Photochemical Rearrangement in the 1,5-Diazabicyclo[5,1,0]octa-3,5-diene System

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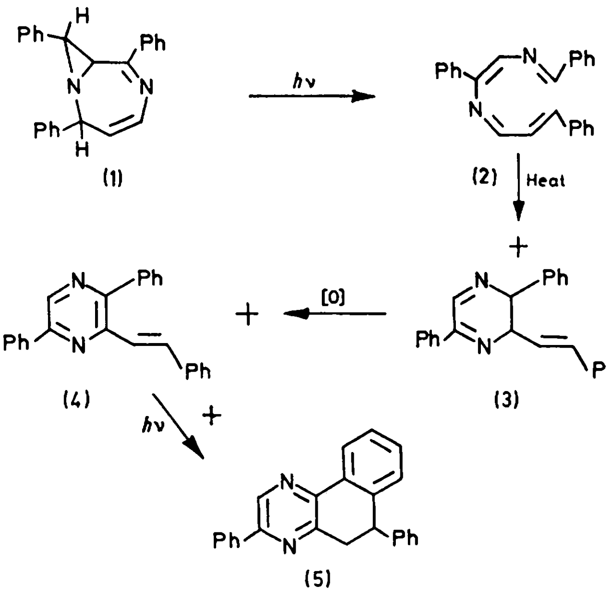
Summary Irradiation of 2,6,8-triphenyl-1,5-diazabicyclo-[5,1,0]octa-3,5-diene affords 3,6-diphenyl-5,6-dihydrobenzo[*f*]quinoxaline, the formation of which can be rationalized by a sequence of four discrete steps.

The mechanism of the photoinduced rearrangement of 1,3-diazabicyclo[3,1,0]hex-3-enes to *cis*-dihydropyrazines has been investigated recently.[1-3] The finding that an azomethine ylide is a key intermediate in the reaction implies that the photochemistry of the system is initiated by cleavage of the C–C bond of the aziridine ring. We here report on the synthesis and photochemistry of the related 1,5-diazabicyclo[5,1,0]octa-3,5-diene system.

The diazabicyclo-octadiene (**1**), m.p. 157—158°, was prepared by treating *trans*-3-benzoyl-2-phenylaziridine with cinnamaldehyde in an ethanolic solution saturated with ammonia and containing small quantities of ammonium bromide.† Spectral data and elemental analysis‡ were in complete agreement with the structure: λ_{max} (95% EtOH) 255 nm (ϵ 33,700); τ(CDCl$_3$) 7·38 br (1H, s), 6·40 br (1H, s), 3·80 (1H, d, *J* 4 Hz), 3·55 (1H, dd, *J* 16 and 4 Hz), 3·24 (1H, d, *J* 16 Hz), and 2·10—2·90 (15H, m).

Irradiation of a solution of (**1**) in benzene at 50° led to complete disappearance of starting material and formation of a complex mixture of photoproducts. Four products (**2**)—(**5**) were isolated whose relative yields depended upon the period of irradiation. As the amount of (**2**) decreased, (**3**) and (**4**) and, more slowly, (**5**) were formed.



U.v. irradiation of a solution of (**1**) in benzene for 1·5 h afforded intermediate (**2**) (80%), m.p. 115—117°, whose structure was assigned on the basis of the following data: (KBr) 6·12 μm; λ_{max} (95% EtOH) 295 and 360 nm (ϵ 53,800 and 26,400); τ (CDCl$_3$) 2·08—3·05 (m). At 50°, thermal rearrangement of (**2**) gave (**3**) and (**4**), but not (**5**). That compounds (**3**) and (**4**) are secondary products derived by thermal isomerization of (**2**) was confirmed by the finding that the photolysis of (**1**) in benzene at 20° gave virtually no (**3**), (**4**), or (**5**). On warming the solution to 50° in the

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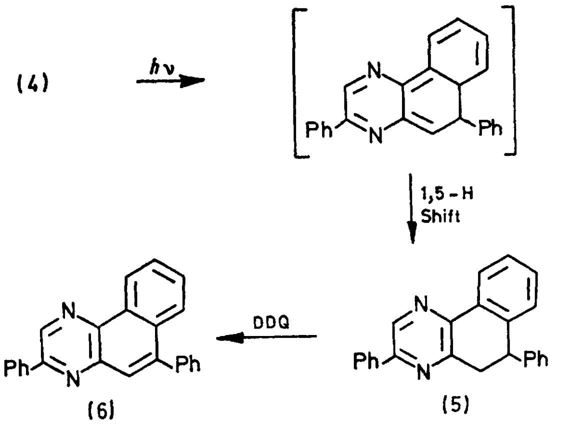
† Only one out of two possible isomers was isolated from this reaction. The stereochemistry of (**1**) is tentatively assigned as *exo, exo* by comparison of its n.m.r. spectrum with that of the *exo,exo* and *exo,endo* isomers from the 1,3-diazabicyclo[3,1,0]hex-2-ene system.

‡ Satisfactory analyses were obtained for all new compounds; complete spectroscopic and degradative details will be given later.

dark, compounds (**3**) and (**4**) were formed but not (**5**). These observations indicate that a photochemically generated precursor of (**3**) and (**4**) persists after the light source is extinguished which then rearranges upon heating to (**3**) and (**4**). Structures (**3**) (m.p. 202—205°) and (**4**) (m.p. 150—151°) were assigned on the basis of the following evidence. Oxidation of (**3**) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) afforded (**4**) in excellent yield. Structure (**4**) was confirmed by unequivocal synthesis[4] from 3-methyl-2,5-diphenylpyrazine,[5] acetic anhydride, and benzaldehyde.



Irradiation of (**4**) in benzene for 2 h afforded the benzo[*f*]-quinoxaline (**5**), m.p. 148—149° (60%), whose structure was assigned on the basis of elemental analysis and spectral data: λ_{max} (95% EtOH), 344, 300, and 287 nm (ϵ 27,100, 13,900, and 13,900); τ ($CDCl_3$) 6·51 (2H, d, *J* 7·5 Hz), 5·62 (1H, t, *J* 7·5 Hz), and 1·87—3·00 (15H, m), and 1·14 (1H, s). Oxidation of (**5**) with DDQ afforded the quinoxaline (**6**), m.p. 190—191°, λ_{max} (95% EtOH): 293, 253, and 221 nm (ϵ 36,500, 30,700, and 35,000).

Isolation of (**5**) from the photolysis of (**1**) can be resolved into a sequence of four discrete reactions. The first step is the light induced 6+2 cycloreversion of (**1**) to 2,5-diazaoctatetraene (**2**). If concerted, this step can be viewed as either a $\pi_s^6 + \pi_s^2$ or a $\pi_a^6 + \pi_a^2$ process.[6] Alternatively, as was noted in the 1,3-diazabicyclic system,[2,3] the opening may proceed in a stepwise manner *via* an azomethine ylide which subsequently opens to diazaoctatetraene (**2**). The second step involves a thermal electrocyclization of (**2**) to (**3**). Under the reaction conditions, (**3**) is partially oxidized to pyrazine (**4**). The final step is analogous to the photochemical isomerization of 1,3,5-hexatrienes to the corresponding cyclohexa-1,3-dienes.[7]

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[5] 2,5-diphenyl-3-methylpyrazine was prepared by treating 2,5-diphenylpyrazine with methyl-lithium according to the procedure of B. Klein and P. E. Spoerri, *J. Amer. Chem. Soc.*, 1950, **72**, 1844.

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