Photochemical Reactions of 1,2-Dihydroquinolines

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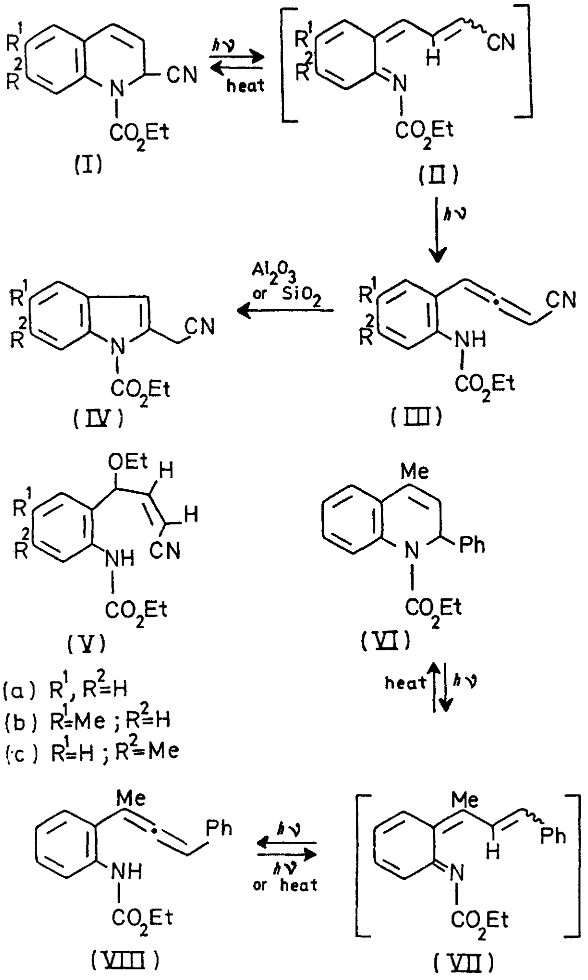
Summary Irradiation of ethyl 2-substituted 1,2-dihydroquinoline-1-carboxylates gives rise to allenic compounds and ethanol adducts depending upon the solvent used; product formation is rationalised in terms of benzoazahexatriene intermediates.

Although the photochemistry of 1,2-dihydronaphthalene[1] and its hetero analogues[2] has received much attention, little is known about the photochemical behaviour of 1,2-dihydroquinolines.[2d,e] We report our results on the photochemistry of a series of ethyl 2-substituted 1,2-dihydroquinoline-1-carboxylates, which provide evidence for benzoazahexatriene intermediates.



Irradiation† of the carboxylate‡ (Ia) followed by evaporation and t.l.c. on alumina or silica gel gave the carboxylate (IVa),§ m.p. 121°, in 52—69% yield. The structural assignment was based on spectral comparisons with ethyl indole-1-carboxylate.[3] However, closer examination of the i.r. and n.m.r. spectra of the crude photolysate indicated the absence of (IVa) and, instead, suggested the presence of allenic compound (IIIa) [ν 3420 (NH), 2220 (CN), and 1950 (C=C=C) cm^{-1}; τ 3·15 (d), 4·38 (d) (two allenic protons, *J* 6·6 Hz)]. Attempts to isolate (IIIa) were unsuccessful, but the results suggest that (IVa) is formed by an intramolecular cyclisation of (IIIa).[4] Compounds (Ib), m.p. 120—121°, and (Ic), m.p. 79—80°, behaved similarly to give the corresponding indole derivative (IVb), m.p. 101—102°, and (IVc), m.p. 98—99°, respectively *via* the allenic intermediates (IIIb) and (IIIc). This reaction could be useful in the syntheses of 2-substituted indole derivatives of potential pharmacological activity, otherwise available only by multistep processes.

When irradiation of (Ia) was carried out in ethanol, an ethanol adduct (Va), m.p. 73—74°, and (IVa) were obtained in 23 and 3% yields, respectively. The structure of (Va) is consistent with its spectral data. The *cis*-stereochemistry of the double bond was tentatively assigned from the coupling constant (*J* 12 Hz) of the two olefinic protons.[5] Under similar conditions, (Ib) gave (Vb) (15%), m.p. 75—76°, and (IVb) (6%), while (Ic) afforded exclusively (Vc) (64%), m.p. 59—60°.

Irradiation of the carboxylate (VI)[6] gave a *ca.* 2:1 mixture of an allenic compound (VIII) and the starting material (VI). Although all attempts to isolate (VIII) failed, the formation of (VIII) was demonstrated by the spectral data of the reaction mixture [ν 1945 (C=C=C) cm^{-1}; τ 3·65 (q, 1H, *J* 3·0 Hz, allenic-H), 7·84 (d, 3H, *J* 3·0 Hz, Me)]. Distillation of the reaction mixture at 120—140 °C and 0·02 mmHg gave only the starting material (VI) in high yield.

These results can be rationalised in terms of benzoazahexatriene intermediates (II, VII) which have been recently proposed for the coloured species in the low-temperature photochromism of 1,2-dihydroquinolines.[2e] The same photochromic behaviour was also observed with (Ia—c) under the photolytic conditions we employed. For example, irradiation of a dilute ethereal or ethanolic solution of (Ia) led to a reddish-brown solution, which faded to colourless

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† Unless otherwise stated, an ether solution of the 1,2-dihydroquinoline (*ca.* 3 × 10^{-2} M) was irradiated at *ca.* 5—10° with a 350 W high-pressure mercury lamp in a Pyrex vessel and the reaction was monitored by u.v. and n.m.r. spectroscopy.

‡ All the Reissert compounds were prepared according to the method described by F. D. Popp, L. E. Katz, C. W. Klinowski, and J. M. Wefer, *J. Org. Chem.*, 1968, **33**, 4447.

§ All new crystalline compounds gave satisfactory elemental and spectral analyses.

within a few minutes in the dark. A [1,5] hydrogen transfer reaction (II→III, VII→VIII)[1,7] may account for the formation of the allenic compounds, and addition of ethanol to (II) for the formation of (V). An analogous example for the latter is the photolysis of 2,2-disubstituted chromenes in ethanol.[2c]

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