Photocyclisation of γ,δ- and δ,ε-Unsaturated Amines. Hydrogen Transfer Reactions *via* Eight-membered Cyclic Transition States

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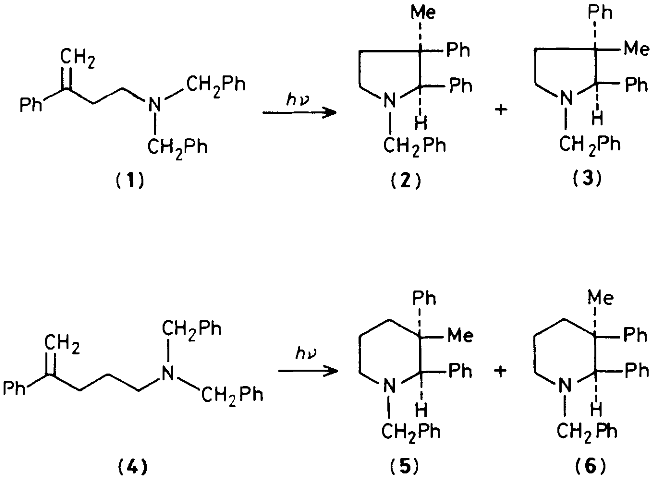
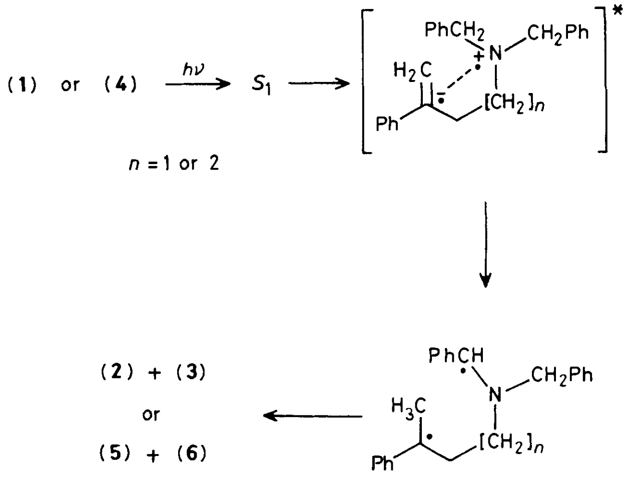
Photolysis 4-(*N,N*-dibenzylamino)-2-phenylbut-1-ene and 5-(*N,N*-dibenzylamino)-2-phenylpent-1-ene gave cyclisation products *via* 1,6- and 1,7-hydrogen shifts respectively.

Photocyclisation *via* intramolecular hydrogen transfer is one of the most important reactions in the photochemistry of carbonyl compounds (type II cyclisation)[1] and thiocarbonyl compounds.[2] Although photochemical hydrogen abstraction of alkenes is less common, some cyclic alkenes are known to undergo such reactions from the π,π^* triplet states.[3] In the case of acyclic alkenes, such a reaction is inefficient because of the presence of competitive processes such as *E–Z* isomerisation.[4] It is well-known that intramolecular hydrogen transfer through a seven-membered cyclic transition state (1,6-hydrogen shift) is less favourable than that through a six-membered one (1,5-hydrogen shift) in the photochemistry of carbonyl compounds,[5] although thiones undergo a 1,6-hydrogen shift selectively.[2] In the case of alkenes, a 1,5-hydrogen shift is common,[3,4] and the 1,6-shift takes place only when γ-hydrogens are absent.[6] A 1,7-hydrogen shift which



Scheme 1



Scheme 2

involves an eight-membered cyclic transition state is extremely rare even in the photochemistry of carbonyl compounds.[7] We now report a rare 1,6-hydrogen shift and an unprecedented 1,7-hydrogen shift in the photoreaction of alkenes.

When 4-(*N*,*N*-dibenzylamino)-2-phenylbut-1-ene (**1**) in hexane was irradiated with a low pressure mercury lamp under argon, pyrrolidines (**2**) and (**3**) were obtained in 22 and 13% yields respectively. Photolysis of (**1**) in MeCN gave a similar result. Irradiation of 5-(*N*,*N*-dibenzylamino)-2-phenylpent-1-ene (**4**) in hexane afforded piperidines (**5**) and (**6**) in 13 and 7% yields respectively. The structures of these products were determined by elemental analyses and spectral data.[†] The stereochemistry of these products was tentatively assigned as shown in Scheme 1 on the basis of the n.m.r. spectra.[‡]

The formation of the products is reasonably explained in terms of a 1,6-hydrogen transfer [in the case of (**1**)] or a 1,7-hydrogen transfer [in the case of (**4**)] and subsequent cyclisation of the resulting diradicals (Scheme 2). The photoreactions of (**1**) and (**4**) were found to be singlet reactions because they were neither sensitizable nor quenchable. Salisbury and coworkers reported that fluorescence quenching of styrenes in cyclohexane with tertiary amines led to the formation of fluorescent charge-transfer exciplexes ($\lambda_{max.}$ 376—410 nm), and that electron–proton transfer took place from the exciplexes to give adducts of the amines to the styrenes.[8] The δ,ε-unsaturated amine (**4**) showed exciplex emission ($\lambda_{max.}$ 382 nm) on excitation, whereas the γ,δ-unsaturated amine (**1**) was non-emissive in contrast to the fact that styrenes exhibit fluorescence ($\lambda_{max.}$ *ca.* 310 nm). These facts suggest that the 1,6- and 1,7-hydrogen shifts involve electron–proton transfer from intramolecular charge-transfer exciplexes.[9] The exciplex from (**1**) may be too short-lived to be emissive. Remote hydrogen transfer *via* charge (or electron) transfer has been reported in the photochemistry of carbonyl compounds.[10,11] The present reactions provide the first examples of such hydrogen transfer in the photoreactions of alkenes.

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[†] *Selected spectroscopic data:* (**5**): ^{1}H n.m.r. ($CDCl_3$) δ 1.47 (s, 3H, Me), 1.5—2.4 and 3.1 (both m, 5H and 1H respectively, CH_2), 2.75 and 3.87 (ABq, 2H, J 14 Hz, CH_2Ph), 3.54 (s, 1H, =CH–), and 6.4—7.6 (m, 15H, Ar); ^{13}C n.m.r. ($CDCl_3$) δ 18.2 (q), 22.1 (t), 39.5 (t), 42.9 (s), 53.3 (t), 60.5 (dd), 77.0 (d), 125.8—129.5 (Ph), 139.8 (s, *ipso*), 140.1 (s, *ipso*), and 147.8 (s, *ipso*); m/z 341 (M^+). (**6**): ^{1}H n.m.r. ($CDCl_3$) δ 1.42 (s, 3H, Me), 1.45—2.4 and 3.1 (both m, 5H and 1H respectively, CH_2), 2.84 and 3.63 (ABq, 2H, J 14 Hz, CH_2Ph), 3.50 (s, 1H, =CH–), and 6.8—7.8 (m, 15H, Ar); ^{13}C n.m.r. ($CDCl_3$) δ 21.7 (t), 29.6 (q), 37.3 (t), 41.5 (s), 51.8 (t), 60.5 (dd), 78.2 (d), 125.6—130.2 (Ph), 139.3 (s, *ipso*), 140.3 (s, *ipso*), 146.3 (s, *ipso*); m/z 341 (M^+). The compounds (**2**) and (**3**) also gave satisfactory analytical and spectroscopic (^{1}H and ^{13}C n.m.r., and mass) data.

[‡] The methyl group of (**5**) was presumed to be axial because in the ^{13}C n.m.r. spectrum of (**5**) the methyl signal (δ 18.2) was at higher field that in the spectrum of (**6**) (δ 29.6).

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