The Reaction of Organic Azides with Boron Trichloride: A New Simple Route for the Production of Fused Heterocycles Containing Nitrogen

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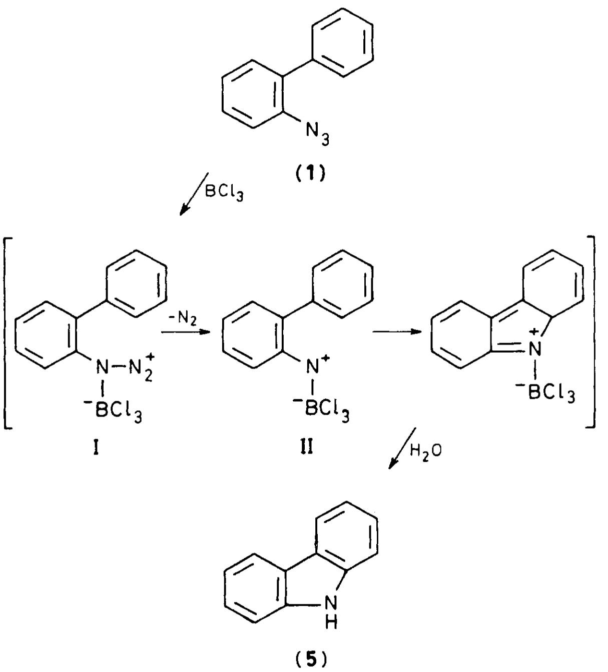
The reaction of boron trichloride with an *ortho*-aryl and *ortho*-diazoaryl phenyl azides at room temperature yielded fused azoles *via* 1,5-cyclization of a probable singlet nitrenium ion intermediate, arising from displacement of molecular nitrogen from the azido group.

Organic azides undergo a facile reaction with a wide variety of trivalent boron compounds to give products derived from fragmentation of the azido group. Secondary amines are readily obtained by reaction of alkyl- or aryl-dichloroboranes with organic azides.[1] Phenyldichloroborane reacts with α,β-unsaturated *o*-aryl azides to give the corresponding *N*-phenyl-1-aza-2-borabenzenes in good yield. The reaction occurs *via* 1,6-cyclization of the intermediate *N*-phenylaminodichloroborane resulting from a 1,2-shift of the phenyl group.[2] The same reaction may be regarded as a possible source of an intermediate nitrenium ion, if the 1,2-shift from boron to nitrogen is inhibited.

Consequently we have studied similar reactions utilizing boron trichloride. These room temperature reactions showed fast loss of nitrogen resulting in a reactive intermediate species which turned out to be able to yield fused azoles. For instance when 2-azidobiphenyl (**1**) was allowed to react with boron trichloride in benzene an exothermic reaction took place with the immediate evolution of molecular nitrogen. The reaction was completed in 10 min (when t.l.c. showed that no starting material was left). After hydrolysis and work up the mixture afforded, in 91 % yield, a solid residue characterized as carbazole (**5**), m.p. 245—246 °C.

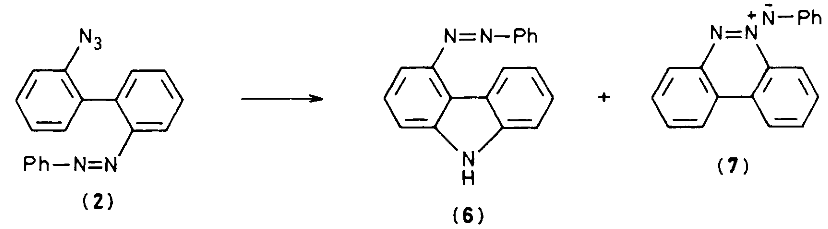


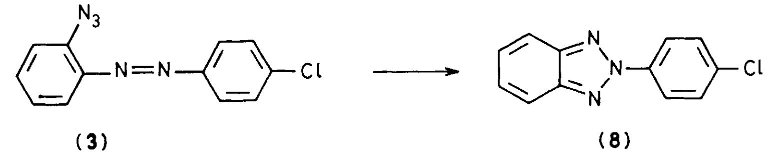
Scheme 1

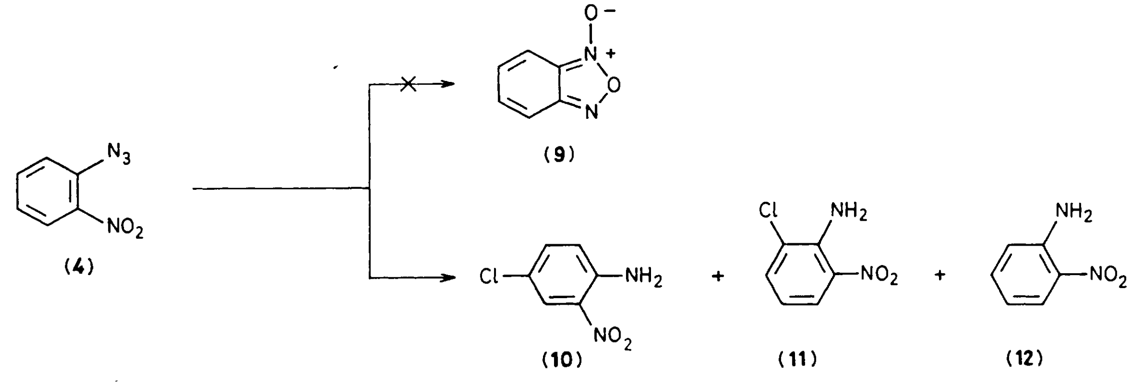
No mechanistic study has yet been undertaken for this reaction. However a nitrenium ion intermediate (II) arising from loss of nitrogen from complex (I) is probably implicated (*cf.* Scheme 1). Intermolecular aromatic substitution or double bond addition of singlet phenylnitrenium ion has recently been reported.[3] Such nitrenium ions are closely related to the nitrenes[4] which are largely produced also by thermal decomposition of aryl azides.[5]

Representative azides, *i.e.* 2-azido-2′-(phenylazo)biphenyl (**2**) and 2-azido-4′-chloroazobenzene (**3**), the thermolyses of which have been reported,[6,7] were allowed to react with boron trichloride at room temperature and in the dark for 10 min. The nature of the products, in both cases, was similar to that of the products obtained in the corresponding decompositions. Thus, the reaction products from the azide (**2**), after chromatography, were 4-phenylazocarbazole (**6**), m.p. 190—191 °C (20 %), and benzo[*c*]cinnoline *N*-phenylimide (**7**), m.p. 130—132 °C (63 %); and from the azide (**3**), 2-(4-chlorophenyl)-benzotriazole (**8**), m.p. 171—172 °C (94 %).

Different behaviour was observed with 2-nitrophenyl azide (**4**), the thermolysis of which has been reported to give mainly benzofuroxan (**9**) through an assisted intramolecular cyclization.[8] Instead, in the reaction with boron trichloride, at room temperature for a few minutes, azide (**4**) provides a new access to chloro-substituted nitroanilines. Chromatographic separation of the reaction mixture gave 2-nitro-6-chloroaniline (**11**), m.p. 74—76 °C (17 %), 2-nitroaniline (**12**), m.p. 69—70 °C







(3%), and 2-nitro-4-chloroaniline (**10**), m.p. 116—118 °C (64%).

Formation of the reduction products (**10**)—(**12**)† from the azide (**4**) is presumably ascribable to an independent process involving the intermediate (II) (Scheme 1) whose inability to cyclize affords (*via* rearrangement)‡ the chloro-substituted nitroanilines (**10**) and (**11**) in good yields. This result suggests that the preferential 1,5-cycloaddition observed with compounds (**1**)—(**3**) is facilitated by the favourable delocalization of the π-bond.

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† Related reactions of phenyl azide with aluminium chloride in the presence aromatic substrates have been reported to give diarylamines and aniline (ref. 9).

‡ The positive charge of a phenylnitrenium ion populates preferentially the *ortho*- and *para*-positions of the aromatic ring rather than the nitrogen atom (ref. 10).

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