

Formation of 1,2,3-Benzotriazines by Oxidation of 1- and 2-Aminoindazoles

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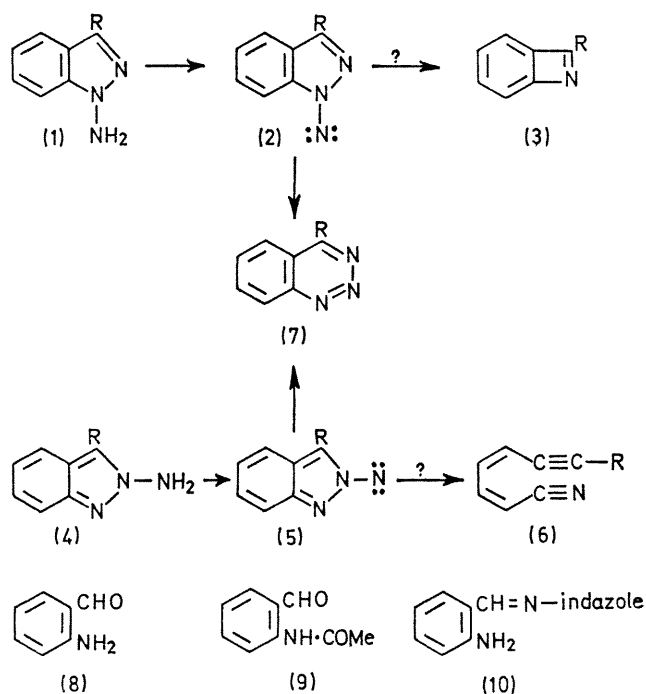
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Summary 4-Substituted 1,2,3-benzotriazines are formed in high yield by oxidation of 1- and 2-amino-3-substituted indazoles; 1,2,3-benzotriazine itself is formed in the same way if nucleophiles are carefully excluded.

OXIDATION of 1- (1) and 2-aminoindazole (4) was investigated since it seemed likely that, by analogy with the oxidation of 1- and 2-aminobenzotriazole and related compounds,¹ nitrogen would be extruded from the resulting nitrenes (2) and (5). The former should lose nitrogen and either collapse to the azabenzocyclobutadiene (3) or fragment further to RCN and benzyne. The latter, (5), should lose nitrogen and ring-open to the cyanoacetylene (6), or possibly collapse to the azabenzocyclobutadiene (3). It was thought that common products from the oxidation of 1- and 2-aminoindazoles would indicate the intermediacy of (3).

The *N*-aminoindazoles [(1) and (4); R = H, Me, and Ph] were readily obtained by amination of the indazoles with hydroxylamine-*O*-sulphonic acid in aqueous alkali. The isomers were separated chromatographically and their structures established spectroscopically and by independent synthesis of the 2-amino-compounds.

Somewhat surprisingly, oxidation of the *N*-amino-3-substituted indazoles [(1) and (4); R = Me and Ph] with lead tetra-acetate in dichloromethane did not lead to the loss of nitrogen, but the 1,2,3-benzotriazines (7; R = Me and Ph) were formed rapidly and almost quantitatively. Similarly, oxidation of 1- and 2-aminoindazole [(1) and (4);



R = H] gave the parent benzotriazine (7; R = H). However the latter is highly susceptible to attack by nucleophiles

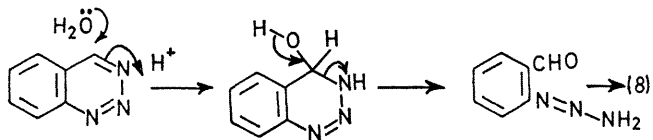
and it could only be isolated when the *N*-aminoindazole was added slowly to lead tetra-acetate in rigorously dried solvents in the presence of excess of powdered calcium oxide to remove acetic acid. In the absence of such precautions the products (**8**), (**9**), and (**10**) were obtained in variable yields, by attack of water, acetic acid, or the starting aminoindazole, respectively, on the triazine. Formation of *o*-aminobenzaldehyde (**8**), for example, is rationalised as shown; the initial "covalent hydration" is well known for related heterocyclic systems.²

Once isolated, as a colourless, crystalline solid, m.p. 119–120°, 1,2,3-benzotriazine (**7**; R = H) is quite stable. Its structure is supported by analytical, spectral, and mass spectral data, by its rapid reaction in solution with nucleophiles to give derivatives of *o*-aminobenzaldehyde, and by its thermal fragmentation in the vapour phase (450° at 0.02 Torr) to give benzyne, isolated as biphenylene (40%).

¹ C. D. Campbell and C. W. Rees, *J. Chem. Soc. (C)*, 1969, 742.

² A. Albert, *Angew. Chem. Internat. Edn.*, 1967, **6**, 919.

The lower reactivity of the 4-substituted benzotriazines towards nucleophiles is attributed to a combination of steric and electronic effects.



Oxidation of 1- and 2-aminoindazoles thus provides a further, and as yet the cleanest, route to 1,2,3-benzotriazines. The reaction promises wide scope; for example 3-methoxyindazole can be converted into 4-methoxy-1,2,3-benzotriazine in high yield by amination and oxidation.

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