The Reaction of Aryldichloroborane with Organic Azides: Preparation of *N*-Substituted Derivatives of 1,2-Dihydro-1-aza-2-borabenzene

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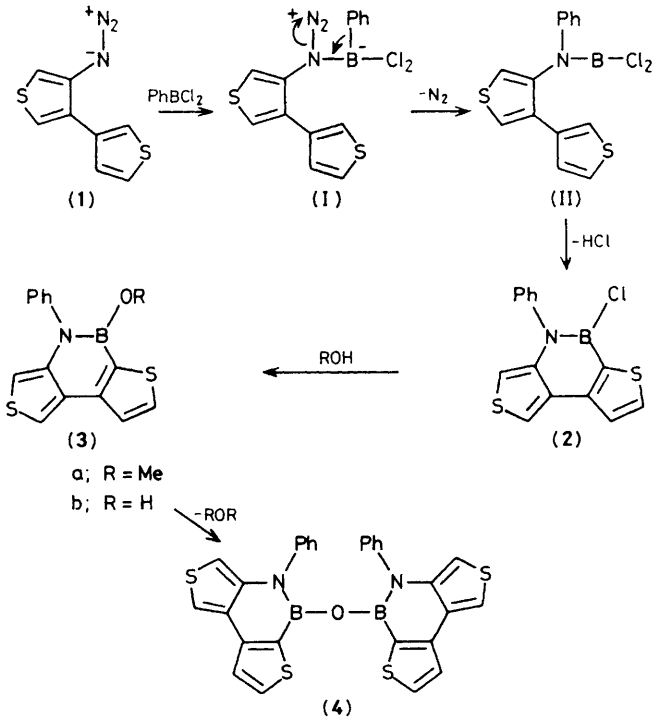
The reaction between phenyldichloroborane and an α,β-unsaturated *o*-aryl azide at room temperature yielded the corresponding 1,2-dihydro-*N*-phenyl-1-azo-2-borabenzenes quantitatively *via* 1,6 cyclization of the intermediate *N*-phenylaminodichloroboranes resulting from a 1,2-shift of the phenyl group.

In recent years much effort has been devoted to the synthesis of 1,2-dihydro-1-aza-2-borabenzenes, a class of pseudo-aromatic boron compounds whose electronic structures have been studied.[1] Their pharmacological properties are well recognized,[2] but no direct synthetic method for 1,2-dihydro-*N*-substituted-1-aza-2-borabenzenes is available.

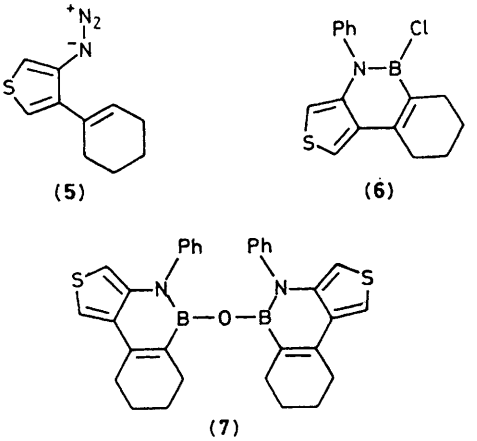
Recent reports on the syntheses of *o*-azidobithienyls[3] and 1,2-dihydro-1-aza-2-borabenzodithiophens[4] prompted us to study the reaction of aryldichloroborane with *o*-azidobithienyls as a possible route to new *N*-substituted 1,2-dihydro-1-aza-2-borabenzodithiophens.[5]



Scheme 1

When 4-azido-3,3′-bithienyl† (**1**) was allowed to react with phenyldichloroborane at room temperature in benzene an exothermic reaction took place with the immediate evolution of molecular nitrogen. The reaction, followed by t.l.c., revealed the disappearance of the starting azide (1 h) and the formation of a single compound which was probably the chloro-derivative (**2**). After solvent removal the solid residue was treated with methanol, to give the ester (**3a**)‡ m.p. 125—126 °C (94%). Compounds (**2**) and (**3a**) proved to be very sensitive to moisture, being smoothly converted into the free acid (**3b**), and ultimately to the ether (**4**) m.p. 226—228 °C. Under the same conditions 3-(cyclohex-1-enyl)-4-azidothiophen (**5**)† gave the chloro-derivative (**6**) whose hydrolysis gave the ether (**7**) m.p. 230—232 °C (95%) directly.

The proposed mechanism, which is in part based on that suggested previously by H. C. Brown *et al.*[5] for the reaction of organic azides with mono-substituted dichloroborane, is outlined in Scheme 1.



† Prepared according to ref. 3.

‡ The structures of the new products were confirmed by analytical data and i.r., n.m.r., and mass spectral data.

Loss of molecular nitrogen from complex (I) and 1,2-migration of the phenyl group from boron to nitrogen would give the *N*-dichloroborane (II). This would lead readily to products (**2**) and (**6**) by intramolecular electrophilic substitution on the more reactive α-position of the thiophen ring and on the vinylic carbon of cyclohexene, respectively.

The ready availability of suitable alkyl- and aryl-azides and alkyl-[6] and aryl-dichloroboranes[7] together with the mild reaction conditions make this procedure a simple and convenient route to 1,2-dihydro-*N*-substituted-1-aza-2-borabenzenes.

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References

1 For a review, see A. J. Fritsch in 'Special Topics in Heterocyclic Chemistry,' in 'The Chemistry of Heterocyclic Compounds,' Vol. 30, eds. A. Weissberger and E. Taylor, Wiley, 1977, p. 381.
2 S. Gronowitz, T. Dahlgren, J. Namtvedt, C. Roos, B. Sjöberg, and V. Forsgren, *Acta Pharm. Suec.*, 1971, **8**, 377; S. Gronowitz, T. Dahlgren, C. Roos, G. Rosen, B. Sjöberg, and U. Forsgren, *ibid.*, p. 623; G. Hogenauer and M. Woistsch Läger, *Nature* (*London*), 1981, **293**, 662.
3 S. Gronowitz, P. Spagnolo, and P. Zanirato, *J. Org. Chem.*, 1982, **47**, 3177.
4 I. Ander, S. Gronowitz, and P. Zanirato, *Chem. Scr.*, to be published.
5 These reactions were proposed initially as a source of secondary amines, H. C. Brown, M. M. Midland, and A. B. Levy, *J. Am. Chem. Soc.*, 1973, **95**, 2394.
6 H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, 1973, **95**, 2396.
7 K. Niedenzu and W. J. Dawson, *J. Am. Chem. Soc.*, 1960, **82**, 4223.