Photochemical Synthesis of Coupled Boranes and Carbaboranes

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Summary The mercury-sensitised photochemical reactions of boranes or carbaboranes at 2537 Å have been found to be a convenient method of synthesising the corresponding boron–boron coupled boranes or carbaboranes; the synthesis of $3,3'\text{-}(2,4\text{-}C_2B_5H_6)_2$ and $2,2'\text{-}(B_5H_8)_2$ is described.

ALTHOUGH several examples of boron–boron coupled boranes [$2,2'\text{-}(B_4H_8)_2$,[1] $1,1'\text{-}(B_5H_8)_2$,[2] and $2,2'\text{-}(B_5H_8)_2$[3]] and carbaboranes [$2,2'\text{-}(1,5\text{-}C_2B_3H_4)_2$)][4] are known, no general method of preparation of these compounds has been developed. We report a convenient method for the preparation of these compounds by gas-phase photolysis of boranes and carbaboranes at 2537 Å in the presence of mercury vapour, as shown in equations (1) and (2).

$$2,4\text{-}C_2B_5H_7 \xrightarrow[\text{Hg vapour}]{h\nu,\ 2537\ \text{Å}} 3,3'\text{-}(2,4\text{-}C_2B_5H_6)_2 + H_2 \qquad (1)$$

$$B_5H_9 \xrightarrow[\text{Hg vapour}]{h\nu,\ 2537\ \text{Å}} 2,2'\text{-}(B_5H_8)_2 + H_2 \qquad (2)$$

In a typical reaction, a cylindrical quartz tube (25 mm dia. × 350 mm) containing 2·31 mmol of $2,4\text{-}C_2B_5H_7$ and 3 drops of mercury (reaction 1) was irradiated at 30 °C in a

Griffin–Rayonet photochemical reactor equipped with 16 2537 Å lamps. After 1 h, the noncondensable material was removed, a further 1·93 mmol of 2,4-$C_2B_5H_7$ was added, and irradiation was continued for an additional 3 h. Fractionation of the volatile products under reduced pressure gave 131·3 mg (47·7%, based on 2,4-$C_2B_5H_7$ consumed) of a material, the mass spectrum and elemental analysis of which are consistent with the formula $C_4B_{10}H_{12}$. The boron–boron coupled structure proposed in the Figure is consistent with the 32·1 MHz ^{11}B n.m.r. spectrum of this compound which shows resonances at $-8{\cdot}3$ (s),† $-5{\cdot}0$ (d, *J* 168 Hz), and 21·0 (d, *J* 175 Hz) p.p.m., relative area 1 : 2 : 2, which may be assigned to 3,3′; 5,5′, 6,6′; and 1,1′,7,7′ boron atoms respectively. The 100 MHz ^1H n.m.r. spectrum consists of signals at τ 4·18 (s, CH), 5·95 [q, *J* 160 Hz, BH (5,5′;6,6)], and 10·00 [q, *J* 177 Hz BH (1,1′;7,7′] of relative areas 1 : 1 : 1. No evidence was found in this reaction for the formation of other possible isomers. The only other product was a viscous oil which has not been characterised.

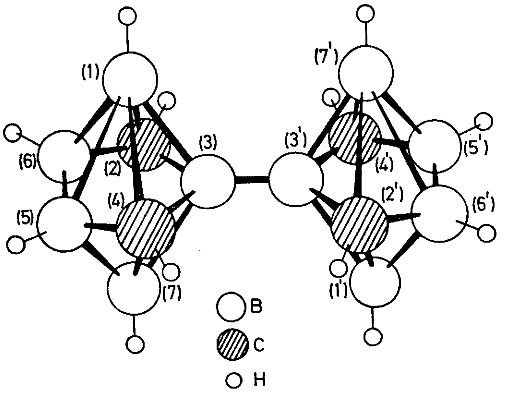

FIGURE. Proposed structure for 3,3′-(2,4-$C_2B_5H_6)_2$.

Reaction (2) was carried out similarly, to give 17% (based on B_5H_9 consumed) of 2,2′-$(B_5H_8)_2$ in 1 h. The product was identified by comparison of its ^{11}B n.m.r., i.r., and mass spectra with those reported previously.[3] The only other products of this reaction were traces of decaborane(14) and a viscous oil which has not been characterised. As in reaction (1), no evidence was found for the formation of other possible isomers. The compound 2,2′-$(B_5H_8)_2$ was originally discovered[3a] in the residue in old pentaborane(9) storage vessels and the only known synthesis[3b] was as a byproduct of the co-pyrolysis of pentaborane(9) and diborane, which gives only traces of impure materials after many days.

Hirata and Gunning[5] had previously studied the mercury-sensitised photolysis of diborane which gives tetraborane(10) and hydrogen as the major products. They proposed a mechanism involving a primary abstraction of hydrogen from diborane by a Hg(^3P) atom followed by a recombination of the resulting diboryl radicals to form tetraborane(10). Such a mechanism seems consistent with our results with B_5H_9 and $2B_5H_7$, since irradiation of these compounds in the absence of mercury vapour gave no reaction.

We have found similar results from the mercury-sensitised photolysis of other small boranes and carbaboranes and these will be reported elsewhere.

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† Relative to external BF_3–OEt_2.

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