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CARBON-CARBON BOND CLEAVAGE IN ORGANOBORANES

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In the application of organoboranes to a wide variety of synthetic problems the transfer of the organic group from boron to its new terminus, whether oxygen (1), nitrogen (2), or carbon (3) occurs cleanly, stereospecifically and without rearrangement or fragmentation of the carbon skeleton. Several groups (4,5,6) have observed the replacement of carbon bound hetero-substituents from one of the alkyl moieties by either a hydrogen or an alkyl group from the boron atom (equation I).

(I)

X = Br, Cl, O-alkyl, S-alkyl
R = H, alkyl

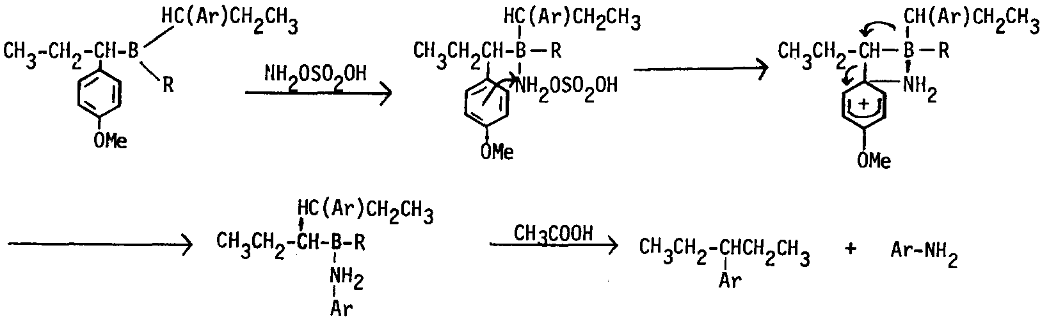
In fact, Brown has made this reaction the basis for a general synthesis of carbon-carbon bonds (7,8).

We wish to report the unusual case of carbon-carbon bond cleavage occurring within the organic moiety of an organoborane. Addition of solid hydroxylamine-O-sulfonic acid to the mixture (9) of organoboranes obtained by hydroboration of 2,4,5-trimethoxy-propenylbenzene produced in 20% yield, 2,4,5-trimethoxyaniline, m.p. 92-93^{0}. Anal. calcd. for $C_9H_{13}NO_3$: C, 50.00; H, 7.15; N, 7.65; ml. wt. 183. Found: C, 58.91; H, 7.31; N, 7.57, mol. wt. 183 (mass spectrum); nmr ($CDCl_3$) in ppm from TMS: 6.68 broad (2H disappears on shaking with D_2O), 6.22

singlet (3H), 6.18 singlet (3H), 6.16 singlet (3H), 3.63 singlet (1H), 3.48 singlet (1H). The absence of any high field signals in the nmr spectrum shows that the alkyl side chain has been removed. Similarly, the lack of any coupling between the aromatic protons indicates that they are para to one another and therefore the amino group occupies the same position held by the side chain. In a similar manner hydroboration of p-methoxypropenylbenzene and subsequent addition of hydroxylamine-O-sulfonic acid gave in 45% yield a mixture of basic products containing 8% p-anisidine (10). In order to decide whether one or both of the isomeric organoboranes formed from the propenylbenzene derivatives are responsible for the aniline products, we performed the following experiment. Hydroboration of p-methoxystyrene proceeds to place the boron atom almost exclusively at the terminal carbon (11). Addition of hydroxylamine-O-sulfonic acid to this intermediate results in a mixture in which p-anisidine could not be detected by GLC. This result indicates that it is the isomer in which the aryl group and boron are bonded to the same carbon that gives rise to the aniline product. Since oxidation of the organoboranes has not been observed to produce phenols (9,12), the organoborane does not rearrange by itself. The aniline products must be due to a rearrangement brought about through the agency of hydroxylamine-O-sulfonic acid.

A thorough search of the reaction mixture to determine the fate of the original side chain failed to uncover any three carbon fragment. However, addition of acetic acid to the reaction mixture followed by combined gas chromatography-mass spectrometry analysis showed the presence of 3-p-anisylhexane. Its identity follows directly from its mass spectrum which in addition to a molecular ion at m/e 192 exhibits major fragments at m/e 77, 78, 91, 92, 107, 121, 134, 135, 149, 150, 163 and 177 (13).

A satisfactory scheme to account for these observations may be constructed as follows:



R = $-CH(Ar)CH_2CH_3$ or $-CH(CHAr)CH_3$

Ar = $p\text{-}CH_3OC_6H_4-$

Electrophillic amination with hydroxylamine-O-sulfonic acid and Lewis acids has been observed (14). In this case it may be an especially favorable intramolecular reaction because of proximity of the aromatic nucleus to the aminating species created by the reaction of the organoborane and hydroxylamine-O-sulfonic acid. The subsequent rearrangement is of a previously observed type (4,6,7).

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9. Oxidation of the mixture of organoboranes gave a 2:1 mixture of 1-(2,4,5-trimethoxyphenyl)-1-propanol and 1-(2,4,5-trimethoxyphenyl)-2-propanol. No phenolic products could be detected.
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