

Photochemical Cyclisation of Stilbazoles to Azaphenanthrenes

By C. E. LOADER, M. V. SARGENT, and C. J. TIMMONS

(Chemistry Department, The University, Nottingham)

WE have extended our recent work on the photochemistry of stilbene¹ to stilbazoles. Contrary to reports by Mallory and his co-workers^{2,3} that 2- and 4-stilbazoles do not cyclise when irradiated with ultraviolet light in cyclohexane solution in the presence of iodine, we have found that 2-, 3- and 4-stilbazole all cyclise in cyclohexane, both in the presence and absence of iodine. Iodine had little effect on the reactions in dilute solution, but

appeared to inhibit the reaction in more concentrated solutions of the stilbazoles. Both *trans*-3-stilbazole and 4'-methyl-*cis*-3-stilbazole cyclise rapidly giving good yields (~60%) of the benz[*f*]isoquinolines (1a), m.p. 98—99.5°, and (1b), m.p. 109—110°, respectively, contaminated with some polymeric material and the *cis*- and *trans*-3-stilbazoles. *trans*-2-Stilbazole and 6-methyl-*trans*-2-stilbazole cyclise more slowly giving fair yields

¹ M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, 1963, **85**, 2186, and *J. Chem. Soc.*, 1964, 5544.

² F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 1964, **86**, 3094.

³ C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.

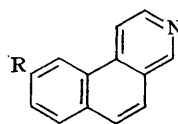
(~30%) of the benzo[*f*]quinolines (IIa), m.p. 90—91° and (IIb), m.p. 80—81°, respectively. *trans*-4-Stilbazole cyclises very slowly giving a poor yield (22%) of benz[*h*]isoquinoline (III). Analogously, 4-styrylquinoline cyclises to benzo[*i*]phenanthridine (IV), m.p. 181—182° (25%). In each case the progress of the reaction was followed by ultraviolet spectroscopy of the reaction mixture, the appearance of bands in the 300—350 m μ region being characteristic of the formation of the azaphenanthrenes.⁴

The initial step in the photochemical reaction of the stilbazoles is the formation of *cis-trans*-mixtures. The following cyclisation presumably proceeds by a similar mechanism to that postulated for the cyclisation of stilbene.^{1,2} The photocyclisations take place most readily in dilute solution, and we have used 0.005M-solutions except in the case of *trans*-4-stilbazole where 0.0025M-solutions gave better results. The stilbazole, in cyclohexane, was irradiated by a 400 w Hanovia medium-pressure mercury-vapour lamp surrounded by a water-cooled silica jacket for the required time. The cyclohexane solution was then filtered, and the cyclohexane was evaporated. The products were isolated by chromatography on alumina or as the picrates.

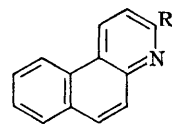
Perkampus and Senger in an investigation of the cyclisation of the related dipyridylethylenes used more dilute solutions (4×10^{-5} M) in *n*-hexane.⁵ 1,2-Di-(2-pyridyl)ethylene and 1,2-di-(4-pyridyl)ethylene also cyclised under the conditions used by

us, but more rapidly than the 2- and 4-stilbazoles. The order of rates for the stilbazoles is 3->2->4-stilbazole, which is similar to that obtained by Perkampus and Senger for the dipyridylethylenes,⁵ 2,3'->2,4'->3,4'->2,2'->4,4'-dipyridylethylene.

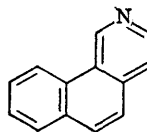
These photocyclisations have possible preparative value, especially in view of the comparative inaccessibility of benz[*f*]- and benz[*h*]-isoquinolines by normal chemical synthesis.



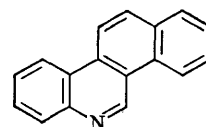
(Ia); R = H
(Ib); R = Me



(IIa); R = H
(IIb); R = Me



(III)



(IV)

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⁴ G. Coppens, *Bull. Soc. chim. belges*, 1960, **69**, 413; Y. Kanda and R. Shimada, *Spectrochim. Acta*, 1959, **15**, 211.

⁵ H.-H. Perkampus and P. Senger, *Ber. Bunsen Gesellschaft Phys. Chem.*, 1963, **67**, 876.