

Photocyclization of (ω -Dialkylamino)alkyl β -Oxoesters *via* Remote Hydrogen Transfer

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The (ω -dialkylamino)alkyl β -oxoesters (**1**) undergo photocyclization *via* remote hydrogen transfer to give the medium-sized azalactones (**2**) and/or aminolactones (**3**). Intramolecular electron transfer from nitrogen to the excited carbonyl group of (**1**) occurs prior to the remote hydrogen transfer.

Intramolecular hydrogen abstraction by the excited carbonyl group is a well-known primary photochemical process. It is very specific in that γ -hydrogen abstraction involving a six-membered cyclic transition state greatly predominates over other possible modes, as in the Norrish Type II reaction.¹ The great facility for this γ -hydrogen abstraction is due to the favourable stereoelectronic² or geometric requirements.³ Hydrogen abstractions from other positions, such as δ^4 or ϵ ,⁵ may occur when the carbonyl compound lacks a suitably aligned hydrogen by reason of substitution or geometry, or when a hydrogen on a carbon atom other than γ is activated by hetero atoms.⁶ Remote hydrogen abstraction through large-^{7,8} or medium-sized cyclic transition states^{9,10} has rarely been observed.

Aminoketones also undergo the Type II photoreaction.¹¹ The primary interaction in the aminoketones is the intramolecular charge-transfer (CT) quenching of the excited carbonyl group by the amino group.¹¹ Proton migration may follow the CT-quenching in contrast to the direct hydrogen migration in normal ketones. The CT-interaction may occur even in systems in which the carbonyl and amino groups are linked by a long flexible chain.¹² We report here photocyclization of (ω -dialkylamino)alkyl β -oxoesters (**1**) *via* remote proton transfer in CT-intermediates, produced by intramolecular CT-interaction between the excited ketone carbonyl group and the amine nitrogen.¹³

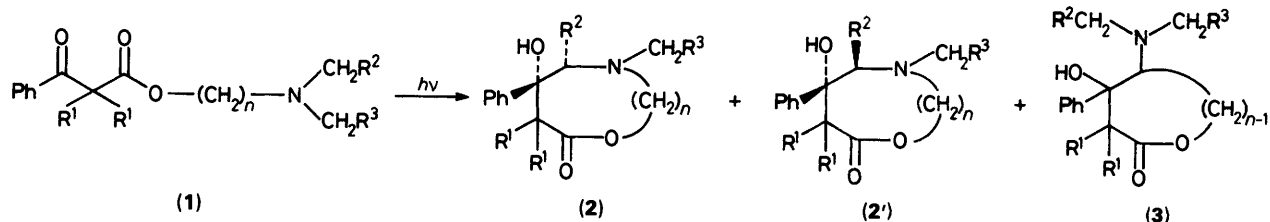
Results and Discussion

Preparative Study.—The β -oxoesters (**1a**) and (**1d-f**) were prepared from ethyl benzoylacetate and the corresponding

amino alcohols. For the preparation of (**1b**), cetyl benzoylacetate was used instead of the ethyl ester in order to facilitate the separation of the product by silica gel column chromatography. The α,α -dimethyl ester (**1c**) was prepared by methylation of (**1b**).

Irradiation of (2-dimethylamino)ethyl benzoylacetate (**1a**) in benzene under nitrogen with a 450 W high-pressure mercury lamp through a Pyrex filter gave the eight-membered azalactone (**2a**) in 33% yield. The structure of (**2a**) was elucidated by spectral data and elemental analysis. The IR spectrum showed characteristic absorptions of the carbonyl and the hydroxy groups at 1715 and 3500 cm^{-1} , respectively, while the ¹³C NMR showed four triplets at δ 44.3, 58.0, 65.7, and 66.6 attributable to the methylene groups. Compound (**2a**) showed a rather complicated ¹H NMR spectrum; four double doublets appeared and were attributable to the ethano group (δ 2.76 and 2.92 for NCH₂ and 4.26 and 4.42 for OCH₂), indicating the presence of two sets of non-equivalent methylene hydrogens and supporting the cyclic structure (**2a**). Formation of the eight-membered azalactone (**2a**) can be reasonably explained in terms of photocyclization *via* remote η -hydrogen transfer to the ketone carbonyl oxygen.

Irradiation of the (dibenzylamino)ethyl ester (**1b**) under the same conditions gave the azalactone isomers (**2b**) and (**2b'**) in 31 and 21% yields, respectively. The structures of (**2b**) and (**2b'**) were assigned from their analytical and spectral data. The mass spectra of (**2b**) and (**2b'**) showed the same parent peaks at m/z 387 and the same fragmentation patterns, and their IR spectra showed characteristic hydroxy and lactone carbonyl absorptions. Eight- and nine-membered cyclic aminoketones, 1-azacyclo-octan-5-ones and -6-ones, show a transannular elec-



	<i>n</i>	R ¹	R ²	R ³
a	2	H	H	H
b	2	H	Ph	Ph
c	2	Me	Ph	Ph
d	2	H	H	Ph
e	3	H	H	H
f	4	H	Ph	Ph

	<i>n</i>	R ¹	R ²	R ³
a	2	H	H	H
b	2	H	Ph	Ph
c	2	Me	Ph	Ph
d(m)	2	H	H	Ph
d(b)	2	H	Ph	H
e	3	H	H	H
f	4	H	Ph	Ph

Table. Product yield in photoreaction of (1).

Compound	Yield (%)		
	(2)	(2')	(3)
a	33		0
b	31	21	0
c	41	22	0
d(m)	7		0
d(b)	32	2	0
e	34		7
f	19	6	6

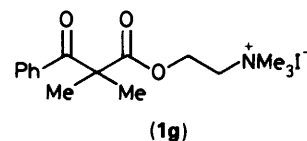
tronic interaction between the carbonyl group and amine nitrogen, and show the C=O stretching absorptions at rather lower wave-numbers than normal ketones.¹⁴ The azalactones (2b) and (2b') also showed this transannular interaction, and the carbonyl absorption was observed at 1 690 and 1 710 cm⁻¹, respectively. These results suggest that the transannular effect is stronger in (2b) than in (2b') and, therefore, the distance separating the carbonyl group and nitrogen is shorter in (2b) than in (2b'). Analysis using Dreiding molecular models indicates that the nitrogen atom can locate close to the carbonyl group in the azalactone (2b), in which the C₇- and C₈-phenyl groups are *trans* to each other. However, in the isomer (2b'), having *cis* phenyl groups, the distance between the carbonyl group and the nitrogen is somewhat longer in the favoured conformation because of steric repulsion between the phenyl groups. Irradiation of (1c) also gave the azalactone isomers (2c) and (2c') in 41 and 22% yields, respectively.

The β-oxoester (1d) has methyl and benzyl hydrogens η to the ketone carbonyl group and was expected to give two different types of azalactones. Indeed, irradiation of (1d) gave two types of azalactones, [2d(m)] and the [(2d(b),d(b)')] pair. The azalactone [2d(m)] arises from methyl hydrogen transfer and [2d(b)] and [2b(b)'] from benzyl hydrogen transfer. The hydrogen transfer in these systems seems to be governed by the strength of the C-H bond involved. In none of the photoreactions of the aminoethyl esters (1a-d) could the ε-hydrogen transfer products, aminolactones (3), be obtained. This is probably due to the eight-membered cyclic transition state for such a hydrogen migration being stereochemically unfavourable.

In contrast to the aminoethyl esters, the aminopropyl and aminobutyl esters underwent competitive photocyclization to give the azalactones (2) and the aminolactones (3). Irradiation of (1e) gave (2e), the θ-hydrogen transfer product, and (3e), the ζ-hydrogen transfer product, in 34 and 7% yield, respectively. Irradiation of (1f) also gave the azalactone isomers (2f) and (2f'), the ι-hydrogen transfer products, and the aminolactone (3f), the η-hydrogen transfer product, in 19, 6, and 6% yield, respectively. The intramolecular hydrogen transfer in the photoreaction of (1) takes place *via* a 9- to 12-membered cyclic transition state, and seems to occur *via* even larger cyclic transition states.*

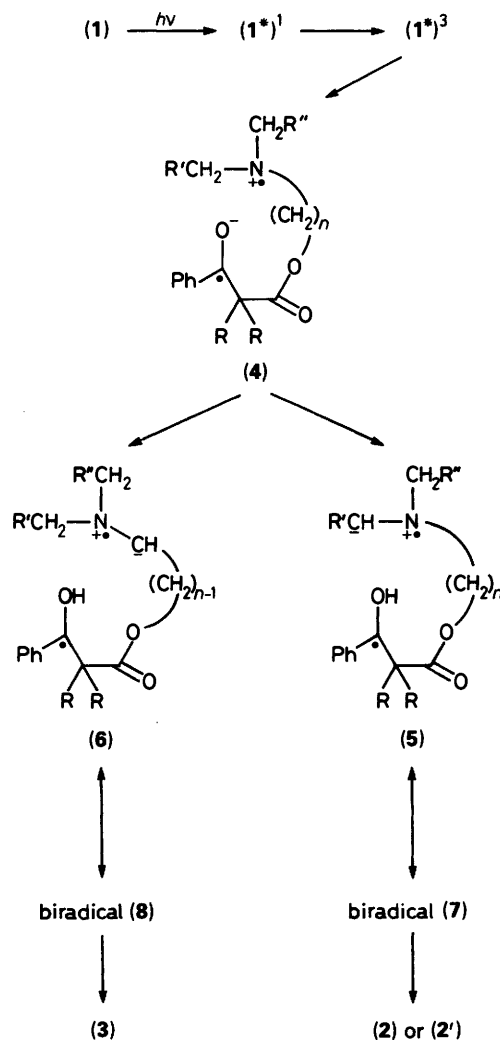
Mechanistic Study.—The quantum yields for formation of the azalactone (2b,b') at 313 nm were determined to be 0.04 and 0.03, respectively, and those for (2c,c') were 0.27 and 0.18, respectively. The β-oxoester (1b) shows keto-enol tautomer-

* Intramolecular hydrogen migration in the CT-intermediates occurs from even more remote positions than 1. We attempted the photocyclization of (10-dibenzylamino)decyl benzoylacetate and obtained the corresponding azalactone and aminolactone in 27 and 21% yields, respectively. However, complete purification of these compounds could not be achieved.



ism; photocyclization occurs only from the more reactive keto form. The lower quantum yields for (2b,b') can be explained in terms of an internal filter effect by the enol form of (1b). Surprisingly, the quantum yields for formation of the η-hydrogen transfer products (2c,c') are comparable to that for acetophenone formation from valerophenone *via* γ-hydrogen abstraction (φ = 0.33).¹⁵

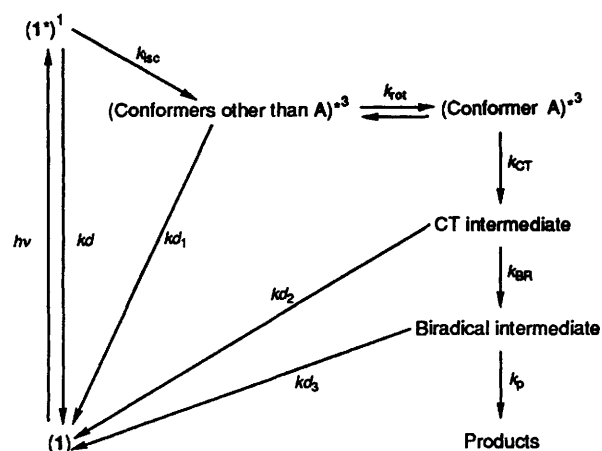
The photoreactions of (1b) and (1c) were effectively quenched with 2,5-dimethylhexa-2,4-diene, indicating that the reactions take place from their n,π* triplet states. These reactions also proceeded in methanol, but were prevented by the addition of



hydrochloric acid. These results suggest the intervention of the CT intermediate (4) (Scheme 1); further support for this is that neither the ammonium salt (1g) nor butyl benzoylacetate showed photoreactivity.

The Type II photoreaction of aminoketones generally occurs *via* the CT intermediate.^{11,16,17} The CT interaction is now fully recognized as one of the most common causes of the excited state quenching process.¹² The rate of the intramolecular CT-

quenching is faster than that of diffusion-controlled bimolecular quenching in aminoketones where the carbonyl and the amino groups are linked by a short flexible chain.^{16,17} The efficient internal quenching is a consequence of the overlap of the half-vacant carbonyl n orbital and the nitrogen sp^3 orbital.^{18,19} The rate of the CT process itself, that is the elementary process of internal electron transfer, must be faster than that of diffusion-controlled bimolecular quenching even in the aminoketones (1); nevertheless, the photoreactions of (1b) and (1c) were effectively quenched with diene. This might be explained in terms of very low population of the conformer which is appropriate for electron transfer from the amine nitrogen to the excited carbonyl group because of conformational flexibility of the long chain. The donor and acceptor orbitals must overlap each other for the CT quenching, and therefore the entropic and conformational demands of the connecting chain become more important.¹⁸ A simplified scheme for the photoreaction of (1) can be written as in Scheme 2. The term k_{rot} refers to the



Scheme 2.

average rate constant for conformational change from conformers unfavourable for the CT interaction to the favourable conformer (conformer A in Scheme 2). The Stern-Volmer equation involving the conformational change can be written as follows:

$$\frac{\phi_0}{\phi} = 1 + kq \frac{1}{kd_1 + k_{rot}} [Q]$$

$$= 1 + kqr [Q]$$

The slope of the Stern-Volmer plots was found to be 32 for the photoreaction of (1c). The life-time τ is calculated to be 6.4×10^{-9} s, assuming the diffusion-controlled rate for kq (5×10^9 s⁻¹). The value is comparable to that of valerophenone (7.2×10^{-9} s)¹⁵ and is 60 times greater than that of γ -dimethylaminobutyrophenone (0.12×10^{-9} s).¹⁷ These results suggest that the conformational flexibility is an important factor in the intramolecular CT quenching process of the long chain aminoketones (1).

Experimental

All m.p.s are uncorrected. IR spectra were recorded with a JASCO A-3 spectrometer, ¹H and ¹³C NMR spectra were measured with a JEOL FX90Q or a Bruker AM400 spectrometer using tetramethylsilane as an internal standard, and mass spectra were recorded with a JEOL JMS-01SG-2 spectrometer.

Preparation of ω -(Alkylamino)alkyl β -Oxoesters (1).—Ethyl benzoylacetate (0.02 mmol) and an excess of the corresponding aminoalcohol (0.04 mmol) in benzene were refluxed for a few days. After removal of the solvent, the residue was chromatographed on a silica gel column (Merck Kieselgel 60), eluting with benzene-hexane or benzene-ethyl acetate, to give (1). For the preparation of (1b), cetyl benzoylacetate was used instead of ethyl benzoylacetate. The β -oxoester (1c) was prepared by methylation of (1b) according to the literature method.²⁰ The β -oxoesters (1a) and (1d-f) could not be purified by vacuum distillation because of partial decomposition on heating. The ammonium salt (1g) was prepared by heating (1b) overnight with methyl iodide in a sealed tube at 100 °C. After the removal of methyl iodide, the residual solid was recrystallized from acetone-benzene.

2-(Dimethylamino)ethyl benzoylacetate (1a); a syrup, 80% yield (Found: C, 66.0; H, 7.7; N, 5.6. $C_{13}H_{17}NO_3$ requires C, 66.4; H, 7.3; N, 6.0%); ν_{max} (neat) 1690 and 1740 cm^{-1} ; δ_H (CDCl₃) 2.26 (6 H, s, 2 \times Me), 2.57 (2 H, t, J 5.8 Hz, NCH₂), 4.03 (1.6 H, s, COCH₂CO), 4.27 (2 H, t, J 5.8 Hz, OCH₂), 5.86 (0.2 H, s, C=CH), 7.3-7.6 (3 H, m, ArH), 7.9-8.1 (2 H, m, ArH), and 16.3 (0.2 H, br s, OH).

2-(Dibenzylamino)ethyl benzoylacetate (1b); white crystals, m.p. 36.8-38.8 °C (from hexane), 44% yield (Found: C, 77.4; H, 6.5; N, 3.6. $C_{25}H_{25}NO_3$ requires C, 77.5; H, 6.5; N, 3.6%); ν_{max} (KBr) 1690 and 1740 cm^{-1} ; δ_H (CDCl₃) 2.74 (1.4 H, t, J 6.1 Hz, NCH₂), 2.81 (0.6 H, t, J 5.9 Hz, NCH₂), 3.63 (2.8 H, s, CH₂), 3.70 (1.2 H, s, CH₂), 3.98 (1.4 H, s, COCH₂CO), 4.26 (1.4 H, t, J 6.1 Hz, OCH₂), 4.31 (0.6 H, t, J 5.9 Hz, OCH₂), 5.66 (0.3 H, s, C=CH), 7.2-7.7 (13 H, m, ArH), 7.7-8.1 (2 H, m, ArH), and 15.4 (0.3 H, br s, OH).

2-(Dibenzylamino)ethyl 2-benzoyl-2-methylpropionate (1c); white crystals, m.p. 58-59 °C (from hexane), 83% yield (Found: C, 77.9; H, 7.0; N, 3.4. $C_{27}H_{29}NO_3$ requires C, 78.0; H, 7.0; N, 3.4%); ν_{max} (KBr) 1675 and 1730 cm^{-1} ; δ_H (CDCl₃) 1.54 (6 H, s, 2 \times Me), 2.56 (2 H, t, J 6.4 Hz, NCH₂), 3.49 (4 H, s, CH₂Ph), 4.13 (2 H, t, J 6.4 Hz, OCH₂), 7.1-7.4 (13 H, m, ArH), and 7.7-7.9 (2 H, m, ArH).

2-(Benzylmethylamino)ethyl benzoylacetate (1d); a syrup, 77% yield (Found: C, 73.5; H, 6.8; N, 4.4. $C_{19}H_{21}NO_3$ requires C, 73.3; H, 6.8; N, 4.5%); ν_{max} (neat) 1690 and 1740 cm^{-1} ; δ_H (CDCl₃) 2.20 (2.5 H, s, NMe), 2.21 (0.5 H, s, NMe), 2.65 (1.7 H, t, J 5.8 Hz, NCH₂), 2.71 (0.3 H, t, J 5.7 Hz, NCH₂), 3.50 (1.7 H, s, CH₂Ph), 3.58 (0.3 H, s, NCH₂Ph), 3.98 (1.7 H, s, CH₂), 4.27 (1.7 H, t, J 5.8 Hz, OCH₂), 4.33 (0.3 H, t, J 5.7 Hz, OCH₂), 5.68 (0.2 H, s, C=CH), 7.2-7.6 (8 H, m, ArH), and 7.8-8.0 (2 H, m, ArH).

3-(Dimethylamino)propyl benzoylacetate (1e); a syrup, 35% yield (Found: C, 67.5; H, 7.4; N, 5.3. $C_{14}H_{19}NO_3$ requires C, 67.4; H, 7.7; N, 5.6%); ν_{max} 1690 and 1740 cm^{-1} ; δ_H (CDCl₃) 1.80 (2 H, tt, J 5.1 and 6.4 Hz, CH₂), 2.23 (6 H, s, 2 \times Me), 2.27 (2 H, t, J 5.1 Hz, NCH₂), 4.01 (1.8 H, s, COCH₂CO), 4.23 (2 H, t, J 6.4 Hz, OCH₂), 5.69 (0.1 H, br s, C=CH), 7.3-7.7 (3 H, m, ArH), 7.8-8.1 (2 H, m, ArH), and 16.2 (0.1 H, br s, OH).

4-(Dibenzylamino)butyl benzoylacetate (1f); a syrup, 64% yield (Found: C, 77.9; H, 7.0; N, 3.4. $C_{27}H_{29}NO_3$ requires C, 78.0; H, 7.0; N, 3.4%); ν_{max} 1690 and 1740 cm^{-1} ; δ_H 1.3-1.7 (4 H, m, 2 \times CH₂), 2.2-2.5 (2 H, m, NCH₂), 3.39 (2.4 H, s, NCH₂Ph), 3.43 (1.6 H, s, NCH₂Ph), 3.70 (1.2 H, s, COCH₂CO), 3.89 (2 H, t, J 6.7 Hz, OCH₂), 5.47 (0.4 H, s, C=CH), 6.9-7.4 (13 H, m, ArH), and 7.5-7.8 (2 H, m, ArH).

2-(Trimethylammonio)ethyl 2-benzoyl-2-methylpropionate iodide (1g); a white solid, 28% yield (Found: C, 47.4; H, 6.0; N, 3.5. $C_{16}H_{24}INO_3$ requires C, 47.4; H, 6.0; N, 3.5%); ν_{max} (KBr) 1685 and 1730 cm^{-1} ; δ_H (CD₃OD) 1.57 (6 H, s, 2 \times Me), 2.98 (9 H, s, 3 \times NMe), 3.32 (2 H, m, NCH₂), 4.53 (2 H, m, OCH₂), 7.5-7.7 (3 H, m, ArH), and 7.8-8.0 (2 H, m, ArH).

General Procedure for Preparative Irradiation.—The β -oxo-ester (1) (ca. 1 mmol) in benzene was irradiated for ca. 20 h under nitrogen with light from a 450 W high-pressure mercury lamp through a Pyrex filter. After removal of the solvent, the residue was chromatographed on silica gel, eluting with benzene–ethyl acetate, to give the azalactone (2) and/or the aminolactone (3).

7-Hydroxy-1-methyl-7-phenyl-1-aza-4-oxacyclo-octan-5-one (2a); a syrup, 33% yield (Found: C, 66.4; H, 7.4; N, 5.7. $C_{13}H_{17}NO_3$ requires C, 66.4; H, 7.3; N, 6.0%); ν_{max} (neat) 1 715 and 3 500 cm^{-1} ; δ_H ($CDCl_3$) 2.55 (3 H, s, Me), 2.62 (1 H, dd, J 12.0 and 1.7 Hz, $COCH_2$), 2.69 (1 H, dd, J 14.1 and 1.7 Hz, 8-H), 2.76 (1 H, ddd, J 13.3, 3.2, and 2.5 Hz, 2-H), 2.92 (1 H, ddd, J 13.3, 10.1, and 4.9 Hz, 2-H), 2.98 (1 H, d, J 12.0 Hz, $COCH_2$), 2.99 (1 H, d, J 14.1 Hz, 8-H), 3.76 (1 H, s, OH), 4.26 (1 H, ddd, J 12.9, 10.1, and 3.2 Hz, OCH_2), 4.42 (1 H, ddd, J 12.9, 4.9, and 2.5 Hz, OCH_2), and 7.1–7.5 (5 H, m, ArH); δ_C ($CDCl_3$) 44.3 (t), 47.1 (q), 58.0 (t), 65.7 (t), 66.6 (t), 77.4 (s), 124.4 (d, 2C), 127.4 (d), 128.3 (d, 2C), 143.7 (s), and 172.9 (s).

1-Benzyl-7-hydroxy-r-7,t-8-diphenyl-1-aza-4-oxacyclo-octan-5-one (2b); white crystals, m.p. 197–198 °C (from benzene), 31% yield (Found: C, 77.4; H, 6.5; N, 3.6. $C_{25}H_{25}NO_3$ requires C, 77.5; H, 6.5; N, 3.6%); ν_{max} (KBr) 1 690 and 3 550 cm^{-1} ; δ_H ($CDCl_3$) 2.63 (1 H, d, J 13.1 Hz, $COCH_2$), 2.92 (2 H, t, J 9.7 Hz, NCH_2), 3.01 (1 H, d, J 13.1 Hz, $COCH_2$), 3.29 (1 H, d, J 14.3 Hz, NCH_2Ph), 3.94 (1 H, d, J 14.3 Hz, NCH_2Ph), 4.22 (1 H, s, OH), 4.38 (2 H, t, J 9.7 Hz, OCH_2), 4.38 (1 H, s, $NCHPh$), and 6.9–7.5 (15 H, m, ArH); δ_C ($CDCl_3$) 48.4 (t), 52.6 (t), 57.1 (t), 67.9 (t), 71.8 (d), 96.3 (s), 124.9 (d, 2C), 126.7 (d), 127.1 (d), 127.3 (d), 127.9 (d, 2C), 128.0 (d, 2C), 128.3 (d, 2C), 129.1 (d, 2C), 130.6 (d, 2C), 137.0 (s), 138.3 (s), 144.0 (s), and 173.4 (s); m/z 387 (M^+).

1-Benzyl-7-hydroxy-r-7,c-8-diphenyl-1-aza-4-oxacyclo-octan-5-one (2b'); white crystals, m.p. 154–155 °C (from benzene–hexane), 21% yield (Found: C, 77.5; H, 6.5; N, 3.6. $C_{25}H_{25}NO_3$ requires C, 77.5; H, 6.5; N, 3.6%); ν_{max} (KBr) 1 710 and 3 500 cm^{-1} ; δ_H ($CDCl_3$) 2.68 (2 H, t, J 5.1 Hz, NCH_2), 2.88 (1 H, d, J 12.8 Hz, NCH_2Ph), 3.75 (1 H, d, J 12.8 Hz, NCH_2Ph), 4.03 (1 H, s, OH), 4.15 (2 H, t, J 5.1 Hz, OCH_2), 4.26 (2 H, s, $COCH_2$), 4.48 (1 H, s, $NCHPh$), and 6.8–7.4 (15 H, m, ArH); δ_C ($CDCl_3$) 41.6 (t), 50.2 (t), 63.3 (t), 69.0 (t), 77.6 (d), 82.2 (s), 125.7 (d, 2C), 127.2 (d), 127.3 (d, 2C), 127.8 (d, 2C), 128.0 (d, 2C), 128.4 (d, 2C), 128.6 (d, 2C), 130.7 (d, 2C), 135.3 (s), 138.9 (s), 143.3 (s), and 174.8 (s); m/z 387 (M^+).

1-Benzyl-7-hydroxy-6,6-dimethyl-r-7,t-8-diphenyl-1-aza-4-oxacyclo-octan-5-one (2c); white crystals, m.p. 134–135 °C (from benzene–hexane), 38% yield (Found: C, 78.1; H, 7.1; N, 3.4. $C_{27}H_{29}NO_3$ requires C, 78.0; H, 7.0; N, 3.4%); ν_{max} (KBr) 1 705 and 3 530 cm^{-1} ; δ_H ($CDCl_3$) 1.15 (3 H, s, Me), 1.22 (3 H, s, Me), 2.68 (1 H, dd, J 13.6 and 4.1 Hz, NCH_2), 2.99 (1 H, d, J 13.5 Hz, NCH_2Ph), 3.22 (1 H, dd, J 13.6, 10.8, and 4.1 Hz, NCH_2), 3.83 (1 H, dd, J 10.5 and 4.1 Hz, OCH_2), 3.96 (1 H, d, J 13.5 Hz, NCH_2Ph), 4.04 (1 H, s, OH), 4.78 (1 H, ddd, J 10.5, 10.8, and 4.1 Hz, OCH_2), 4.94 (1 H, s, $NCHPh$), and 6.7–7.9 (15 H, m, ArH); δ_C ($CDCl_3$) 20.3 (q), 22.6 (q), 50.6 (s), 56.0 (t), 56.7 (t), 69.3 (t), 72.5 (d), 89.2 (s), 125.3 (d), 126.2 (d), 126.5 (d), 127.1 (d, 2C), 127.5 (d, 4C), 128.2 (d, 4C), 128.5 (d, 2C), 129.7 (s), 138.6 (s), 139.1 (s), and 181.2 (s).

1-Benzyl-7-hydroxy-6,6-dimethyl-r-7,c-8-diphenyl-1-aza-4-oxacyclo-octan-5-one (2c'); white crystals, m.p. 174–175 °C (from benzene–hexane), 25% yield (Found: C, 78.0; H, 7.0; N, 3.3. $C_{27}H_{29}NO_3$ requires C, 78.0; H, 7.0; N, 3.4%); ν_{max} (KBr) 1 705 and 3 500 cm^{-1} ; δ_H ($CDCl_3$) 0.91 (3 H, s, Me), 1.47 (3 H, s, Me), 1.75 (1 H, s, OH), 2.45 (1 H, dd, J 14.3 and 4.6 Hz, NCH_2), 2.56 (1 H, d, J 13.5 Hz, NCH_2Ph), 3.04 (1 H, ddd, J 14.3, 11.8, and 4.6 Hz, NCH_2), 3.43 (1 H, d, J 13.5 Hz, NCH_2Ph), 3.98 (1 H, dd, J 11.3 and 4.6 Hz, OCH_2), 4.94 (1 H, s, $NCHPh$), 5.09 (1 H, ddd, J 11.8, 11.3, and 4.6 Hz, OCH_2), 6.8–7.4 (13 H, m, ArH), 7.5–7.7 (1 H, m, ArH), and 8.3–8.6 (1 H, m, ArH); δ_C ($CDCl_3$)

22.2 (q), 22.8 (q), 50.8 (s), 53.8 (t), 58.0 (t), 68.9 (t), 75.3 (d), 83.0 (s), 126.8 (d, 2C), 127.2 (d), 127.4 (d, 2C), 127.6 (d, 4C), 128.4 (d, 4C), 131.5 (d, 2C), 134.8 (s), 139.3 (s), 142.1 (s), and 180.4 (s).

1-Benzyl-7-hydroxy-7-phenyl-1-aza-4-oxacyclo-octan-5-one [2d(m)]; white crystals, m.p. 155–163 °C (decomp.) (from benzene–hexane), 7% yield (Found: C, 72.9; H, 6.7; N, 4.5. $C_{19}H_{21}NO_3$ requires C, 73.3; H, 6.8; N, 4.5%); ν_{max} (KBr) 1 700 and 3 500 cm^{-1} ; δ_H ($CDCl_3$) 2.80 (2 H, ABq, J 12.6 Hz, CH_2CO), 2.8–3.0 (2 H, m, 2- H_2), 3.04 (2 H, s, 8- H_2), 3.93 (2 H, s, NCH_2), 4.2–4.4 (2 H, m, OCH_2), 4.34 (1 H, br, OH), and 7.0–7.7 (10 H, m, ArH); δ_C ($CDCl_3$) 44.8 (t), 54.9 (t), 63.1 (t), 64.9 (t), 67.0 (t), 96.2 (s), 124.5 (d, 2C), 127.5 (d, 2C), 128.5 (d, 4C), 128.7 (d, 2C), 137.9 (s), 143.7 (s), and 173.5 (s).

7-Hydroxy-1-methyl-r-7,t-8-diphenyl-1-aza-4-oxacyclo-octan-5-one [2d(b)]; white crystals, m.p. 171–172 °C (from benzene–hexane), 32% yield (Found: C, 73.1; H, 6.8; N, 4.5. $C_{19}H_{21}NO_3$ requires C, 73.3; H, 6.8; N, 4.5%); ν_{max} (KBr) 1 660 and 3 450 cm^{-1} ; δ_H ($CDCl_3$) 2.19 (3 H, s, Me), 2.74 (2 H, ABq, J 13.4 Hz, $COCH_2$), 2.7–3.3 (2 H, m, NCH_2), 4.14 (1 H, s, $NCHPh$), 4.3–4.5 (3 H, m, OCH_2 and OH), and 7.0–7.6 (10 H, m, ArH); δ_C ($CDCl_3$) 39.9 (q), 47.2 (t), 56.4 (t), 67.2 (t), 70.6 (d), 83.8 (s), 124.9 (d, 2C), 126.8 (d), 127.2 (d), 127.7 (d, 2C), 128.1 (d, 2C), 130.1 (d, 2C), 136.0 (s), 143.1 (s), and 172.4 (s).

7-Hydroxy-1-methyl-r-7,c-8-diphenyl-1-aza-4-oxacyclo-octan-5-one [2d(b)]; obtained in 2% yield; however, complete purification could not be achieved; ν_{max} (neat) 1 710 and 3 400 cm^{-1} ; δ_H ($CDCl_3$) 2.40 (5 H, s, Me and $COCH_2$), 3.36 (2 H, t, J 5.4 Hz, NCH_2), 3.60 (2 H, s, $NCHPh$ and OH), 4.39 (2 H, t, J 5.4 Hz, OCH_2), and 7.0–7.4 (10 H, m, ArH); δ_C ($CDCl_3$) 41.0 (q), 42.7 (t), 56.8 (t), 66.1 (t), 75.6 (d), 96.2 (s), 126.9 (d), 127.5 (d), 127.9 (d, 2C), 128.1 (d, 2C), 129.3 (d, 2C), 129.9 (d, 2C), 131.2 (s), 139.4 (s), and 176.6 (s).

8-Hydroxy-1-methyl-8-phenyl-1-aza-5-oxacyclononan-6-one (2e); white crystals, m.p. 52–53 °C (from benzene–hexane), 34% yield (Found: C, 67.6; H, 7.7; N, 5.6. $C_{14}H_{17}NO_3$ requires C, 67.4; H, 7.7; N, 5.6%); ν_{max} (KBr) 1 720 and 3 400 cm^{-1} ; δ_H ($CDCl_3$) 1.5–2.1 (2 H, m, 3- H_2), 2.39 (3 H, s, Me), 2.4–3.3 (6 H, m, $COCH_2$, 2- and 9- H_2), 3.9–4.5 (2 H, m, OH and OCH_2), 4.5–5.0 (1 H, m, OCH_2), and 7.2–7.8 (5 H, m, ArH); δ_C ($CDCl_3$) 23.7 (t), 44.1 (q), 47.4 (t), 57.4 (t), 61.7 (t), 69.5 (t), 76.9 (s), 124.5 (d, 2C), 126.9 (d), 128.1 (d, 2C), 144.7 (s), and 171.7 (s).

5-Dimethylamino-4-hydroxy-4-phenyl-1-oxacycloheptan-2-one (2e); white crystals, m.p. 146 °C (decomp.), 7% yield (Found: C, 67.8; H, 7.7; N, 5.4. $C_{14}H_{19}NO_3$ requires C, 67.4; H, 7.7; N, 5.6%); ν_{max} (KBr) 1 720 and 3 340 cm^{-1} ; δ_H ($CDCl_3$) 1.8–3.6 (2 H, m, 6- H_2), 2.09 (7 H, s, NMe_2 and OH), 2.79 (1 H, d, J 14.4 Hz, $COCH_2$), 2.94 (1 H, dd, J 11.3 and 4.6 Hz, NCH), 3.32 (1 H, d, J 14.4 Hz, $COCH_2$), 4.1–4.6 (2 H, m, OCH_2), and 7.1–7.5 (5 H, m, ArH); δ_C ($CDCl_3$) 25.0 (t), 43.1 (q, 2C), 46.5 (t), 67.0 (t), 71.3 (d), 76.3 (s), 124.3 (d, 2C), 126.9 (d), 128.2 (d, 2C), 147.4 (s), and 171.9 (s).

1-Benzyl-3-hydroxy-r-2,t-3-diphenyl-1-aza-6-oxacyclodecan-5-one (2f); white crystals, m.p. 119–112 °C (from methanol), 19% yield (Found: C, 77.9; H, 7.0; N, 3.4. $C_{27}H_{29}NO_3$ requires C, 78.0; H, 7.0; N, 3.4%); ν_{max} (KBr) 1 685 and 3 470 cm^{-1} ; δ_H ($CDCl_3$) 1.4–2.1 (6 H, m, 8-, 9-, and 10- H_2), 2.70 (1 H, d, J 14.1 Hz, NCH_2Ph), 3.47 (2 H, ABq, J 10.3 Hz, $COCH_2$), 3.98 (1 H, d, J 14.1 Hz, NCH_2Ph), 4.06 (1 H, s, $CHPh$), 4.43 (2 H, t, J 11.1 Hz, OCH_2), 4.55 (1 H, s, OH), and 6.7–7.5 (15 H, m, ArH); δ_C 23.4 (t), 26.2 (t), 42.2 (t), 49.8 (t), 57.4 (t), 65.8 (t), 76.3 (d), 78.1 (s), 125.2 (d), 126.5 (d), 127.1 (d, 2C), 127.3 (d, 3C), 127.5 (d, 2C), 128.2 (d, 2C), 128.5 (d, 2C), 130.0 (d), 131.5 (d), 134.6 (s), 138.6 (s), 145.0 (s), and 172.8 (s); m/z 415 (M^+).

1-Benzyl-3-hydroxy-r-2,c-3-diphenyl-1-aza-6-oxacyclodecan-5-one (2f'); white crystals, m.p. 143–147 °C (from benzene–hexane), 6% yield (Found: C, 77.9; H, 7.0; N, 3.4. $C_{27}H_{29}NO_3$ requires C, 78.0; H, 7.0; N, 3.4%); ν_{max} (KBr) 1 725 and 3 300 cm^{-1} ; δ_H ($CDCl_3$) 1.2–2.3 (6 H, m, 8-, 9-, and 10- H_2), 2.71 (2 H,

ABq, J 16.5 Hz, COCH₂), 2.82 (1 H, d, J 13.3 Hz, NCH₂Ph), 3.82 (1 H, s, CHPh), 3.83 (1 H, d, J 13.3 Hz, NCH₂Ph), 4.03 (2 H, t, J 10.3 Hz, OCH₂), 5.09 (1 H, s, OH), and 6.9–7.7 (15 H, m, ArH); δ_c (CDCl₃) 23.8 (t), 25.7 (t), 47.1 (t), 50.7 (t), 56.1 (t), 67.0 (t), 69.6 (d), 80.2 (s), 124.7 (d, 2C), 126.1 (d), 126.6 (d, 2C), 126.8 (d, 2C), 127.2 (d), 127.5 (d, 2C), 128.2 (d), 129.9 (d, 2C), 131.7 (d, 2C), 133.3 (s), 139.0 (s), 145.5 (s), and 170.4 (s); m/z 415 (M^+).

5-Dibenzylamino-4-hydroxy-4-phenyl-1-oxacyclo-octan-2-one (**3f**); white crystals, m.p. 123–124 °C (from benzene–hexane), 6% yield (Found: C, 77.9; H, 7.1; N, 3.7. C₂₇H₂₉NO₃ requires C, 78.0; H, 7.0; N, 3.4%); ν_{\max} (KBr) 1 710 and 3 420 cm⁻¹; δ_H (CDCl₃) 1.1–1.4 (2 H, m, 7-H₂), 1.5–2.1 (2 H, m, 6-H₂), 2.42 (1 H, d, J 12.9 Hz, COCH₂), 3.04 (1 H, d, J 12.9 Hz, COCH₂), 3.07 (1 H, t, J 16.4 Hz, NCH), 3.14 (2 H, d, J 13.9 Hz, NCH₂Ph), 3.14 (1 H, s, OH), 3.91 (1 H, d, J 13.9 Hz, NCH₂Ph), 3.92 (1 H, d, J 13.9 Hz, NCH₂Ph), 4.1–4.6 (2 H, m, OCH₂), and 6.7–7.6 (15 H, m, ArH); δ_c (CDCl₃) 16.5 (t), 30.3 (t), 47.0 (t), 54.6 (t, 2C), 63.1 (d), 67.1 (t), 80.1 (s), 125.2 (d, 2C), 126.6 (d), 126.7 (d, 2C), 127.8 (d, 4C), 128.2 (d), 128.7 (d), 129.2 (d, 4C), 139.4 (s, 2C), 146.3 (s), and 173.3 (s); m/z 415 (M^+).

Quantum Yield Determination.—The β -oxoester (**1**) was dissolved in purified benzene* (ca. 0.05 mol l⁻¹) and placed in 15 × 150 mm Pyrex culture tubes. In quenching experiments, the solution also contained appropriate concentrations of 2,5-dimethylhexa-2,4-diene. The tubes were degassed by three freeze-pump-thaw cycles and then sealed. Irradiation was performed on a 'merry-go-round' apparatus with an Ushio 450 W high-pressure mercury lamp. Potassium chromate filter solution was used to isolate the 313 nm line.²¹ Product analyses were performed using a Gasukuro Kogyo 570B high-pressure liquid chromatograph with a Model 511 single-wave UV detector (254 nm). A Unishil QC18 column (4 × 250 mm) was used, and methanol–water (7:3 v/v) was employed as the moving phase at a flow rate of 0.7 ml min⁻¹. Phenanthrene was used as a calibrant for the analyses and valerophenone was used as an actinometer.¹⁵

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* Washed with sulphuric acid, neutralized, dried, and distilled from phosphorus pentoxide using Shibata HP-1000B fractional distillation apparatus with a Helipak (No. 2) packed column (15 × 1 000 mm).