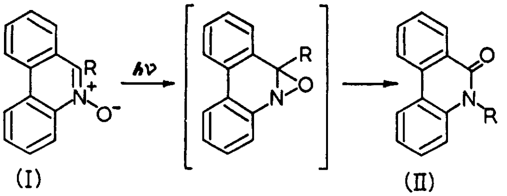
Group Migration in the Photolysis of 6-Substituted Phenanthridine 5-Oxides

By EDWARD C. TAYLOR and GAVIN G. SPENCE
(*Department of Chemistry, Princeton University, Princeton, New Jersey*)

THE photochemical rearrangement of nitrones to amides is a well-established reaction and has been shown to involve the intermediate formation of oxazirans,[1a-e] which in several instances have been isolated and characterized.[1a,b,2-4] An analogous rearrangement is characteristic of a variety of aromatic *N*-oxides;[5-10] oxazirans have been isolated from the photolysis of 2-cyanoquinoline 1-oxides in aprotic solvents,[11,12] and implicated in the photolytic conversion of pyridine 1-oxide into pyrrole-2-carboxyaldehyde.[13] A few nitrone → amide rearrangements have been observed to involve group migration from an intermediate oxaziran as a minor pathway.[6,8-10,12]

We comment briefly upon a related photochemical rearrangement of 6-substituted phenanthridine 5-oxides where conditions for group migration during photolysis are optimal.



Thus, irradiation of (I) in ethanol solution using a medium-pressure mercury vapour lamp (2537 Å) yielded (II) (yield 93% where R = Ph, 79% where R = Me). The conversion is extremely rapid; a study the rate of product formation showed that the reaction was essentially complete within 30 sec. (conc. 10^{-4} M in a Rayonet photochemical reactor), and that further irradiation served only to effect decomposition of (II). A rough kinetic study of the rearrangement showed that it was first order up to 50—60% conversion; the rate then tapered off as absorption of light by the product increased. The photolytic conversion of (I) into (II) (R = Ph) was much more effective in ethanol than in chloroform solution, probably because in the former solvent (II) is appreciably less soluble and crystallizes out directly as it is formed, whereas in chloroform it remains in solution and is thus subject to photochemical decomposition. Quantum yields for the conversion of (I) into (II) in ethanol were found to be $\phi_{254} = 0{\cdot}19$, $\phi_{350} = 0{\cdot}08$ (R = Ph); $\phi_{254} = 0{\cdot}37$, $\phi_{350} = 0{\cdot}11$ (R = Me). There was no evidence for oxaziran accumulation, even in dichloromethane solution ($\phi_{350} = 0{\cdot}12$) (R = Me).[11]

The photolytic conversion of 6-substituted phenanthridine 5-oxides into 5-substituted 6-(5*H*)-phenanthridinones occurs so readily that considerable care must be taken in the preparation of the former intermediates to avoid exposure to laboratory light, even when operations are carried out in Pyrex vessels. We are currently investigating the nature of this extremely rapid group migration by the use of optically active substrates.

(*Received, June 13th*, 1966; *Com.* 404.)

[1] (a) J. S. Splitter and M. Calvin, *J. Org. Chem.*, 1958, **23**, 651; (b) R. Bonnett, V. M. Clark, and A. Todd, *J. Chem. Soc.*, 1959, 2102; (c) F. Kröhnke, *Annalen*, 1957, **604**, 203; (d) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, 1957, **22**, 576; (e) For further examples, see A. Mustafa, *Adv. Photochem.*, 1964, **2**, 63.

[2] L. H. Sternbach, B. A. Koechlin, and E. Reeder, *J. Org. Chem.*, 1962, **27**, 4671.

[3] L. Kaminsky and M. Lamchen, *Chem. Comm.*, 1965, 130.

[4] L. Brehm, K. G. Jensen, and B. Jerslev, *Acta Chem. Scand.*, 1966, **20**, 915.

[5] O. Buchardt, *Acta Chem. Scand.*, 1963, **17**, 1461.

[6] M. Ishikawa, S. Yamada, and C. Kaneko, *Chem. and Pharm. Bull. (Japan)*, 1965, **13**, 747.

[7] E. C. Taylor, B. Furth, and M. Pfau, *J. Amer. Chem. Soc.*, 1965, **87**, 1400.

[8] O. Buchardt, J. Becher, and C. Lohse, *Acta Chem. Scand.*, 1965, **19**, 1120.

[9] O. Buchardt and C. Lohse, *Tetrahedron Letters*, 1966, 4355.

[10] O. Buchardt, J. Becher, and C. Lohse, *Acta Chem. Scand.*, 1966, **20**, 262.

[11] C. Kaneko, S. Yamada, and M. Ishikawa, *Tetrahedron Letters*, 1966, 2145.

[12] C. Kaneko and S. Yamada, *Chem. and Pharm. Bull. (Japan)*, 1966, **14**, 555.

[13] J. Streith and C. Sigwalt, *Tetrahedron Letters*, 1966, 1347.