Oxidation of 1- and 2-Aminobenzotriazole

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BENZYNE is formed rapidly and quantitatively by the oxidation of 1-aminobenzotriazole with lead tetra-acetate in cold benzene.[1] This amine, m.p. 84° [$\lambda_{\text{max.}}$ 211 (log ϵ 3·84), 263 (3·76), 280 mμ (inf.) (3·65), $\nu_{\text{max.}}$ 3230, 3130, 1650, 1415, 1275, 1250, 790, 752 cm.$^{-1}$] is readily prepared by direct amination of benzotriazole with hydroxylamine-*O*-sulphonic acid in aqueous potassium hydroxide at 60°. However the isomeric 2-aminobenzotriazole (I), m.p. 122° [$\lambda_{\text{max.}}$ 216 (log ϵ 4·12), 285 mμ (4·08), $\nu_{\text{max.}}$ 3285, 3140, 1500, 1429, 1172, 978, 743, 738, 689 cm.$^{-1}$, benzylidene derivative m.p. 123°, picrate m.p. 105°] is also formed and its relative yield increases with temperature. The structures of these amines are confirmed by their rapid deamination with nitrous acid, to give benzotriazole in high yield, and by the oxidations now reported.

When 2-aminobenzotriazole in benzene is oxidised with lead tetra-acetate, nitrogen is rapidly evolved and *cis, cis*-mucononitrile (IV), m.p. 127°, is formed in 64% yield, presumably by way of the (possibly triplet) nitrenes (II) and (III). The same intermediates have been postulated in the

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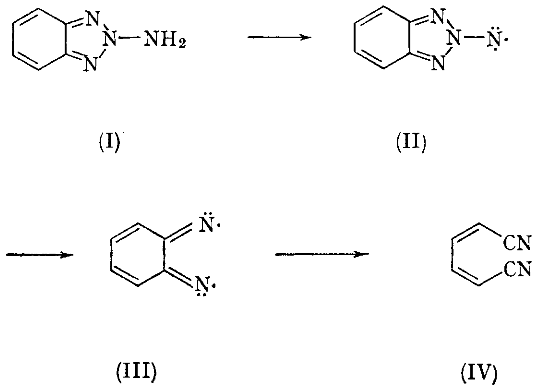
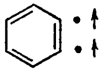
[1] C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 1964, 296.

thermal decomposition of *o*-diazidobenzene to mucononitrile by Hall,[2] whose report prompts this preliminary communication. Three mucononitriles, m.p. 95—96°,[3] 124—125°,[4] and 159—161°[3] have been reported without stereochemical assignments; that ours is the expected *cis*, *cis*-isomer follows from its n.m.r. spectrum [quartets centred on τ 2·57 and 4·20; J = 2·6 and 6·0 c./sec.]. The dinitrene (III) could not be trapped by reaction with ethyl acetylenedicarboxylate, presumably because of the much faster bond isomerisation to mucononitrile, isolated in 63% yield.





(V)

When 1-aminobenzotriazole is oxidised with lead tetra-acetate in the absence of a benzyne trap nitrogen is again rapidly evolved and biphenylene formed in high yield (83%) together with very small amounts of triphenylene (*ca.* 0·5%). Benzyne generated in this way shows a marked tendency to dimerise; biphenylene was often the major product (up to 86%) in attempted additions of benzyne to heterocyclic dienes. 1-Amino-5-methylbenzotriazole similarly gave 2,6-dimethylbiphenylene (67%). This is in striking contrast with benzyne generated in most other ways where the amounts of biphenylene formed are small. (An exception is irradiation of 1,2,3-benzothiadiazole 1,1-dioxide which gave 52%).[5] Reasons for this difference, including the possibility that our benzyne is formed in a triplet (V) rather than a singlet state, the original nitrene having been generated in its triplet ground state, are under investigation.

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[2] J. H. Hall, *J. Amer. Chem. Soc.*, 1965, **87**, 1147.
[3] H.-F. Piepenbrink, *Annalen*, 1951, **572**, 83.
[4] P. Kurtz, H. Gold, and H. Disselnkötter, *Annalen*, 1959, **624**, 1.
[5] G. Wittig and R. W. Hoffmann, *Chem. Ber.*, 1962, **95**, 2718.