Reaction of 5,6-Benzo-1,2,4-triazine 1-Oxides with Grignard Reagents

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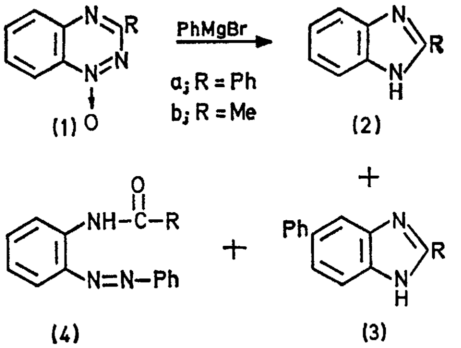
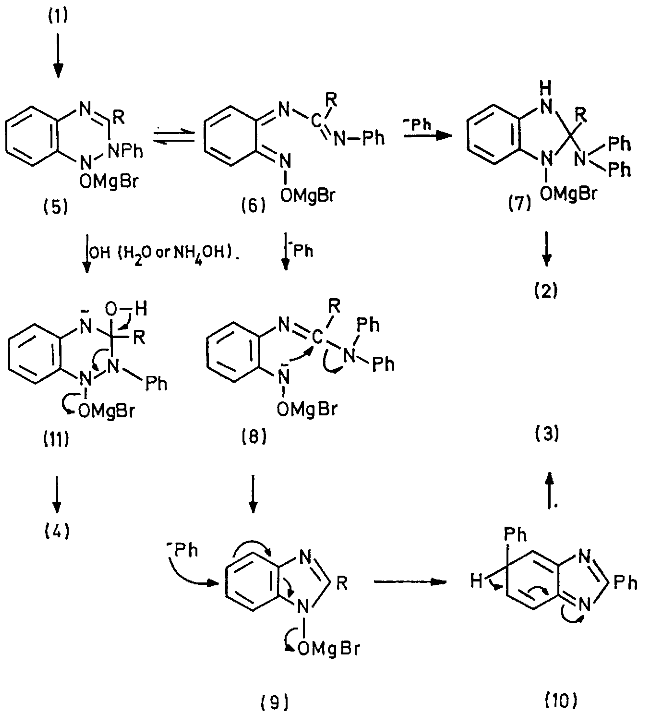
Summary Reaction of 5,6-benzo-1,2,4-triazine 1-oxides with phenylmagnesium bromide results in ring fission to afford benzimidazoles and 2-acylaminoazobenzenes.

SOME reactions of 1,2-diazine *N*-oxides, and also triazine *N*-oxides, with Grignard reagents are specific, *e.g.*, ring fission and elimination of molecular nitrogen. Thus, pyridazine *N*-oxides afford[1] buta-1,3-dienes and vinylacetylenes, and results for cinnoline 2-oxides[2] and 5,6-benzo-1,2,3-triazine 3-oxides[3] have been reported. However, the carbon atom α to the *N*-oxide group in cinnoline 1-oxide[4] is relatively insensitive to this addition, and we therefore examined the reactions of the structurally analogous benzo-1,2,4-triazine 1-oxides.



To a solution of the oxide[5] (**1a**) in benzene, ethereal PhMgBr was added at room temperature. Work up afforded the benzimidazoles (**2a**)[6] (8%) and (**3a**)[7] (6%), and the azobenzene (**4a**)[8] (5—6%). The 3-methyl compound† (**1b**) did not afford (**2b**) and (**3b**), but gave the azobenzene (**4b**) (15—20%). In all cases traces of several unidentified substances were detected besides (**2**)—(**4**).

Use of MeMgI instead of PhMgI gave the parent triazine (30—35%) and starting material (40%), and no other product was identified, as was the case with cinnoline 2-oxide.‡



Scheme

We suggest that compounds (**2**)—(**4**) might be formed by the mechanism in the Scheme. The formation[9] of (**2a**) by electrolytic reduction of the 1,4-dihydro-derivative of (**1a**) and the formation[10] of 1,2,3-benzotriazoles by treatment of (**1**) with alkali, are known.

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† Compound (**1b**) was obtained by oxidation of 3-methyl-5,6-benzo-1,2,4-triazine with H_2O_2 in AcOH, m.p. 92—93°; δ (CCl_4): 2·70 (s, 3H, Me), 7·54 (q, 1H, 7-H), 7·80 (m, 1H, 6-H), 7·83 (d, 1H, 5-H), and 8·33 (q, 1H, 8-H).

‡ 4-Methyl-1,4-dihydrocinnolines, 1,4-dimethyl-1,4-dihydrocinnolines, and deoxygenated cinnolines were obtained in 2—4% yields.

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