The Preparation of n-$B_{18}H_{22}$ *via* the Protonolysis of the Tetradecahydroundecaborate Ion, $B_{11}H_{14}^-$

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Summary A simple two-step stereospecific synthesis of pure n-$B_{18}H_{22}$ from decaborane is reported *via* protonolysis of the $B_{11}H_{14}^-$ ion: a possible reaction pathway involves both $B_{11}H_{13}L$ and $B_9H_{13}L$ species.

FEW neutral boranes containing more than ten boron atoms are known, and their chemistry is relatively undeveloped. This is partly due to the lack of convenient preparative methods. For example, the two established routes to octadecaborane are summarised in equations (1)[1–3] and (2)[4–6]

$$(1)\quad B_{10}H_{14} \xrightarrow{R_3N} B_{10}H_{10}^{2-} \xrightarrow{Fe^{3+}} B_{20}H_{18}^{2-} \xrightarrow{H^+} \text{iso- and n-}B_{18}H_{22}$$

$$(2)\quad B_{10}H_{14} \xrightarrow[ROH]{Me_2S} B_9H_{13}(Me_2S) \xrightarrow{100^\circ} \text{n-}B_{18}H_{22} + (B_5H_9 + B_{10}H_{14} + B_{16}H_{20}) + Me_2S.BH_3$$

$$\text{or } B_9H_{13}(Bu_2O) \xrightarrow{140^\circ} \text{n-}B_{18}H_{22}$$

We now report a simple two-step synthesis [equation (3)] from decaborane involving protonolysis of the $B_{11}H_{14}^-$ ion, which produces the n-$B_{18}H_{22}$ isomer *exclusively* in moderate yield.

$$(3)\quad B_{10}H_{14} + BH_4^- \rightarrow B_{11}H_{14}^- \xrightarrow{H^+} \text{n-}B_{18}H_{22}$$

The $B_{11}H_{14}^-$ ion may be easily prepared by the action of $NaBH_4$ on decaborane in dioxan under reflux using a molar ratio $NaBH_4 : B_{10}H_{14}$ of 1 : 1, and is isolated as the pale yellow dioxanate $NaB_{11}H_{14}{\cdot}nC_4H_8O_2$ (where $n = 2{\cdot}5$—$3{\cdot}0$).[7] The protonation reaction occurs conveniently using anhydrous HCl in dioxan solution at 25° with a molar ratio of $NaB_{11}H_{14} : HCl = 1 : 2$. The hydride, n-$B_{18}H_{22}$, is then recovered, after removal of the dioxan, by sublimation *in vacuo* at 100—120°. The reaction also occurs in the absence of solvent, or in the presence of Me_2S, although with a reduced yield of n-$B_{18}H_{22}$. The only other detectable product in the sublimate was trace amounts of decaborane. The product contained only the n-$B_{18}H_{22}$ isomer identified from (i) the u.v. spectrum[8] (ii) conversion into the n-$B_{18}H_{21}^-$ ion by addition of Et_3N to form $Et_3NH^+B_{18}H_{21}^-$ (also identified as the n-isomer from its u.v. spectrum[8]), and (iii) the mass spectrum in which a parent ion is observed at an *m/e* value of 220 ($B_{18}H_{22}^+$),[9] and by comparison with the mass spectra of the n- and iso-$B_{18}H_{22}$ isomers in which small but distinct differences are observed in the fragmentation patterns of the two isomers at *m/e* values of 202, 203, 210, and 211.[10]

Protonolysis reactions of other borane anions have yielded neutral boranes *e.g.*[6,11,12]

$$BH_4^- + H^+ \longrightarrow (BH_3)_2 + H_2$$

$$B_9H_{14}^- + H^+ \longrightarrow \text{iso-}B_9H_{15} + (B_2H_6 + B_4H_{10} + B_5H_9\ \textit{etc.})$$

A rearrangement reaction occurs with $B_3H_8^-$ yielding tetraborane as the major product.[13,14]

$$B_3H_8^- + H^+ \longrightarrow B_4H_{10} + (B_6H_{12} + B_9H_{15} + B_{10}H_{14}\ \textit{etc.})$$

Reaction (3), therefore, illustrates an extension of these protonolysis reactions involving both coupling and elimination of borane fragments stereospecifically.

In view of reactions (2) it is possible that intermediates possessing the boron skeleton of $B_9H_{13}L$ are involved. However, our studies of the reaction mixture after protonolysis and *prior to heating for sublimation*, suggest the presence of $B_{11}H_{13}L$ similar to that postulated from earlier preliminary studies of the protonation of $B_{11}H_{14}^-$ in Me_2S.[15] No evidence for the presence of $B_9H_{13}L$ could be found.

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