040 m, 1030 m, 1010 m, 975 ms, 965 s, 955 m, 860 w, 760 m, 750 ms, 740 m, 715 m, and 700 m. The above assignments correspond to those given for the normal species. There was no absorption in the 2300- or 770-cm^{-1} region where C–D frequencies should appear, and also the H^1 nmr spectrum showed no decrease in the C–H signal at τ 3.7.

$(CH_3)_2C_2B_4H_6$–DCl Exchange.—Preliminary experiments showed that there was no deuterium exchange between either $(CH_3)_2C_2B_4H_6$ or $C_2B_4H_8$ and DCl at temperatures up to 100°. A mixture of DCl and Al_2Cl_6 destroyed $C_2B_4H_8$ even at 0° forming hydrogen and unidentified products. However $(CH_3)_2C_2B_4H_6$ and DCl in the presence of Al_2Cl_6 exchanged deuterium during a 2-hr period at 25° after which about 95% of the starting dicarbahexaborane could be recovered. In the ^{11}B nmr spectrum of this material the high-field doublet (apex) collapsed to a broad single peak. The low-field component also changed to a pattern similar to that found in the $C_2B_4H_8$–B_2D_6 exchange,[4] but it is not possible to tell whether or not all of the basal positions have exchanged. The infrared spectrum showed decreased absorption at 2680, 900, and 750 cm^{-1} and increased absorption at 1940 cm^{-1}. There was no increase in absorption at 1400 or 1100 cm^{-1} where deuterium present in the bridge positions would be indicated.

$C_2B_4H_8$–B_2D_6 Exchange in Diglyme.—Deuteriodiborane (1.95 mmol), 2,3-dicarbahexaborane(8) (1.50 mmol), and 1 ml of diglyme were condensed into a 100-ml reaction flask. After stirring the mixture at 25° for 4 hr the mixture was vacuum fractionated through traps at −40° (diglyme), −120° (2,3-dicarbahexaborane), and −190° (diborane). Infrared spectra of the −120° fraction indicated the growth of a strong band at 1960 cm^{-1} (B–D stretch). The −190° fraction exhibited the spectrum of a mixture of partially protonated and deuterated diboranes.[2b] All of the fractions were condensed back into the reaction flask for further reaction. The reaction was stopped at intervals, the mixture was fractionated, and spectra were taken in order to determine optimal conditions for establishing equilibrium between the most readily exchangeable positions. After 20 hr of reaction further changes in the infrared spectrum of the −120° fraction appeared to be negligible. For further isotope enrichment the −120° fraction was combined with a fresh portion of deuteriodiborane and allowed to exchange in the presence of diglyme for another 20-hr period. Final work-up afforded 1.37 mmol of deuterated 2,3-dicarbahexaborane(8) which exhibited bands (cm^{-1}) at 3050 m (C–H stretch), 2620 vs (terminal B–H), 1960 vs (terminal B–D overlapping with a weaker bridge hydrogen symmetric stretch), 1510 s (bridge hydrogen asymmetric stretch), and many other unassigned bands in the fingerprint region of the infrared spectrum.

2,3-Dicarbahexaborane(8)-2,3-d_2.—2,3-Dicarbahexaborane(8) with deuterium substituted at the carbon atoms was synthesized by the thermal process previously described.[3] Acetylene-d_2 was produced by passing D_2O vapor over fresh CaC_2 and purified by fractional distillation. The infrared spectrum indicated that the protium content was about 4.5%. A mixture of C_2D_2 (39 mmol) and B_5H_9 (7.6 mmol) was heated in a 2-l. bulb at 215° for 7 days to give a 40% yield of the dicarbahexaborane. The infrared spectrum showed (in cm^{-1}): 3050 nil (C–H stretch), 2620 vs, 2260 m (C–D stretch), 1940 m, 1510 s, 1080 w, 955 ms, 920 m, 850 m, 770 mw, and 735 ms. When compared with the undeuterated material, there was no increase in absorption at 1960 or 1120 cm^{-1} where B–D terminal or bridge substitution would be indicated. From the H^1 nmr spectrum a comparison of the area of the residual C–H peak at τ 3.68 with one of the B–H components indicated 5% H.

Discussion

Exchange with D_2.—All terminal and bridge hydrogen atoms bonded to boron exchange with D_2 in the presence of Cr_2O_3 on activated alumina. This result is similar to that found by Hrostowski and Pimentel,[5] who used the same type of catalyst for the B_5H_9–D_2 exchange. Unfortunately no other studies of this type seem to have been made on the boron hydrides. It is, therefore, difficult to comment on the role the catalyst plays in this exchange. It is surprising that all hydrogen atoms bonded to boron exchange under relatively mild conditions, but those bonded to carbon do not, as indicated by the ^1H nmr and infrared spectra.

Exchange with DCl.—In the $(CH_3)_2C_2B_4H_6$–DCl exchange it is apparent from the ^{11}B nmr that exchange occurs in basal positions of the molecule as well as the apex. It is not possible to tell from the nmr spectrum whether or not all three of the base terminal hydrogen atoms have exchanged, but the infrared spectrum clearly shows that there is no bridge hydrogen exchange. The exchange of nearly all (if not all) of the terminal hydro-

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[1] Metal Hydrides Inc., Beverly, Mass.

[2] (a) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952); (b) W. J. Lehmann, J. F. Ditter, and I. Shapiro, *J. Chem. Phys.*, **29**, 1248 (1958).

[3] T. Onak, R. Drake, and G. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

[4] T. Onak and G. Dunks, *ibid.*, **5**, 439 (1966).

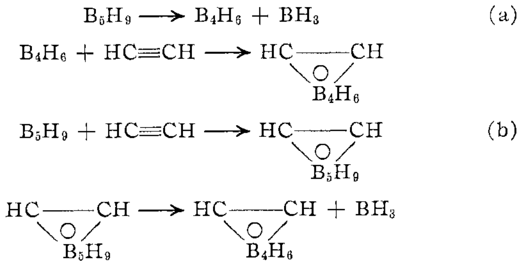
[5] H. J. Hrostowski and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954).

gen positions in the dicarbahexaborane is in striking contrast to the selective apical deuteration of pentaborane under similar conditions. It is noted, however, that a comparison of estimated charge distribution in both systems offers a partial explanation for the observed differences.[6]

Diglyme-Catalyzed Exchange with B_2D_6.—It has been reported that protium–deuterium exchange between deuteriodiborane and 2,3-dicarbahexaborane(8) occurs slowly at 100°.[4] Exchange was observed primarily in the 4, 5, and 6 terminal positions.

The deuterated derivative of 2,3-dicarbahexaborane(8) obtained from the diglyme-catalyzed exchange reaction retains the high-field doublet pattern (B_1–H) of the parent compound in the ^{11}B nmr.[4,7] The change in the doublet structure at low field ($B_{4,5,6}$–H) is somewhat similar to that observed from the thermal exchange.[8] From ^{11}B nmr alone it is clear that hydrogens attached to some or all of the basal boron atoms have exchanged. From the ^1H nmr an area comparison to the unchanged high-field member of the H–B_1 quartet (τ 11.13[3,4]) shows that neither the bridge hydrogens (τ 12.6) nor the carbon-attached hydrogens (τ 3.68) have participated in the exchange.[9] The absence of a C–D stretch in the infrared spectrum supports the latter conclusion. Of the remaining positions (terminal hydrogen atoms as $B_{4,6}$ and B_5) a sharp cutoff at mass 78, corresponding to $^{12}C_2{}^{11}B_4{}^1H_6{}^2D_2{}^+$, in the mass spectrum argues for H_t–$B_{4,6}$ exchange only. This conclusion is in agreement with the observation that the overlapping H_t–$B_{4,6}$ and H_t–B_5 quartets at τ 6.56 in the ^1H nmr never dropped in measured area below that of the unchanged H–B_1 quartet after the sample had been exchanged several times with B_2D_6. Only after prolonged contact (several weeks) is there evidence that a third hydrogen of the carborane is undergoing exchange in the diglyme solution. The mass spectrum begins to show a peak at mass 79 which is slightly higher in intensity than can be accounted for by the normal $P + 1$ contributions (*e.g.*, $^{13}C^{12}C^{11}B_4{}^1H_6{}^2D_2{}^+$) of a dideuterated material.

In addition to giving useful spectroscopic comparisons, the 2,3-dicarbahexaborane(8)-2,3-d_2 produced from C_2D_2 and B_5H_9 had the same carbon-bonded protium content as the reactant acetylene within experimental error. It is significant to note that this rules out the possibility of 2-methylcarbahexaborane-(9)[10] as an intermediate in the formation of $C_2B_4H_8$ from pentaborane and acetylene. Formation of such an intermediate by 1,1 addition to the alkyne followed by appropriate rearrangement and elimination steps to give the observed $C_2B_4H_8$ would have led to a minimum 33% total protium content attached to the carbon. The present work supports a 1,2-boron addition but does not differentiate between several reasonable pathways, two of which are shown below in a rather general fashion



$$B_5H_9 \longrightarrow B_4H_6 + BH_3 \qquad (a)$$

$$B_4H_6 + HC{\equiv}CH \longrightarrow \underset{B_4H_6}{\underset{\diagdown O \diagup}{HC{-}{-}CH}}$$

$$B_5H_9 + HC{\equiv}CH \longrightarrow \underset{B_5H_9}{\underset{\diagdown O \diagup}{HC{-}{-}CH}} \qquad (b)$$

$$\underset{B_5H_9}{\underset{\diagdown O \diagup}{HC{-}{-}CH}} \longrightarrow \underset{B_4H_6}{\underset{\diagdown O \diagup}{HC{-}{-}CH}} + BH_3$$

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(6) W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2331 (1963); W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 110.

(7) (a) T. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962); (b) R. E. Williams and T. Onak, *ibid.*, **86**, 3159 (1964).

(8) See Figure 2c of ref 4

(9) The proton area comparison was checked against a sample of undeuterated $C_2B_4H_8$ run at the same instrument settings. The area measurements are good to within 5%

(10) T. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **88**, 2061 (1966).