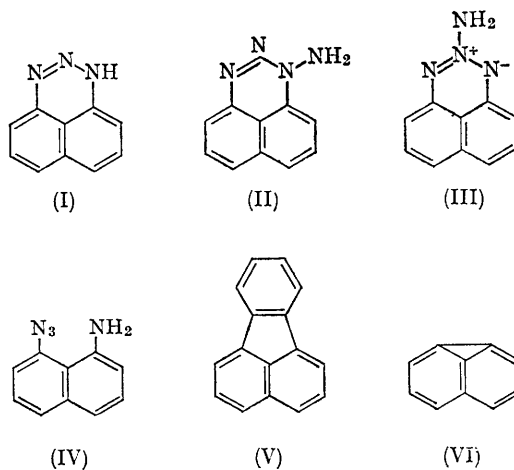


1,8-Dehydronaphthalene (*peri*-Naphthalene)

By C. W. REES and R. C. STORR
(King's College, Strand, London, W.C.2)

SINCE benzyne generated by the oxidation of 1-aminobenzotriazole with lead tetra-acetate dimerises very readily it could be a triplet state diradical.¹ If this is so, similarly produced *meta*- and *para*-benzynes should be of comparable stability. We have generated the "*meta*-benzyne" 1,8-dehydronaphthalene by this route.

Amination of the triazine (I) with hydroxylamine-*O*-sulphonic acid in aqueous alkali gave the red 1-amino-derivative (II), m.p. 135–140° decomp. [λ_{\max} . 232.5 (log ϵ 4.42), 339 m μ (4.01), ν_{\max} . 3415, 3205, 1630, 1584, 842, 772, 757 cm.⁻¹] together with the almost colourless isomer 1-azido-8-naphthylamine (IV), m.p. 78–80° [λ_{\max} . 232 (4.20), 252.5 (4.19), 346 m μ (3.94), ν_{\max} . 3500, 3380, 2110, 1594, 1578, 1300, 810, 750 cm.⁻¹]



¹ C. D. Campbell and C. W. Rees, preceding communication.

probably derived from the unstable 2-amino-derivatve (III) [cf. the similar amination of benzotriazole¹ and the alkylation of the triazine (I)²].

Nitrogen was eliminated very rapidly from the aminotriazine (II) by oxidation with lead tetraacetate in cold benzene to give, not the naphthalene dimer perylene, but fluoranthene (V). This must presumably result from 1,2-addition of 1,8-dehydronaphthalene to benzene to give 9,14-dihydrofluoranthene which is oxidised further. Similar oxidation in tetrachloroethylene gave 1,1,2,2-tetrachloroacenaphthene. Oxidation in *cis*- and *trans*-dichloroethylene gave very largely *cis*- and *trans*-dichloroacenaphthene,³ respectively, together with a minor amount of the other isomer (thin-layer chromatography) in each case. Thus the additions are stereospecific and are most simply explained by the formation of 1,8-dehydronaphthalene and the simultaneous formation of both new bonds in its addition to the olefins. Oxidation of (II) in cyclohexene has so far given naphthalene

as the only crystalline product, presumably by abstraction of allylic hydrogen atoms from the solvent by the naphthalene. In all these oxidations the products were isolated in low yields (5–45%) and identified by comparison with authentic compounds.

peri-Naphthalene appears to be much more reactive than benzyne, generated by this route under the same conditions, since it reacts with benzene in the cold and it does not dimerise; perylene could not be detected in any of the above oxidations. Thus the question of spin multiplicity in these species must remain open; the two reactive centres in *peri*-naphthalene are not conjugated however and the only classical structure for it is the highly strained trimethylenecyclopropane (VI). 1,3- and 1,4-Dehydrobenzene have now been detected mass spectrometrically in the flash photolysis of the corresponding benzenediazonium carboxylates by Berry, Clardy, and Schafer whose reports⁴ prompt this preliminary communication.

(Received, April 7th, 1965.)

² M. J. Perkins, *J. Chem. Soc.*, 1964, 3005.

³ S. J. Cristol, F. R. Stermitz and P. S. Ramey, *J. Amer. Chem. Soc.*, 1956, **78**, 4940.

⁴ R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Letters*, 1965, 1003, 1011.