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TRANSFER REACTIONS INVOLVING BORON. XIII. CARBON-CARBON BOND CLEAVAGE DURING THE OXIDATION OF VICINAL AND GEMINAL BIS-BORONIC ESTERS (1)

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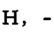
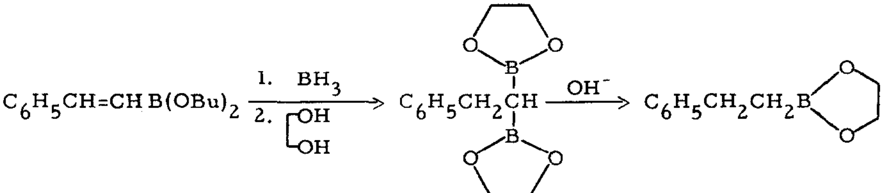
A recent publication from our laboratories proposed a complex mechanistic scheme for the formation of the multitude of products formed by dihydroboration of acetylenes followed by basic hydrolysis and oxidation. (2) The intermediate formed on dihydroboration of an acetylene has a highly cross-linked polymeric structure and the type of products formed on hydrolysis and oxidation may well depend on the structure of the intermediate and state of oxidation of the boron atoms during the hydrolysis and oxidation steps. The substantiation or refutation of the proposed mechanisms awaits the preparation of model compounds and a study of their chemistry.

We have now prepared two bis-boronic esters formally derivable from phenylacetylene on dihydroboration. Compound I was prepared by treating $\underline{\beta}$-styryl magnesium bromide with trimethyl borate followed by hydrolysis and extraction with n-butanol. Hydroboration of I with an excess of borane in tetrahydrofuran followed by the addition of ethylene glycol and distillation produced II in greater than 95% isomeric purity (NMR: 1. 06 ppm (relative to TMS) triplet (1H, -C$\underline{H}$(-B)$_2$), 2. 83 ppm doublet (2H, $C_6H_5C\underline{H}_2$–), 3. 91 ppm singlet (8H, –$C\underline{H}_2O$) and 7. 11 ppm multiplet (5H, aromatic hydrogens)).

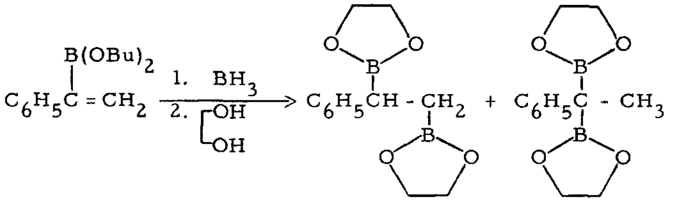
Treatment of II with aqueous base followed by oxidation with hydrogen peroxide produced varying yields (dependent on the base concentration) of benzaldehyde (up to 60%), benzyl alcohol (10-20%), 1-phenylethanol (1-2%), 2-phenylethanol (5-40%) and phenylacetaldehyde (0-10%). These observations are consistent with our earlier report in which benzaldehyde (1. 7-4. 4%) and benzyl alcohol (1. 1-2. 4%) were detected in the product mixture derived from the dihydroboration of phenylacetylene (2). Similar treatment of C-14 labelled II in the benzyl position yields benzaldehyde with retains <u>all</u> of the C-14. Treatment of II with base alone causes only a slow hydrolysis of one of the carbon-boron bonds to give III as evidenced by the isolation of only 2-phenylethanol on oxidation with hydrogen peroxide. Therefore the cleavage



I II III

of the carbon-carbon bond is not base-catalyzed but occurs in the oxidation step. Treatment of II with Fenton's reagent (hydrogen peroxide and ferrous ion) produces benzaldehyde (41%), phenylacetaldehyde (40%), acetophenone (19%) and a trace amount of styrene. Thus the cleavage appears to be radical induced; however, attempts at initiation with di-t-butylperoxide (equal molar amounts) and azo-bis-isobutyronitrile led to the complete recovery of II even though the initiator was completely decomposed. Treatment of II with m-chloroperbenzoic acid in chloroform produced predominantly phenylacetaldehyde, however, low yields of cleavage products were present.

Hydroboration of IV with an excess of borane in tetrahydrofuran followed by the addition of ethylene glycol and distillation produced a mixture of V and VI (90-95% V by NMR analysis).



IV V VI

Recrystallization of the mixture from carbon-tetrachloride produced in low yield pure V (mp 113-115^{o}; Anal: Calcd. B, 8.80: Found: B, 8.64; NMR: 1.19 ppm AB portion of an ABX system, (2 H, -C$\underline{H}_2$-B<), 2.50 ppm X portion (1H, C_6H_5C$\underline{H}$-), 3.90 ppm singlet (8 H, -C$\underline{H}_2$O-) and 7.1 ppm multiplet (5 H, aromatic hydrogens): NMR of mixture of V and VI displays a 1.10 ppm singlet (-C$\underline{H}_3$)).

Treatment of the mixture of V and VI with aqueous base followed by oxidation with hydrogen peroxide produces benzaldehyde (up to 55%), acetophenone (6%), 1-phenylethanol (up to 70%), 2-phenylethanol (up to 12%) and varying low yields of phenylethanediol (all of the yields vary with base concentration). Treatment of the mixture of V and VI with m-chloroperbenzoic acid in chloroform produced predominantly acetophenone along with lesser amounts of benzaldehyde, 1-phenylethanol and phenylethanediol and trace amounts of benzyl and 2-phenylethyl alcohols. Treatment of a sample of pure V with Fenton's reagent produced predominantly styrene (81%) and benzaldehyde (19%) with only trace amounts of the other products. Treatment of pure V with aqueous base resulted in a reasonably rapid hydrolysis of V to give 2-phenylethylboronic acid which on oxidation gave only 2-phenylethanol As with II the carbon-carbon bond cleavages and elimination reactions involving V are apparently not base catalyzed but are of a radical nature. Decomposition of di-t-butylperoxide and azo-bis-isobutrylnitrile in the presence of pure V led to the complete recovery of V.

The nature of the cleavage and elimination reactions is under further study and will be discussed at greater length in a later publication.

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