Synthesis of Heterocycles by Photochemical Cyclization of *ortho*-Substituted Benzene Derivatives

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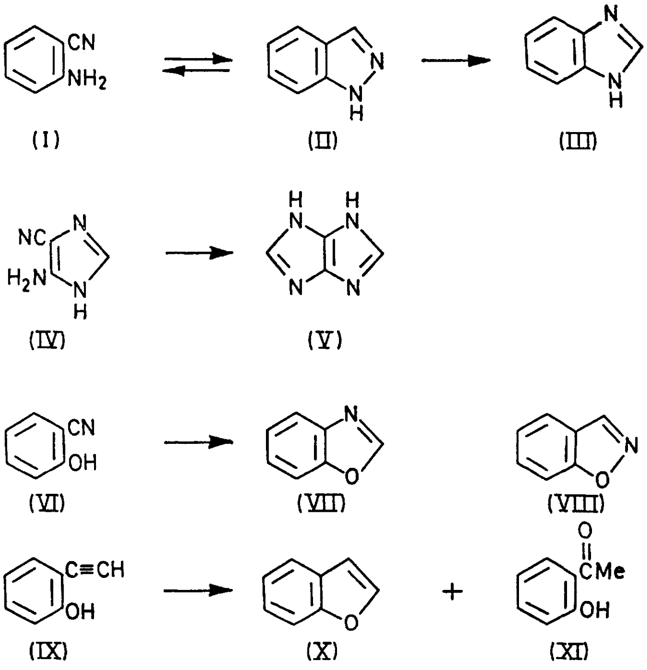
Summary Photochemical cyclization of *ortho*-substituted benzene derivatives to the corresponding benzimidazole, indazole, benzoxazole, and benzofuran ring systems is described.

ALKYL-SUBSTITUTED imidazoles may be conveniently prepared by the photochemical cyclization of aliphatic enaminonitriles.[1] We now report the extension of this photochemical cyclization to various aromatic compounds with the formation of the benzimidazole, indazole, benzoxazole, and benzofuran ring systems.†

Irradiation of degassed acetonitrile solutions of (I) first gives (II) which upon further irradiation yields benzimidazole (III) [20% from (I)]. *N*-Methylanthranilonitrile is photochemically converted into 1-methylindazole (17%). The 1-alkylindazoles do not yield the corresponding benzimidazoles on irradiation.[2] The formation of the pyrazole ring in these photolyses is in marked contrast with the findings using aliphatic enaminonitriles where it was established that pyrazoles were not intermediates.[1] However, irradiation of (IV)[3] yields the novel bicycle (V)‡ with no evidence for the prior formation of the corresponding pyrazole.

A completely different reaction pathway was observed when *N*-phenylanthranilonitrile was irradiated. Carbazole (87%) formed by intramolecular displacement of CN by the *N*-phenyl ring, was obtained.

Photochemical cyclization was observed when the amino-group of anthranilonitrile was replaced by OH. However, the oxazole ring system was formed directly without the intermediacy of the corresponding isoxazole. For example, irradiation of an aqueous degassed solution of 2-cyanophenol resulted in a 60% yield of benzoxazole (VII). When this irradiation was carried out with low conversion under conditions where the cyanophenol was absorbing > 95% of the light only benzoxazole was observed as product. No benzisoxazole (VIII) could be detected. Furthermore, it was established that cyanophenol does not sensitize the conversion of benzisoxazole into benzoxazole.[4]



Finally the cyclization was still observed when both the cyano- and amino-groups of anthranilonitrile were replaced

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† Photolyses were carried out on a 10^{-4}—10^{-2} M scale (λ 254 or 300 nm). Products were identified by comparison with authentic samples.

‡ I.r., u.v., n.m.r., and mass spectra of this compound are in accord with this structural assignment.

with acetylene and hydroxy-groups. Irradiation of (IX) in acetonitrile or 10^{-2}M aqueous OH^- gave (X) [60% in aqueous base together with (XI) (20%)]. Compound (XI) was the only product in neutral aqueous solution. The surprising scope of these heterocyclic preparations suggests that this synthetic approach may also be applied to the formation of indole, thiophen, and thiazole rings.

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[1] J. P. Ferris and J. E. Kuder, *J. Amer. Chem. Soc.*, 1970, **92**, 2527 and references given therein.

[2] The photochemical rearrangement of indazole to benzimidazole was reported by H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Helv. Chim. Acta*, 1967, **50**, 2244.

[3] J. P. Ferris and L. E. Orgel, *J. Amer. Chem. Soc.*, 1966, **88**, 3829.

[4] The photochemical conversion of benzisoxazole into benzoxazole was reported by H. Göth and H. Schmid, *Chimia* (*Switz.*) 1966, **20**, 148.