

4-Alkyl- and 4-Aryl-1,2,3-benzotriazines

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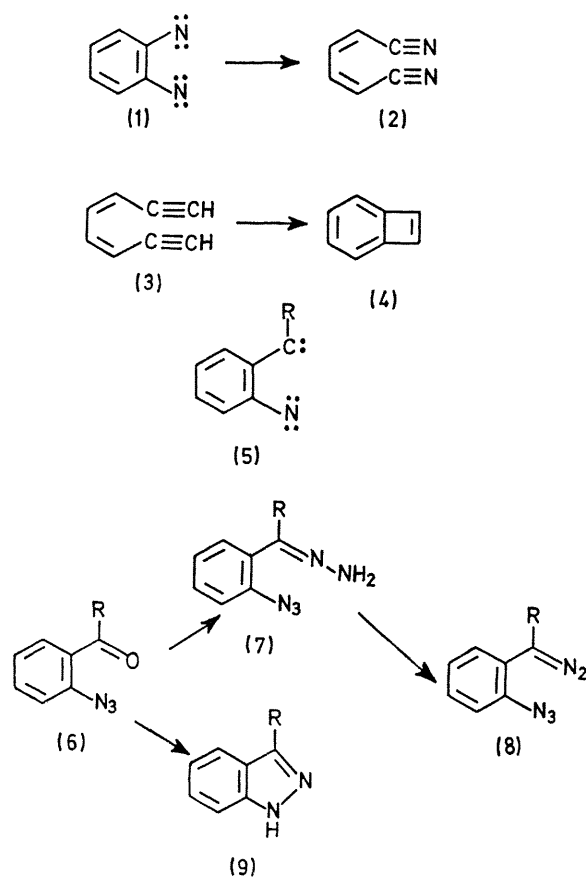
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Summary Oxidation of the hydrazones of *o*-aminophenyl alkyl and aryl ketones provides a simple route to the previously virtually unknown 4-alkyl- and 4-aryl-1,2,3-benzotriazines; 1-(*o*-azidophenyl)diazoethane on thermolysis also gives the 4-methyltriazine in high yield; on pyrolysis in the vapour phase, the triazines fragment to give benzyne and hence biphenylene (40%).

cis,cis-1,4-DICYANOBUTADIENE (2) is the stable product of several reactions which formally involve *o*-dinitrenobenzene (1), such as the pyrolysis of *o*-diazidobenzene¹ and the oxidation of *o*-phenylenediamine² and 2-aminobenzotriazole.³ In contrast, *cis,cis*-octa-3,5-diene-1,7-diyne (3) is unstable and rapidly isomerises to benzocyclobutadiene (4).⁴ Species with the intermediate stoichiometry of *o*-nitrenophenylcarbene (5) are therefore of considerable interest, particularly as potential precursors of azabenzocyclobutadiene.

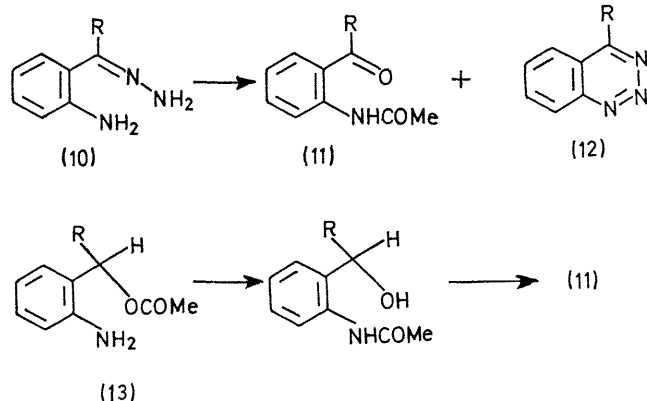
o-Azidophenyldiazo-compounds (8) were obvious precursors of the nitrenocarbenes (5). However, attempts to convert the readily available azides (6; R = H, Me, or Ph) into the azido-hydrazones (7), by treatment with hydrazine in refluxing ethanol containing a small amount of acetic acid, gave the indazoles (9) in high yield. In fact this is a useful synthetic route to 3-substituted indazoles; it possibly involves intramolecular nucleophilic displacement of azide from the aromatic ring, under surprisingly mild conditions.

In view of this failure to obtain the desired azido-hydrazones (7), the amino-hydrazones (10) were oxidised in the hope that they would give, successively, the *o*-amino-diazo-compound, the *o*-nitreno-diazo-compound, and, with loss of nitrogen the nitreno-carbene (5) or a valence tautomer. Oxidation of (10; R = Me, Ph, or *p*-MeO·C₆H₄) with lead tetra-acetate gave two products in each case. The first was the corresponding acetamido-ketone (11) (10, 30, and 70%, respectively), most simply rationalised in terms of



reaction of the amino-diazo-compound with acetic acid to give the acetate (13), followed by intramolecular acetyl

transfer to nitrogen and further oxidation of the benzyl alcohol.



More interesting, the second product was the 4-substituted 1,2,3-benzotriazine (12) (50, 50, and 30%, respectively). Spectral, mass spectral, and analytical data

support the proposed benzotriazine structure. Chemical support came from their fragmentation in relatively mild vapour-phase pyrolyses (450° and 0.1 Torr) to give benzyne, isolated as biphenylene (*ca.* 40%). The benzotriazine (12; R = *p*-MeO·C₆H₄)[†] was identical with the product obtained by diazotisation of 2-amino-4'-methoxybenzophenone imine.⁵ The 4-substituted benzotriazines are stable, colourless, crystalline solids. Their formation by oxidation of the *o*-aminophenyl hydrazones (10) can be readily envisaged *via* the amino-diazo-compound and cyclisation of this to the dihydrotriazine which is then oxidised.

The diazo-azide (8; R = Me) has subsequently been obtained from the azido-ketone (6; R = Me) by treatment with hydrazine under very mild conditions, with iodine catalysis. In refluxing benzene, (8; R = Me) decomposed smoothly with loss of one mol. of nitrogen to give 4-methyl-1,2,3-benzotriazine in 70% yield. Probably the azido-carbene is formed and undergoes 1,6-dipolar cyclisation in an 8 π -electron pericyclic process.

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[†] This is the only previously reported example of a simple aryl, or alkyl, 1,2,3-benzotriazine.

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⁴ G. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, 1969, **91**, 7520.

⁵ A. J. Nunn and K. Schofield, *J. Chem. Soc.*, 1953, 716.