

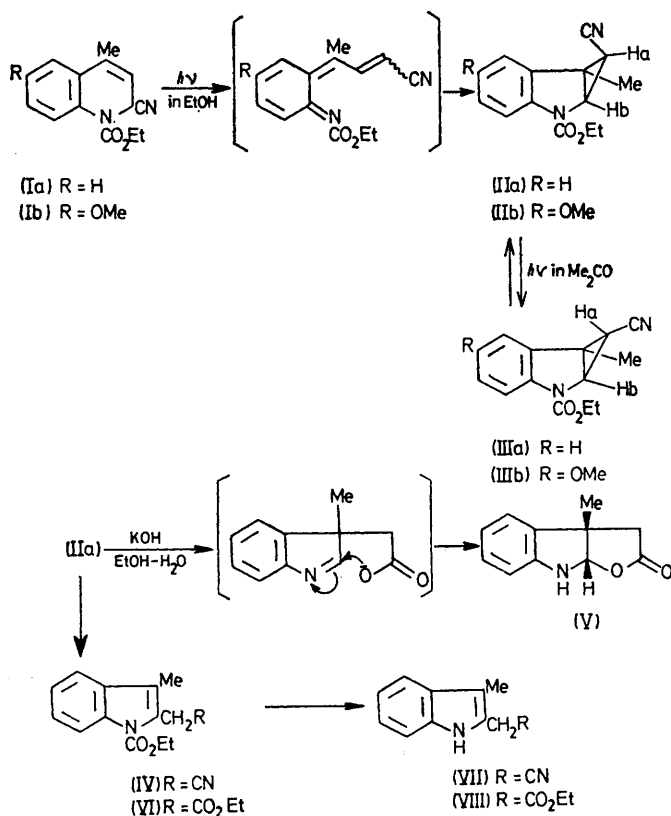
Photochemical Synthesis of 2,3-Homoindoles

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Summary Irradiation of ethyl 2-cyano-4-methyl-1,2-dihydroquinoline-1-carboxylates in ethanol gives stereospecifically ethyl *endo*-1-cyano-6b-methyl-1,1a,2,6b-tetrahydrocycloprop[*b*]indole-2-carboxylates (2,3-homoindoles) in 59—61% yields, which are shown to be useful synthetic intermediates for indole derivatives.

PREVIOUSLY we reported¹ that irradiation of ethyl 2-cyano-1,2-dihydroquinoline-1-carboxylates (Reisert compounds) gives either allenic compounds or ethanol adducts depending upon the solvent used. The allenic compounds can be transformed into indole derivatives. We now report a variation of the reaction course by the introduction of a



methyl group at the 4 position of the Reissert compounds; namely stereospecific formation of 2,3-homoindoles (II).²

When the dihydroquinoline (Ia),[†] was irradiated[‡] in ether two products (IIa) (10%), m.p. 104–105°,§ and (IV) (32%), m.p. 88–89°, were obtained (t.l.c.). Irradiation of (Ia) in ethanol gave exclusively (IIa) (61%).

The structure of (IIa) was determined from its mass, u.v., i.r., and n.m.r. spectra. Chemical confirmation was obtained by alkaline hydrolysis (KOH–EtOH–H₂O, 110°) of (IIa) to (V) (72%), m.p. 99–100°, and by ring opening of (IIa) (conc. HCl, reflux) to (IV) (42%) or (HCl–EtOH, r.t.) to (VI) (90%), m.p. 151–153°, which were hydrolysed (K₂CO₃–MeOH) to (VII) (71%), m.p. 99–101°, and the known compound (VIII) (52%),³ respectively. This result also confirmed the structure of the photoproduct (IV). The stereochemistry of the cyclopropane ring in (IIa) was determined by comparison of the chemical shift⁴ of Ha [τ 8.28 for (IIa) and 8.88 for (IIIa)] and the coupling constant^{4a} between Ha and Hb [$J_{a,b}$ 6 Hz for (IIa) and 2.5 Hz for (IIIa)] with those of the *exo*-isomer (IIIa), m.p. 98–99°, which was isolated from an equilibrium mixture (IIa : IIIa = ca. 2 : 3) obtained by the acetone-sensitized photolysis of (IIa).[¶]

Similarly, irradiation of (Ib) in ethanol gave (IIb), m.p. 124–125° (59%), which was also transformed into (IIIb), m.p. 119–120°.

The formation of (II) may be visualized as analogous to the photochemical transformation of 1,2-dihydronaphthalenes into benzobicyclo[3,1,0]hexenes⁵ and the formation of (IV) is analogous to the reaction described previously.¹

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[†] Reissert compounds (Ia,b) 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.

[‡] Irradiation was carried out with a 350W high-pressure mercury lamp in a Pyrex vessel until all of the starting material had disappeared as determined by t.l.c.

[§] All new compounds gave satisfactory elemental and spectral analyses.

[¶] Both (IIa) and (IIIa) are stable on irradiation in ether or ethanol.

¹ M. Ikeda, S. Matsugashita, H. Ishibashi, and Y. Tamura, *J.C.S. Chem. Comm.*, 1973, 922.

² The only reported example in this class of compounds is limited to ethyl 2-benzoyl-1,1a,2,6b-tetrahydrocycloprop[b]indole-1-carboxylates which have been synthesised by the reaction of 1-benzoylindoles with ethyl diazoacetate in low yields: J. W. Welstead, U.S.P. 2,103,295/1970 (*Chem. Abs.*, 1971, **75**, 98,444).

³ H.-H. Stroh and H. Beitz, *Annalen*, 1966, **700**, 78.

⁴ (a) V. Rautenstrauch and F. Wingler, *Tetrahedron Letters*, 1965, 4703; (b) F. W. Fowler, *Chem. Comm.*, 1969, 1359.

⁵ (a) H. Heimgarter, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1972, **55**, 3005 and references therein; (b) D. A. Seeley, *J. Amer. Chem. Soc.*, 1972, **94**, 4378.