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BENZYNE FORMATION FROM ORTHO - AMINOPHENYLBORONIC ACID

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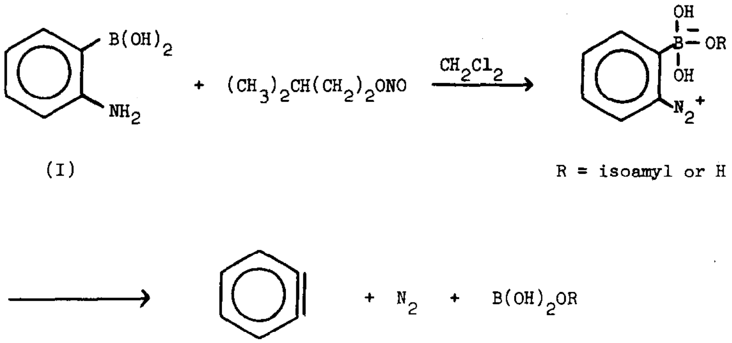
The loss of two ortho-substituents from appropriately substituted benzenes leads to the formation of benzyne.[1] We report the generation of benzyne, as evidenced by trapping experiments, from the aprotic diazotization of ortho-aminophenylboronic acid (I). Benzyne is generated rapidly under similar mild conditions used by Friedman and Logullo[2] for anthranilic acid, and in the presence of anthracene, triptycene is isolated in 45 - 60% yield.



(I)

R = isoamyl or H

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<u>ortho</u>-Nitrophenylboronic acid was synthesized by the selective nitration of phenylboronic acid in acetic anhydride solution.[3] The nitro-compound had m.p. 140-142° (lit.[3] m.p. 139-141°) and displayed the following strong bands in the infra red spectrum (KBr): 3300, 1515, 1350, and 1275 cm.$^{-1}$

Catalytic hydrogenation (30% Pd/C, 60 p.s.i.g., 1:3 MeOH-H_2O) of the nitro-compound afforded (I) in 65% yield, m.p. 175-176° (lit.[4] m.p. 179-180°) with the following strong infra red bands (KBr): 3450, 3350, 1604, 1465, and 768 cm.$^{-1}$

In a typical run, (I), in acetone solution was added dropwise to a refluxing solution of isoamyl nitrite and anthracene in methylene chloride. Equimolar amounts of reagents were used. Injection of a sample of the crude reaction mixture onto a F & M Model 720 gas chromatograph (2 ft. SE-30 silicone rubber columns, He flow 65 ml./min., column temp. 225°) allowed the identification of unreacted anthracene (3.9 min.) and triptycene (12.1 min.); retention times identical with those of authentic samples. Under the operating conditions (I) decomposed in the injection port. Work-up of the reaction mixture in the usual manner[2] afforded off-white platelets of triptycene (from EtOH-φH) m.p. and mixed m.p. 255-256° in 55% yield.

From the mild conditions (40°) of the decomposition, it may be inferred that the boron becomes tetra-coordinated before leaving. Kuivila, <u>et al</u>.[5] have shown that in aromatic protodeboronation $\mathrm{Ar\bar{B}(OH)_3}$ is about a million times more reactive than is $\mathrm{ArB(OH)_2}$.

Hydroxide ion and isoamyl alcohol are formed in the aprotic diazotization. One of these bases coordinates with the boron but it is not yet clear whether the boron leaves as boric acid or as the mono-isoamyl ester of boric acid. Alkyl borates are thermally unstable and extremely susceptible to hydrolysis.[6] Further experiments are currently underway.

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References

1. For a recent review with leading references, see G. Wittig, Angew. Chem. Internat. Edit., **4**, 731 (1965).
2. L. Friedman and F. M. Logullo, J. Am. Chem. Soc., **85**, 1549 (1963).
3. W. Seaman and J. R. Johnson, J. Am. Chem. Soc., **53**, 711 (1931).
4. F. R. Bean and J. R. Johnson, J. Am. Chem. Soc., **54**, 4415 (1932).
5. H. G. Kuivila, J. F. Reuwer, Jr., and J. A. Mangravite, Can. J. Chem., **41**, 3081 (1963).
6. H. Steinberg, Organoboron Chemistry, Vol. I, chapter 21, John Wiley and Sons, Inc., New York (1964).