An Insertion Reaction Involving Pentaborane(9). The Synthesis of the Tetradecahydrononaborate(1−) Ion, $B_9H_{14}^-$

By C. G. SAVORY and M. G. H. WALLBRIDGE*

(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary The synthesis of the *nido*-$B_9H_{14}^-$ ion has been achieved by an insertion reaction into the B_5 cage of pentaborane(9) at low temperatures using an alkali-metal hydroborate, the results also providing strong evidence that the $B_9H_{14}^-$ ion is an intermediate in the formation of the *closo*-$B_{12}H_{12}^{2-}$ ion.

IN general, three alternative routes are available for the synthesis of borane anions: (i) cage insertion reactions, (ii) pyrolysis of borane anions, and (iii) degradation of a boron hydride.[1] The useful cage expansion reactions (i) and (ii) have not yet been established as viable routes to the lower borane ions, indeed only one well defined example exists for a cage containing *less* than ten boron atoms, that is the one-atom insertion in the synthesis of the $B_3H_8^-$ ion from the action of the hydroborate ion on diborane, although the *closo*-$B_6H_6^{2-}$ ion has also been mentioned as a product apparently from a similar reaction.[1] We now report an extension of method (i) carried out under very mild conditions which involves a specific insertion reaction into the B_5 cage of pentaborane(9).

Pentaborane(9) and lithium (or sodium) hydroborate react in a 1 : 1 molar ratio in diglyme at −78° to +25° over 48 h with the evolution of hydrogen (0·5 to 0·7 mole per mole of B_5H_9 used). The solution becomes yellow but only trace quantities of solid are precipitated. Addition of an aqueous solution of tetramethylammonium hydroxide causes some effervescence and precipitates almost pure $Me_4NB_9H_{14}$ (identified from the ^{11}B n.m.r. spectrum[2] and elemental analysis) in 40% yield (based on the boron content of the B_5H_9 used). The addition of dioxan also precipitates the $B_9H_{14}^-$ ion, probably as the dioxanate, $LiB_9H_{14},nC_4H_8O_2$, and after removal of this solid a further reaction product, the octahydrotriborate ion, $B_3H_8^-$, may also be readily recovered from the filtrate by precipitation either as the tetramethylammonium salt, $Me_4NB_3H_8$, by the addition of aqueous tetramethylammonium hydroxide, or as the dioxanate, $LiB_3H_8,nC_4H_8O_2$, by concentration of the filtrate.

The reaction may be followed from variations in the ^{11}B n.m.r. spectrum when the reactants (B_5H_9–$LiBH_4$–diglyme) are sealed in an n.m.r. tube. Thus immediately after mixing at −196°, and recording the spectrum at −78°, the distinctive feature is that no signals attributable to either of the reactants are observed, but an unresolved multiplet arising from the $B_3H_8^-$ ion (centred at +29·1 p.p.m., relative to BF_3,Et_2O = 0) together with two other doublets (at +13·4 and +60·2 p.p.m., with $J_{B\text{-}H}$ = 114 and 110 Hz, respectively) may be recognised. After warming to 25°, the two doublets disappear, and the signals from the $B_9H_{14}^-$ ion develop continually until the reaction is complete. The final spectrum contains only three sets of signals arising from the $B_9H_{14}^-$ ion (three doublets centred at +8·16, +20·43, and +23·60 p.p.m.), the $B_3H_8^-$ ion[3,4] (a multiplet centred at +29·5 p.p.m.), and two other signals (a probable singlet at +13·90 p.p.m. and a triplet at +39·5 p.p.m.) which we are unable to assign at present. The relative areas of the three sets of signals are 2·0 : 2·1 : 1·1, and the unknown species therefore accounts for only about 20% of the total boron content. When lithium deuterioborate is used the final spectrum is similar but shows a loss of resolution on all the peaks indicating that the BD_4^- ion enters fully into the reaction, which therefore appears to be significantly different from that between pentaborane(9) and the hydride ion.[5]

These reactions offer an alternative synthesis of the $B_9H_{14}^-$ ion [the only other reported method involves the degradation of decaborane(14)[6]], and illustrates a hitherto unreported example of a specific insertion reaction into a smaller boron cage compound. Further, it is significant that at the low temperatures used in the present work no borane anions containing more than nine boron atoms are detected, and the results strongly suggest that the $B_9H_{14}^-$ ion is a vital intermediate in the formation of the *nido*-$B_{11}H_{14}^-$ and *closo*-$B_{12}H_{12}^{2-}$ ions since it is known that all the boron hydrides up to decaborane(14) react with the hydroborate ion at elevated temperatures yielding complicated mixtures which contain these B_{11} and B_{12} anions.[7]

(*Received, October 9th,* 1970; *Com.* 1733.

---

[1] E. L. Muetterties and W. H. Knoth, "Polyhedral Borones," Marcel Dekker, New York, 1968, pp. 86—92, and references therein.

[2] N. N. Greenwood, H. J. Gysling, J. A. McGinnety, and J. D. Owen, *Chem. Comm.*, 1970, 505.

[3] R. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 2669.

[4] D. Marynick and T. Onak, *J. Chem. Soc.* (*A*), 1970, 1160.

[5] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 1967, **89**, 3375; T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, 1967, **6**, 1465; H. D. Johnson, R. A. Geanangel, and S. G. Shore, *ibid.*, 1970, **9**, 908.

[6] L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Amer. Chem. Soc.*, 1963, **85**, 2674.

[7] H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, 1964, **3**, 1457.