Photo-isomerisation of 1-Acetyl-2-cyano-1,2-dihydroquinolines to *N*-Acetylbenzoazetines

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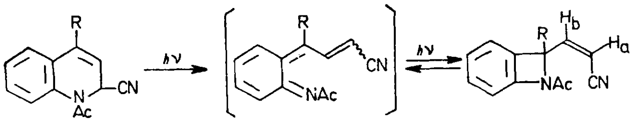
Summary 1-Acetyl-2-cyano-1,2-dihydroquinolines isomerise photochemically to give *N*-acetylbenzoazetines, the formation of which is rationalised in terms of benzoazahexatriene intermediates.

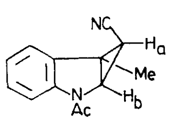
1,2-DIHYDROQUINOLINES have been shown to undergo a number of photochemical reactions.[1,2] We now report a new photochemical isomerisation of 1,2-dihydroquinolines to benzoazetines.[3]



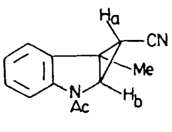
(Ia) R = Me
(Ib) R = H

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

(IIIa) R = Me
(IIIb) R = H_c



(IV)



(V)

Irradiation of the dihydroquinoline (Ia)† in ether or ethanol with a 350 W high-pressure lamp through Pyrex gave (IIIa) and (IV), whose relative yields depended upon the period of irradiation and the solvent. In a typical experiment, (Ia) (300 mg) when irradiated in ethanol for 5 h gave (IIIa) (an unstable oil) and (IV) (m.p. 207—208 °C)‡ in 30 and 54% yields, respectively. After a shorter period of irradiation (1—3 h), (IIIa) was the major product; longer periods (10 h) resulted in the complete disappearance of (IIIa) and an increase in the amount of (IV) and polymer. Irradiation of (IIIa) (isolated) gave (IV). The structure of (IIIa) was assigned from its mass, i.r., and n.m.r. spectra; M^+ 212; ν_{max} ($CHCl_3$) 2200 (CN), and 1640 (CO) cm^{-1}, δ ($CDCl_3$) 7·02—7·35 (4H, m, ArH), 6·56 (1H, d, H_b), 5·43 (1H, d, H_a), 2·22 (3H, s, COMe), and 1·89 (3H, s, Me). The *cis* stereochemistry of the double bond of (IIIa) was tentatively assigned from the coupling constant (*J* 12 Hz) of

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† Reissert compounds (Ia,b) were prepared according to the method described by F. P. Popp, L. E. Katz, C. W. Klinowski, and J. M. Weter, *J. Org. Chem.*, 1968, **33**, 4447.

‡ All new crystalline compounds gave satisfactory elemental and spectral analysis.

the two olefinic protons.[4] The structure of (IV) (H_a, δ 1·82, J_{ab} 6 Hz) was assigned by comparison of its n.m.r. spectrum with that of the *exo*-isomer (V) (H_a, δ 1·21, J_{ab} 2 Hz), m.p. 180—181 °C, obtained by isomerisation of (IV), § as well as with those of ethyl *endo*- and *exo*-1-cyano-6b-methyl-1,1a,2,6b - tetrahydrocycloprop[*b*]indole - 2 - carboxylates.[2] Similarly, irradiation of (Ib) in ether gave (IIIb) in quantitative yield as an unstable solid which rapidly decomposed on exposure to air. The structure was assigned on the basis of the following spectral data; ν_{max} ($CHCl_3$) 2250 (CN), and 1650 (CO) cm^{-1}; δ ($CDCl_3$) 7·00—7·35 (4H, m, ArH), 6·62 (1H, dd, J_{ab} 11 Hz, J_{bc} 9 Hz, H_b), 6·19 (1H, d, J_{bc} 9 Hz, H_c), 5·50 (1H, d, J_{ab} 11 Hz, H_a), and 2·12 (3H, s, COMe).

These results can be rationalised in terms of benzoazahexatriene (II), which undergoes a fast and reversible isomerisation to (III), and a slow and irreversible isomerisation to (IV).

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§ Isomerisation of (IV) to (V) was effected (i) by refluxing in decalin, (ii) by photolysis in acetone, and (iii) by treatment with BF_3–etherate to give a *ca.* 1 : 1 equilibrium mixture of (IV) and (V) (by n.m.r.).

[1] P. T. Izzo and A. S. Kende, *Tetrahedron Letters*, 1966, 5731; J. Kolc and R. S. Becker, *J. Amer. Chem. Soc.*, 1969, **91**, 6513; *J. Chem. Soc.* (*B*), 1972, 17; M. Ikeda, S. Matsugashita, H. Ishibashi, and Y. Tamura, *J.C.S. Chem. Comm.*, 1973, 922.

[2] M. Ikeda, S. Matsugashita, F. Tabusa, H. Ishibashi, and Y. Tamura, *J.C.S. Chem. Comm.*, 1974, 433.

[3] For other benzoazetines, see E. M. Burgess and L. McCullagh, *J. Amer. Chem. Soc.*, 1966, **88**, 1580; M. Fischer and F. Wagner, *Chem. Ber.*, 1969, **102**, 3486.

[4] P. Laszlo and P. R. Schleyer, *Bull. Soc. chim. France*, 1964, 87.