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SHORT COMMUNICATION

On the mechanism of 2,4-dimethylenetetraborane formation

In recent years a number of new boron–carbon–hydrogen compounds, clearly distinguishable from traditional alkylboranes or alkylboron hydrides, have been reported. These compounds (or their alkyl derivatives), called carboranes include the so-called *closo*-compounds*, $C_2B_nH_{n+2}$ ($n = 3$–10)[1–5], and the *nido*-compounds, CB_5H_9[6], $C_2B_4H_8$[7], $C_3B_3H_7$[8], and $C_4B_2H_6$[9], as well as $C_2B_9H_{13}$[10], all of which are formed, directly or indirectly, by reactions between acetylenic compounds and boranes.

2,4-Dimethylenetetraborane, on the other hand, is formed by reaction of ethylene with tetraborane-10[10,11], and its structure consists of a tetraborane skeleton bridged diagonally by a $-CH_2CH_2-$ group. Consequently, it is more logically classified as an alkylborane than as a carborane. The mode of reaction between B_4H_{10} and C_2H_4 is the subject of this communication.

When deutero-acetylene was utilized in the first syntheses[1,2] of carboranes, the reaction produced the corresponding dideuterocarboranes (containing two CD groups in the molecular skeleton), indicating that hydroboration of the acetylene had not taken place. Analogous reactions involving ethylene are not known, although hydroboration reactions of ethylene and boranes have been reported[12].

Intuitively, as one candidate mechanism, a hydrogen in B_4H_{10} might be expected to add across the double bond of ethylene to form ethyltetraborane, as has been observed for other BH_2-containing boranes. But if this is the case, there has to be a subsequent formation of a B–C bond and ejection of H_2 in order to create the dimethylene product. This is an unlikely reaction under such mild conditions, and it is without precedent. As a second possibility, the B_4H_{10} could lose H_2 to form the already postulated intermediate $[B_4H_8]$[13,14], and this in turn might add to the ethylene molecule without hydrogen transfer. No other borane–*alkene* reactions which exclude hydroboration are known.

In order to determine which of the two candidate routes is correct, we carried out a reaction with deuterated ethylene and tetraborane. If B_4H_8 was formed as an intermediate, the product would be pure $D_4C_2B_4H_8$, whereas if hydroboration took place only one-third of the product would be $D_4C_2B_4H_8$ while the remaining two-thirds would be $D_3C_2B_4H_9$ as shown in the following equations.

$$\begin{tikzcd}
 & {[HCD_2CD_2\text{-}B_4H_9]} \arrow[r, "-HD", "-H_2"'] & \left\{\begin{array}{c} 67\%\ D_3C_2B_4H_9\ (m/e_{max}\ 83) \\ + \\ 33\%\ D_4C_2B_4H_8\ (m/e_{max}\ 84) \end{array}\right. & (1) \\
B_4H_{10} \arrow[ur, "C_2D_4"] \arrow[dr, "-H_2"'] & & & \\
 & {[B_4H_8]} \arrow[r, "C_2D_4"] & 100\%\ D_4C_2B_4H_8\ (m/e_{max}\ 84) & (2)
\end{tikzcd}$$

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* The terms *closo*-carborane and *nido*-carborane are the latest names chosen for the "closed-cage" and "open" carboranes.

Mass spectrometric analysis of the product showed a shift upward of four mass numbers from the normal protiated compound, and unequivocally demonstrated that all four deuterium atoms were retained on the carbon in 100% of the product. Therefore, the addition mechanism 2 is correct*. That the C–H(C–D) bonds survive fragmentation allows a simple first-order interpretation of the data and demonstrates that ethylene in this case, as well as the aforementioned acetylene may react without hydroboration.

In addition to the unambiguous mass spectrometric analysis which demonstrated that four deuterium atoms were retained in the product as $C_2B_4D_4H_8$, we also obtained infrared spectra of the purified product. The results (Table 1) confirmed the fact that all of the deuteriums were attached to carbon and none were on boron; C–D bonds and B–H bonds were observed, whereas C–H was absent. The 12.8 Mc ^{11}B NMR spectrum of $D_4C_2B_4H_8$ appeared to be identical to that obtained from $C_2B_4H_{12}$[11], as would be expected.

TABLE 1

INFRARED ADSORPTION SPECTRA OF DIMETHYLENE-d_4-TETRABORANE (MICRONS)

s = strong, m = medium, w = weak, sh = shoulder, b = broad.

3.89 sh	4.65 s	9.22 s, b	10.0 sh	11.1 s	14.3 w, b
3.97 s	7.40 w, b	9.71 m	10.1 m	13.2 w, b	

Experimental

Both the preparation (in a hot–cold reactor) and separation (standard high-vacuum fractionation techniques) of 2,4-dimethylenetetraborane were accomplished as previously described[10]. The mass spectra were obtained with a Consolidated Model 21-103 mass spectrometer, the ^{11}B NMR spectra on a Varian V-4300 high-resolution nuclear magnetic resonance spectrometer at 12.8 Mc, and the infrared spectra on a Perkin–Elmer Model 137.

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* For such a mass spectral analysis to be susceptible to a simple first-order interpretation requires that the largest m/e fragments must retain all (or nearly all) of the carbon-attached hydrogens. For example, the polyisotopic mass spectra of B_5H_9 and B_5H_8–C_2H_5 in the "parent peak group" (that region where only hydrogens are lost) are quite similar, merely displaced by 28 m/e units, reflecting the loss of boron-attached hydrogens and the retention of carbon-attached hydrogens on fragmentation. In contrast, B_5H_9 and B_5D_9 differ greatly in the B_5^+ to $B_5H_9^+$ (B_5^+ to $B_5D_9^+$) region because of the H–D mass difference upon fragmentation. $B_5H_8C_2H_5$ and $B_5H_8C_2D_5$ also have quite similar mass spectra (displaced by 5 m/e units) again reflecting loss of hydrogens from the B_5H_8 skeletal structure and retention of hydrogens (deuteriums) on the appended ethyl groups. It follows that the reaction of B_4H_{10} and C_2D_4 yields a product with an easily interpretable mass spectrum, whereas B_4D_{10} and C_2H_4 would yield $(CH_2)_2B_4D_8$ and which would produce a mass spectrum difficult to interpret.

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