Remote Photocyclization of (Dibenzylamino)ethyl Benzoylacetate. Intramolecular Hydrogen Abstraction through a Ten-membered Cyclic Transition State

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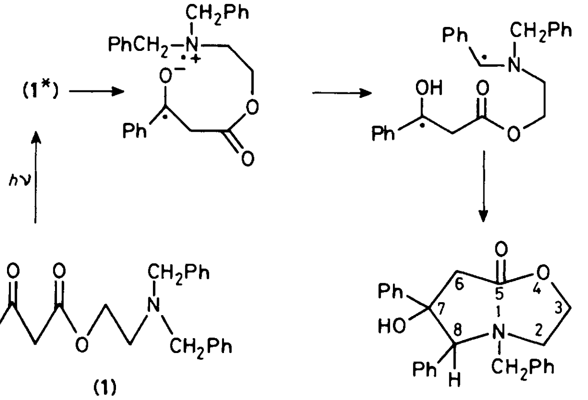
(Dibenzylamino)ethyl benzoylacetate (**1**) undergoes photocyclization *via* intramolecular hydrogen abstraction through a ten-membered cyclic transition state to give eight-membered azalactones (**2**) and (**3**).

Intramolecular hydrogen abstraction by the excited carbonyl group of phenyl ketones is very specific in that γ-hydrogen abstraction involving a six-membered cyclic transition state greatly predominates over other possible modes.[1] The great facility for the γ-hydrogen abstraction is due to the stereoelectronic requirement for the abstraction.[2] Efficient intramolecular abstraction of hydrogen requires that the C–H bond axis should be directed towards the half-vacant n orbital of the carbonyl oxygen atom. Hydrogen abstractions from positions other than γ take place when there are no γ-hydrogens or when the required transition state for the hydrogen abstraction is achieved without severe distortion. The n-alkyl esters of 4-benzoylbenzoic acid undergo photocyclization *via* remote hydrogen abstraction through a cyclic transition state with more than eighteen members.[3,4] In the photochemistry of phenyl ketones, no examples of photocyclization involving remote hydrogen abstraction to give medium-sized cyclic alcohols have been found.[5] We report here the photocyclization of benzoylacetate (**1**) involving remote hydrogen abstraction through a ten-membered cyclic transition state to give eight-membered azalactones (**2**) and (**3**).



(**2**), 7-and 8-Ph *trans*
(**3**), 7-and 8-Ph *cis*

Irradiation of (dibenzylamino)ethyl benzoylacetate (**1**) in benzene with Pyrex-filtered light gave the eight-membered azalactones (**2**) (m.p. 197—198 °C; 31%) and (**3**) (m.p. 154—155 °C; 21%). Their structures were assigned on the basis of their spectral data and elemental analyses. The mass spectra of (**2**) and (**3**) showed the same parent peak at *m/z* 387 and similar fragment peaks. The lactone carbonyl i.r. absorption for (**2**) was at 1690 cm^{-1} whereas that of (**3**) appeared at 1710 cm^{-1}. The rather lower wavenumbers for these compounds than oxacycloalkan-2-ones can be explained in terms of transannular electronic interaction between the carbonyl group and the nitrogen atom. In azacyclo-octan-5-one ring systems there is an attractive transannular interaction between the nitrogen atom and the carbon atom of the carbonyl group, which shifts the carbonyl stretching absorption in the i.r. spectrum to lower wavenumbers than normal for ketones.[6] The i.r. spectra of (**2**) and (**3**) support the cyclic structures of these compounds and indicate that the distance separating the carbonyl group and the nitrogen atom is larger in (**3**) than in (**2**).† The ^{1}H n.m.r. spectra of both (**2**) and (**3**) showed two triplets due to the $-CH_2CH_2-$ group [(**2**): δ 2.92 and 4.40; (**3**): δ 2.68 and 4.14] and a singlet due to 8-H [(**2**): δ 4.40; (**3**): δ 4.48].

Formation of the eight-membered azalactones (**2**) and (**3**) can reasonably be explained in terms of remote photocyclization involving η-hydrogen abstraction by the phenyl carbonyl oxygen. The phenyl carbonyl oxygen of (**1**) may abstract hydrogen from the δ-, ε-, or η-positions. We could not detect any products arising from δ- or ε-hydrogen abstraction.

The photoreaction of (**1**) to yield the azalactones was efficiently quenched by penta-1,3-diene suggesting a triplet state reaction. The charge-transfer process probably precedes the η-hydrogen abstraction, although photoreactions of α-, γ-, or δ-aminoketones which involve charge-transfer processes are not quenched by dienes.[7] The slower rate of the charge transfer in (**1**) than that of diffusion-controlled bimolecular quenching might be explained in terms of conformational flexibility.[1] Charge transfer requires close approach between the donor nitrogen and the excited carbonyl group. The probability of obtaining the required conformation for charge transfer would be much smaller for (**1**) than for the α-, γ-, or δ-aminoketones.

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† Examination of molecular models of (**2**) and (**3**) showed that the distance between the carbonyl group and the nitrogen atom is larger in (**3**) than in (**2**) in the most favourable conformation.

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