The reaction of acetylene with diborane: formation of 1,2-diboroethanes

Although hydroboration of substituted acetylenes[1] and reactions of acetylene with higher boranes[2] have been investigated, the direct reaction of acetylene with diborane in a solvent has not been studied. We have found that, after a mixture of these two gases in 1,2-dimethoxyethane had been allowed to stand, hydrolysis yielded one mole less hydrogen than that expected for unreacted diborane per mole of acetylene used (diborane in excess). With propionic acid, the solid hydrolysate yielded only ethane, equivalent in amount to the acetylene added. These observations suggest initial formation of the diboroethane (I) (X = H) in the solution,

$$\begin{matrix} X \\ X \end{matrix}\!\!>\!B\!-\!CH_2\!-\!CH_2\!-\!B\!<\!\!\begin{matrix} X \\ X \end{matrix}$$

(I)

this being converted to the diboric acid (I; X = OH) on hydrolysis, which is known to yield ethane quantitatively with propionic acid[3]. The diboric acid was separated from boric acid and identified by paper chromatography. Attempts to remove excess diborane from the original reaction mixture, to isolate (I) (X = H), were unsuccessful, more diborane being evolved to leave a viscous, non-volatile residue. However, with excess acetylene in the original reaction, the latter was very vigorous even below 0° C, and gave an insoluble white solid from which solvent and excess acetylene could be removed to leave a highly reactive product of composition $3C_2H_2 + B_2H_6$. The latter gave no hydrogen on hydrolysis, but gave an almost quantitative yield of ethane, with a trace of ethylene, on reaction with propionic acid; this suggests formulation as a polymeric species $[B_2(C_2H_4)_3]_n$ (II) made up of $-(CH_2)_2B(CH_2)_2B(CH_2)_2-$ units and probably containing a small number of terminal vinyl groups. This formulation is supported by reaction of (II) with boron trifluoride or trichloride, which gave the respective 1,2-bis(dihaloboro)ethanes (I; X = F, Cl) in good yield:

$$[B_2(C_2H_4)_3]_n + 4nBX_3 \longrightarrow 3nX_2B(CH_2)_2BX_2 \qquad (1)$$

It is worth nothing that the compound (I) with X = CH_3 has been found[4] to be thermally unstable, losing ~ 75 % of its boron content as trimethylborane and leaving a glassy residue for which a formula similar to (II) has been suggested; this decomposition reaction corresponds closely to the reverse of eqn. (1) with X = CH_3.

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