Identification of a Reaction Pathway for Photochemical Ring Scrambling of a Heterocycle: Observation of Two Oxa-azabicyclo[2.2.0]hexenone Intermediates

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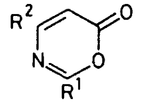
Summary The oxa-azabicyclo[2.2.0]hexenones (**7**) and (**8**) are shown to be intermediates in the reversible photochemical isomerization of (**1**) to (**2**).

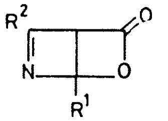
The formation of Dewar-benzene structures during the irradiation of benzene derivatives and six-membered heterocycles is well authenticated.[1] Also, photochemical isomerizations of aromatic compounds and six-membered heterocycles, involving movement of ring atoms ('ring scrambling'), are common[2] and have frequently been postulated as proceeding through Dewar-benzene, benzvalene, or prismane structures; proof of their intermediacy is rare. We present here evidence for the intermediacy of two such species, oxa-azabicyclo[2.2.0]hexenones, in the photo-isomerization of a six-membered heterocycle.

Irradiation† of the oxazinone (**1**)[3] in toluene at room temperature resulted in the establishment of a photochemical equilibrium (*ca.* 2 : 3) between (**1**) and the isomeric oxazinone (**2**). The oxazinone (**2**) was isolated by fractional crystallization and was identical with an authentic sample.‡

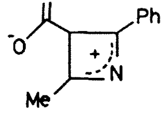
It has been reported[4] that irradiation of the unsubstituted oxazinone (**3**) in an argon matrix at 8 K gives a species tentatively assigned the bicyclic structure (**5**) (ν_{max} 1840 cm^{-1}), whilst Maier has reported[5] that irradiation of the oxazinone (**4**) at −70 °C gives a species assigned the structure (**6**) {ν_{max} 1865 cm^{-1}; τ ([$^2H_8$]tetrahydrofuran; −70 °C) 8·87 (9H, s), 7·74 (3H, d, *J* 0·5 Hz), and 5·26 (1H, q, *J* 0·5 Hz)}. When the oxazinone (**1**) was irradiated† in [$^2H_8$]toluene at −78 °C conversion into an intermediate identified as (**7**) occurred, which had τ ($C_6D_5CD_3$; −78 °C) 8·71 (3H, s), 6·69 (1H, s), 2·96 (3H, m), and 2·57 (2H, m) and ν_{max} 1830 cm^{-1}. Warming to −40 °C caused quantitative conversion into a second intermediate identified as (**8**), τ ($C_6D_5CD_3$; −20 °C) 8·55 (3H, s), 6·21 (1H, s), 2·93 (3H, m), and 2·49 (2H, m), ν_{max} 1830 cm^{-1}. Species (**8**) was stable in solution at 0 °C, but at room temperature quantitatively gave approximately equal amounts of the oxazinones (**1**) and (**2**).



(1) R^1 = Ph, R^2 = Me
(2) R^1 = Me, R^2 = Ph
(3) R^1 = R^2 = H
(4) R^1 = Bu^t, R^2 = Me



(5) R^1 = R^2 = H
(6) R^1 = Bu^t, R^2 = Me
(7) R^1 = Ph, R^2 = Me
(8) R^1 = Me, R^2 = Ph



(9)

In the reverse process, irradiation of (**2**) at −78 °C in [$^2H_8$]toluene resulted in direct conversion into (**8**), no change was observed on warming to 0 °C, but at room temperature approximately equal amounts of (**1**) and (**2**) were again formed.

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† Irradiations were performed on degassed samples through Pyrex using high pressure mercury or xenon lamps.

§ The oxazinone (**2**) was prepared by intramolecular condensation of ethyl 3-acetamidocinnamate in refluxing diphenyl ether.

When either (**1**) or (**2**) was irradiated in [$^2H_2$]methylene chloride at −78 °C only conversion into (**8**) was observed, and in both cases no change occurred on warming to 0 °C At room temperature a mixture of approximately equal amounts of (**1**) and (**2**) was found quantitatively

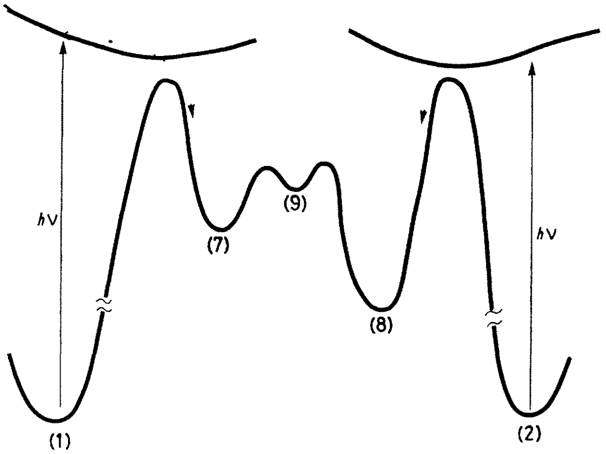

FIGURE Potential energy diagram showing parts of the proposed ground state and excited state surfaces for compounds (**1**) and (**2**) and intermediates (**7**), (**8**), and (**9**)

The u v spectra of (**7**) and (**8**) were also recorded, irradiation† of (**1**) (10^{-4} M) in hexanes at −78 °C resulted in the disappearance of its absorption spectrum and appearance of a weak band (*ε ca* 250) centred around 260 nm This band possessed vibrational structure and was similar in position and intensity to the band in the spectrum of toluene when recorded under identical conditions It is assigned to the isolated phenyl group of (**7**) Warming the solution to −40 °C caused this band to disappear and be replaced by a more intense absorption, with a band at 255 nm (*ε ca* 6000), assigned to the conjugated phenyl group of (**8**) Warming to room temperature gave a spectrum consistent with a mixture of (**1**) and (**2**) Repetition of the experiment with (**2**) in hexanes, or with either (**1**) or (**2**) in methylene chloride, resulted in the observation of only the u v spectrum assigned to (**8**), and this, also, was transformed into a spectrum consistent with a mixture of (**1**) and (**2**) on warming to room temperature

The observations described are summarized in the Figure We suggest that the intermediate (**8**) is thermodynamically more stable than (**7**) and that they interconvert through the zwitterionic species (**9**)[6] In more polar solvents (methylene chloride as opposed to toluene) the activation energy for the transformation (**7**) to (**8**) is sufficiently small that at −78 °C only (**8**) is observed

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