

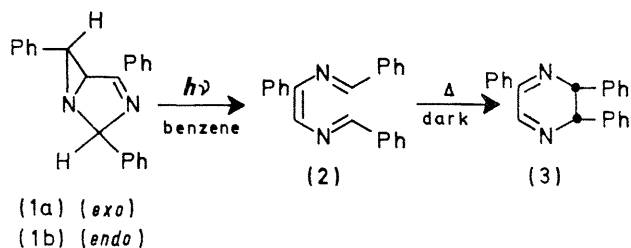
The Effect of Solvent on the Photorearrangement of the 1,3-Diazabicyclo[3,1,0]hex-3-ene System

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Summary The irradiation of *exo*- and/or *endo*-2,4,6-triphenyl-1,3-diazabicyclo[3,1,0]hex-3-ene in methanol to give 2,4-diphenyl-1-methoxybenzylimidazoline proceeds *via* photochemical ring opening to an enedi-imine which undergoes subsequent intramolecular nucleophilic addition at the imine carbon atom; the solvent controls the mode of cyclization.

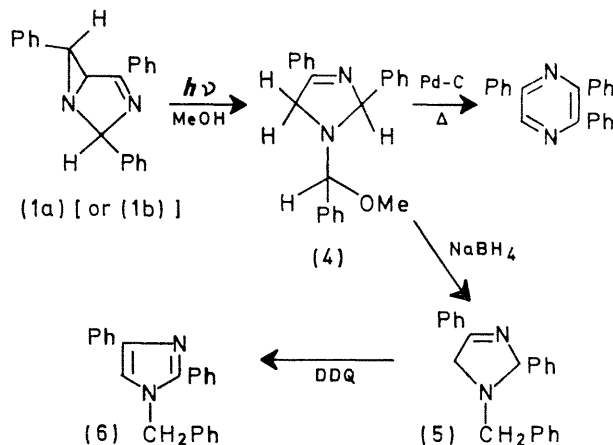
THE photoisomerization of 1,3,5-hexatrienes to bicyclo[3,1,0]hex-2-enes is of considerable interest.¹⁻⁴ Recently, we reported the photochemistry of the related 1,3-diazabicyclo[3,1,0]hex-2-ene system in non-polar solvents.⁵ The proposed mechanism of the photoreaction involved photoisomerization to enedi-imine (2) which thermally cyclized to *cis*-dihydropyrazine (3).^{5,6} We now report a variation of the reaction when the irradiation is carried out in methanol.



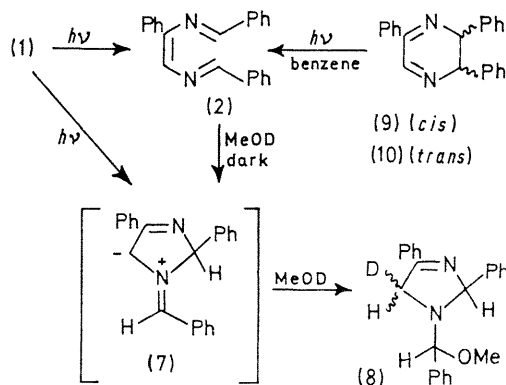
Irradiation of a dilute solution of (1a) or (1b) in methanol gave the imidazoline (4), as the major product (60%). Almost no dihydropyrazine (3) was formed. The structure of (4) was determined from its u.v., i.r., n.m.r., and mass spectra; ν_{\max} (neat) 3.45, 6.15, 6.70, 7.80, 8.55, 9.72, and 10.45 μm ; λ_{\max} (95% ethanol) 245 (ϵ 10,500) and 280 nm (1300); τ (CDCl_3) 6.70 (3H, s), 6.15 (1H, dd, J 14.0 Hz), 5.62 (1H, dd, J 14.0, 5.0 Hz), 5.07 (1H, s), 3.80 (1H, J 5.0 Hz), and 2.60 (15H, m). Chemical confirmation was obtained by the oxidation of (4) with palladium-charcoal to 2,3,5-triphenylpyrazine,⁵ and by reduction with sodium borohydride to the imidazoline (5),[†] m.p. 89–90°, followed by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to the imidazole (6), m.p. 122–124°.

The photoconversion of (1) into (4) may be formulated as proceeding *via* enedi-imine (2) which undergoes ground-state ring closure by intramolecular nucleophilic addition at the imine carbon atom to give (7) and thence (4) by addition of methanol. The cyclization of (2) to (7) as a non-photochemical reaction is known.^{7,8} Alternatively, the reaction could proceed *via* the azomethine ylide (7) by cleavage of the aziridine C–C bond⁶ prior to the formation of (2). Support for this intermediate is provided by the deuterium incorporation observed in the course of the

photolysis. Irradiation of (1) in methan[²H]ol gave (8). The extent of deuterium incorporation was determined by mass spectrometry, and the position of deuteration was determined by n.m.r. The incorporation of deuterium in the 5-position of the product is expected for an intermediate corresponding to (7).



Further support was obtained by generation of (2) by irradiating (9) or (10) in benzene. Removal of the solvent followed by addition of methanol (in the dark) gave the imidazoline (4).



The foregoing data demonstrate that the direction of cyclization of the enedi-imine (2) is dependent on the solvent. In non-polar solvents such as benzene, electrocyclization is preferred. A different mode of cyclization

[†] Satisfactory analyses were obtained for all new compounds; complete spectroscopic and degradative details will be given in our full publication.

occurs when polar solvents such as methanol are used. This undoubtedly is related to the ability of methanol to solvate the developing charge centres.

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