

Notes

Contribution from the Evans Laboratory of Chemistry,
The Ohio State University, Columbus, Ohio 43210

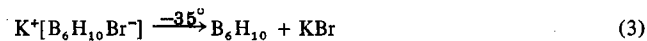
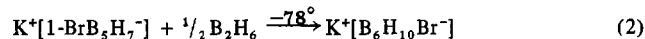
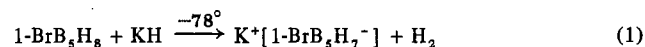
An Improved Synthesis of Hexaborane(10). Preparation of 2-Methylhexaborane(10)

H. D. Johnson, II, V. T. Brice, and S. G. Shore*

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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 structure² the answers to which have only recently been unequivocally 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 B₆H₁₀ 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 B₆H₁₀ from 1-BrB₅H₇ in 75% yield. The process may be represented by the equations



This preparation is superior to the previous one⁴ 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 easy and rapidly accomplished. The intermediate, B₆H₁₀Br⁻, produced by the addition of BH₃ to 1-BrB₅H₇⁻ is probably structurally similar to B₆H₁₁⁻ produced by the addition of BH₃ to B₅H₈⁻ 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-CH₃B₆H₉ from 1-Br-2-CH₃B₅H₇. At room temperature 2-CH₃B₆H₉ 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-CH₃B₆H₉ as well as B₆H₁₀ 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 BH₃ 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/ROC⁷ and stripped of oil with pentane under vacuum, and 1-BrB₅H₈⁸ and 1-Br-2-CH₃B₅H₇⁹ were prepared by methods described in the literature. Preparation of K⁺[1-BrB₅H₇⁻] has been previously reported.¹⁰

Preparation of B₆H₁₀. 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-BrB₅H₈ 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° (C₂H₄Cl₂ 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 B₆H₁₀ 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 B₆H₁₀ 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-CH₃B₆H₉. 2-Methylhexaborane(10) was prepared from 1-Br-2-CH₃B₅H₇ by the procedure described above for the conversion of 1-BrB₅H₈ to B₆H₁₀. The 2-CH₃B₆H₉ 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 BF₃·OEt₂ (*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. B₆H₁₀, 23777-80-2; 2-CH₃B₆H₉, 36863-02-2.

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(7) RIC/ROC, Sun Valley, Calif.

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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-BrB₅H₇⁻] in (CH₃)₂O does not show evidence of decomposition for yellow solutions prepared as described above.