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An Improved Synthesis of Hexaborane(10). Preparation of 2-Methylhexaborane(10)

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Hexaborane(10) is of considerable interest from the point of view of reactivity.[1] Proton and boron-11 nmr spectroscopy have raised questions concerning solution *vs.* solid state structure[2] the answers to which have only recently been unequivically confirmed.[3] Development of the chemistry of this boron hydride and its derivatives has been severely hampered by the difficulty of preparing and purifying sufficient quantities. Preparation of B_6H_{10} in 25-30% yield from commercially available starting materials was recently reported;[4] however, the purification process is time consuming.

We report herein the preparation of B_6H_{10} from 1-BrB_5H_8 in 75% yield. The process may be represented by the equations

$$\text{1-BrB}_5\text{H}_8 + \text{KH} \xrightarrow{-78^\circ} \text{K}^+[\text{1-BrB}_5\text{H}_7^-] + \text{H}_2 \qquad (1)$$

$$\text{K}^+[\text{1-BrB}_5\text{H}_7^-] + {}^1/_2\,\text{B}_2\text{H}_6 \xrightarrow{-78^\circ} \text{K}^+[\text{B}_6\text{H}_{10}\text{Br}^-] \qquad (2)$$

$$\text{K}^+[\text{B}_6\text{H}_{10}\text{Br}^-] \xrightarrow{-35^\circ} \text{B}_6\text{H}_{10} + \text{KBr} \qquad (3)$$

This preparation is superior to the previous one[4] in that the yield is more than doubled, only one half as much diborane(6) is needed and significant quantities of volatile contaminants are not produced so that isolation of the pure product is easily and rapidly accomplished. The intermediate, $B_6H_{10}Br^-$, produced by the addition of BH_3 to 1-Br-$B_5H_7^-$ is probably structurally similar to $B_6H_{11}^-$ produced by the addition of BH_3 to $B_5H_8^-$ in which it is believed the borane group adds to the B–B bond in the base of the pyramidal framework.[5] Hexaborane(10) is then produced by elimination of bromide ion and minor rearrangement.

This apparently general reaction has been extended to the preparation of 2-$CH_3B_6H_9$ from 1-Br-2-$CH_3B_5H_7$. At room temperature 2-$CH_3B_6H_9$ is a colorless liquid of low volatility and like the previously reported dimethylhexaborane(10)[6] is more stable than hexaborane(10) under vacuum. The proton and boron-11 nmr spectra of 2-CH_3-B_6H_9 as well as B_6H_{10} are temperature dependent.[3]

The reactions described herein extend and further demonstrate the utility of the stepwise buildup of boron hydride frameworks by the addition of BH_3 to boron hydride anions.[5]

Experimental Section

Methods and Materials. Standard vacuum-line techniques were used in the manipulation of volatile materials. Nonvolatile materials were transferred in a drybox in a nitrogen atmosphere. Proton magnetic resonance spectra were recorded on a Varian HA-100 spectrometer. Boron-11 nmr spectra were obtained on the same instrument at 32.1 MHz. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. Pentaborane(9) and diborane(6) were obtained from the Callery Chemical Co. KH was obtained from RIC/ROC[7] and stripped of oil with pentane under vacuum, and 1-BrB_5H_8[8] and 1-Br-2-$CH_3B_5H_7$[9] were prepared by methods described in the literature. Preparation of $K^+[1\text{-}BrB_5H_7^-]$ has been previously reported.[10]

Preparation of B_6H_{10}. A reaction tube 20 cm long and 4.5 cm in diameter with a side arm for the controlled addition of KH was used. In the drybox 2.612 g of KH was loaded and the reaction vessel was attached to the vacuum line and evacuated. Then 8.643 g of 1-BrB_5H_8 was condensed in, melted, and refrozen at the bottom. Dimethyl ether, 60 ml, was condensed in at −196° and stirred at −78°. Potassium hydride was added in small increments (approximately 1-3 mmol) and the hydrogen produced was pumped out at intervals. At this point the solution is clear and yellow.[11] Diborane(6), 30.4 mmol, was allowed to expand into the well-stirred reaction mixture at −78° and it was rapidly absorbed. As the reaction mixture was warmed to −35° ($C_2H_4Cl_2$ slush), a white solid rapidly formed. It was stirred at this temperature for 30 min and then cooled to −78° while the bulk of the solvent was distilled away and discarded. The vessel was opened to U traps maintained at −78 and −196° and then warmed to −35° and the bulk of the B_6H_{10} was collected in the −78° trap. The −35° slush was then placed on the trap preceding the −78° trap and the vessel was allowed to warm to room temperature while pumping through the −35, −78, and −196° traps. The fraction collected at −78° was 4.9 ml of B_6H_{10} measured at 0°, 75% yield. No impurities were detected by boron-11 or proton nmr. Vapor pressure at 0° was 7.5 mm.

Preparation of 2-$CH_3B_6H_9$. 2-Methylhexaborane(10) was prepared from 1-Br-2-$CH_3B_5H_7$ by the procedure described above for the conversion of 1-BrB_5H_8 to B_6H_{10}. The 2-$CH_3B_6H_9$ collected in the −78° trap and was obtained in 55% yield. The vapor pressure is 6 mm at 0° and 14.0 mm at 25°. *Anal.* (Schwarzkopf Microanalytical Laboratories). Calcd: C, 13.51; H, 13.51; B, 72.97. Found: C, 13.41; H, 13.27; B, 72.51. The 32.1-MHz boron-11 nmr spectrum contains (reading from low field to high field) a singlet and three doublets with relative areas of 1:2:2:1. The chemical shifts at ambient temperature in parts per million relative to $BF_3 \cdot OEt_2$ (J_{BH} in hertz) are −29.4, −17.6 (145), −6.5 (145), and 49.4 (153). The spectrum is markedly temperature dependent.[3] The infrared spectrum contains absorptions at 2960 (w), 2910 (w), 2570 (s), 1940 (br,w), 1870 (br,w), 1455 (s), 1320 (m), 1150 (br,w), 1102 (m), 1000 (w), 960 (w), 885 (m), 755 (m), 735 (m), and 681 (m) cm^{-1}.

Registry No. B_6H_{10}, 23777-80-2; 2-$CH_3B_6H_9$, 36863-02-2.

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(11) The color is apparently due to a small amount of decomposition. Smaller scale reactions carried out at −97° over a shorter time period yield colorless solutions. The boron-11 nmr spectrum of $K^+[1\text{-}BrB_5H_7^-]$ in $(CH_3)_2O$ does not show evidence of decomposition for yellow solutions prepared as described above.