

Nature of the Intermediates in the Photolysis of Benzotriazoles

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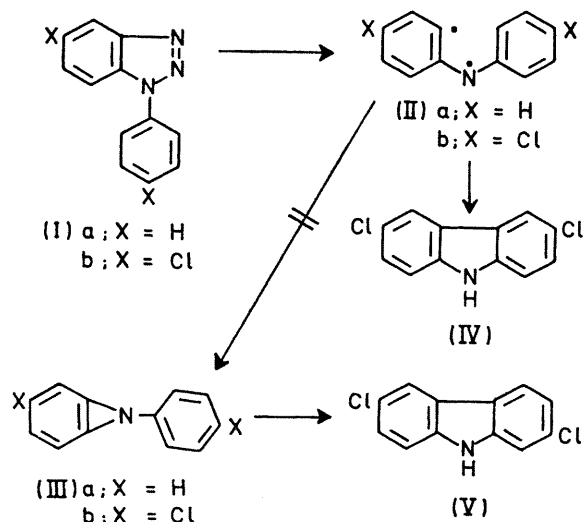
Summary The photochemical transformations of 5-chloro-1-(4-chlorophenyl)benzotriazole and 1-benzoylbenzotriazole have been investigated.

ON irradiation, 1-phenylbenzotriazole loses a molecule of nitrogen to give carbazole.^{1,2} Two structures, the diradical (IIa) and the azirine (IIIa), are conceivable as the reactive intermediate even though the latter is expected to be unstable on account of its antiaromaticity.³

In order to investigate this point, 5-chloro-1-(4-chlorophenyl)benzotriazole (Ib)⁴ was photolysed. If (IIb) were the intermediate, the symmetrical carbazole (IV) should be produced while if the azirine (IIIb) were the real precursor, the unsymmetrical (V) should be the product because of the electronegativity of the chlorine atom at C-5.⁵

Irradiation of (Ib) in acetonitrile with a low-pressure mercury arc for 14 h gave (IV), m.p. 201° (lit. 202°)⁴ in 89% yield as a sole product. Its structure was confirmed by its n.m.r. spectrum; δ 7.03(dd, 2H, J 8.5 and 2.0 Hz), 7.21 (d, 2H, J 8.5 Hz), 7.83(d, 2H, J 2.0 Hz), and 10.0br (s, 1H) p.p.m. (acetone).[†]

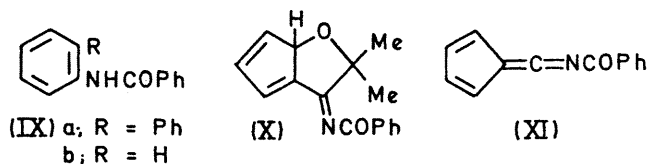
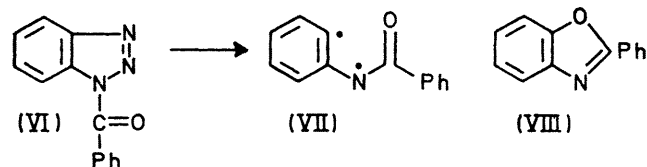
This result indicates that the structure of the reactive intermediate should be (IIb) and the intramolecular



1,5-cyclization must have taken place, not the formation of the antiaromatic compound.

† The n.m.r. spectra were measured with a Varian H-220 instrument and analysed in the first-order approximation

In order to study the electronic state of the intermediate diradical, the photolysis of 1-benzoylbenzotriazole (VI) was examined. Extended Hückel molecular orbital calculations on the intermediate diradical (VII) indicated that the atomic bond population of the C(2)-O linkage is bonding



(+0.050) in the ground state and antibonding (-0.006) in the first excited state. In accord with these calculations the thermolytic decomposition of (VI) gave 2-phenylbenzoxazole (VIII) in reasonable yield.⁶ Photolysis of (VI) in benzene and in acetonitrile gave (IXa) and (IXb), respectively. The acetone-sensitized photolysis of (VI) gave (X), m.p. 122°, m/e 253 (M^+); λ_{\max} 311 nm (EtOH); ν_{\max} (KBr) 1650 cm^{-1} ; δ 1.93 (s, 6H), 5.73 (d, 1H, J 7.5 Hz), 6.48 (td, 1H, J 7.5 and 1.5 Hz), 6.75 (dd, 1H, J 7.5 and 1.5 Hz), 6.84 (t, 1H, J 7.5 Hz), and 7.5 (m, 5H) p.p.m. (CDCl_3).[†] In these reactions no trace of (VIII) was detected. This is in sharp contrast to thermolytic and mass spectrometric fragmentations of (VI).⁷ The formation of (X) may be accounted for in terms of the rearrangement of the diradical to the ketenimine (XI) as in the case of triazoles.¹

We conclude that the electronic state of the diradical intermediate must be the first excited state, as is the case for 3*H*-indazole⁸ and some diazo compounds.⁹

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