JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 9, 221–226 (1996)

PHOTOCYCLIZATION OF 2-(DIALKYLAMINO)ETHYL ACETOACETATES: REMOTE PROTON TRANSFER AND STERN–VOLMER QUENCHING KINETICS IN THE SYSTEM INVOLVING TWO REACTIVE EXCITED STATES

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Upon irradiation, 2-(dibenzylamino)ethyl and 2-(*N*-benzyl-*N*-methylamino)ethyl acetoacetate (1a and 1b) undergo photocyclization via remote proton transfer from the benzyl group to the acetyl carbonyl oxygen to give eight-membered azalactones. Irradiation of the corresponding (diisopropylamino)- and (dimethylamino)ethyl esters gave no azalactones. Introduction of the methyl group on C–2 of 1a brought about a complicated photoreaction, probably due to competition of α-cleavage. The Stern–Volmer plots for the photoreaction of 1a did not show the linear relationship, indicating that the photoreaction proceeds from two reactive excited states. The Stern–Volmer quenching equation for the system was obtained by applying the steady-state approximation and was used for the analysis of the photoreaction of 1a. The triplet lifetime was determined to be $1{\cdot}6 \times 10^{-8}$ s.

INTRODUCTION

Intramolecular remote hydrogen transfer to ketone carbonyl oxygen via a medium-sized cyclic transition state is a rare process even in widely studied ketone photochemistry.[1] A few aryl ketones bearing an activated remote hydrogen on their side-chain have been reported to undergo photocyclization via remote hydrogen transfer.[2–6] Although both aryl and alkyl ketones undergo Type II photoreactions via γ-hydrogen abstraction,[7] only one report on remote hydrogen abstraction, concerning ε-hydrogen, in the aliphatic ketones has been observed.[8] We report here the first examples of photocyclization in aliphatic ketones via η-hydrogen transfer to give eight-membered ring compounds.

EXPERIMENTAL

IR spectra were recorded with a JASCO A–3 spectrometer. ^{1}H and ^{13}C NMR spectra were determined with a JEOL FX9OQ spectrometer using tetramethylsilane as an internal standard. An Ushio 450 W high-pressure mercury lamp was used as the irradiation source.

The acetoacetates **1a–d** and **1g** were prepared from ethyl acetoacetate and the corresponding amino or benzyloxy alcohol and **1e** was prepared by methylation of **1a**. Acetoacetates freshly purified by column chromatography were used as irradiation samples because the acetoacetates **1a–e** were partially decomposed by distillation under reduced pressure and also gradually decomposed on standing even in the dark.

2-(Dibenzylamino)ethyl acetoacetate (**1a**): IR (neat), 1760 and 1730 cm^{-1}; ^{1}H NMR (CDCl$_3$), δ 2·21 (3H, s, COCH$_3$), 2·73 (2H, t, $J = 5{\cdot}9$ Hz, NCH$_2$), 3·36 (2H, s, COCH$_2$), 3·61 (4H, s, 2 × CH$_2$Ph), 4·20 (2H, t, $J = 5{\cdot}9$ Hz, OCH$_2$) and 7·2–7·4 (10H, m, aromatic).

2-(Benzylmethylamino)ethyl acetoacetate (**1b**): IR (neat), 1760 and 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$), δ 2·25 (3H, s, COCH$_3$), 2·26 (3H, s, NCH$_3$), 2·66 (2H, t, $J = 5{\cdot}7$ Hz, NCH$_2$), 3·44 (2H, s, COCH$_2$), 3·54 (2H, s,

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CCC 0894–3230/96/040221–06

Received 26 August 1995
Revised 11 December 1995

CH_2Ph), 4·25 (2H, t, $J = 5·7$ Hz, OCH2) and 7·2–7·4 (5H, m, aromatic).

2-(Diisopropylamino)ethyl acetoacetate (**1c**): IR (neat), 1750 and 1720 cm^{-1}; ^1H NMR ($CDCl_3$), δ 1·00 [12H, d, $J = 6·7$ Hz, $2 \times C(CH_3)_2$], 2·29 (3H, s, $COCH_3$), 2·69 (2H, t, $J = 7·2$ Hz, NCH_2), 3·03 (2H, sept, $J = 6·7$ Hz, $2 \times CH$), 3·46 (2H, s, CH_2CO) and 4·09 (2H, t, $J = 7·2$ Hz, OCH_2).

2-(Dimethylamino)ethyl acetoacetate (**1d**): IR (neat), 1750 and 1720 cm^{-1}; ^1H NMR ($CDCl_3$), δ 2·27 (9H, s, $COCH_3 + 2 \times NCH_3$), 2·57 (2H, t, $J = 5·8$ Hz, NCH_2), 3·49 (2H, s, $COCH_2$) and 4·23 (2H, t, $J = 5·8$ Hz, OCH_2).

2-(Dibenzylamino)ethyl 2,2-dimethylacetoacetate (**1e**): IR (neat), 1750 and 1725 cm^{-1}; ^1H NMR ($CDCl_3$), δ 1·33 (6H, s, $2 \times CH_3$), 2·10 (3H, s, CH_3CO), 2·73 (2H, t, $J = 5·4$ Hz, NCH_2), 3·60 (4H, s, $2 \times CH_2Ph$), 4·21 (2H, t, $J = 5·4$ Hz, OCH_2) and 7·2–7·4 (10H, m, aromatic).

2-Benzyloxyethyl acetoacetate (**1g**): b.p. 125–130 °C/4 mm Hg; IR (neat), 1760 and 1720 cm^{-1}; ^1H NMR ($CDCl_3$), δ 2·22 (3H, s, CH_3), 3·44 (2H, s, $COCH_2$), 3·65 (2H, t, $J = 4·7$ Hz, NCH_2), 4·30 (2H, t, $J = 4·7$ Hz, OCH_2), 4·52 (2H, s, CH_2Ph) and 7·2–7·4 (5H, m, aromatic). Found: C, 66·34; H, 6·97%. Calculated for $C_{13}H_{16}O_4$: C, 66·09; H, 6·83%.

*Preparative irradiation of **1a**.* A solution of the β-oxo ester **1a** (426 mg) in 100 cm^3 of benzene was irradiated for 16 h with a 450 W high-pressure mercury lamp under nitrogen. After removal of the solvent, the residue was chromatographed on a silica gel column. Elution with benzene–ethyl acetate (3 : 1), v/v gave the starting ketone (100 mg), **2a** (117 mg, 36%) and **2a**′ (90 mg, 28%).

1-Benzyl-7-hydroxy-7-methyl-8-phenyl-1-aza-4-oxacyclooctan-5-one (**2a**): m.p. 121–121.5 °C; IR (KBr), 3420 and 1720 cm^{-1}; ^1H NMR ($CDCl_3$), δ 1·36 (3H, s, CH_3), 2·3–2·7 (m, 2H, NCH_2), 2·63 (1H, s, OH), 2·83 (2H, ABq, $J = 12·6$Hz, CH_2CO), 3·93 (2H, ABq, $J = 14·4$ Hz, N–CH_2Ph), 4·13 (2H, dd, $J = 3·6$ and 10·8 Hz, OCH_2), 4·14 (1H, s, CHPh) and 7·1–7·5 (10H, m, aromatic); ^{13}C NMR ($CDCl_3$), δ 26·4 (q), 45·0 (t), 50·2 (t), 62·5 (t), 68·0 (t), 76·1 (d), 79·1 (s), 127·4 (d), 127·9 (d), 128·6 (d, 2C), 128·7 (d, 4C), 130·4 (d, 2C), 136·5 (s), 139·0 (s) and 174·3 (s). Found: C, 73·54; H, 7·07; N, 4·24%. Calculated for $C_{20}H_{23}O_3N$: C, 73·82; H, 7·12; N, 4·30%.

2a′: b.p. 143–148 °C/3 mm Hg; IR (neat), 3460 and 1705 cm^{-1}; ^1H NMR ($CDCl_3$), δ 1·19 (3H, s, CH_3), 2·64 (2H, s, CH_2CO), 2·80 (2H, ddABq, $J = 3·6$, 7·2 and 14·4 Hz, NCH_2), 3·26 (1H, d, $J = 14·1$ Hz, NCH_2Ph), 3·67 (1H, s, OH), 3·87 (1H, d, $J = 14·1$ Hz, NCHPh), 4·29 (2H, dd, $J = 3·6$ and 7·2 Hz, OCH_2) and 6·9–7·6 (10H, m, aromatic); ^{13}C NMR ($CDCl_3$), δ 26·8 (q), 46·4 (t), 51·8 (t), 57·0 (t), 60·3 (t), 64·6 (d), 72·6 (s), 127·1 (d), 127·9 (d), 128·4 (d, 4C), 129·1 (d, 2C), 130·8 (d, 2C), 137·3 (s), 138·6 (s), and 174·0 (s). Found: C, 73·63; H, 7·06; N, 4·21%. Calculated for $C_{20}H_{23}O_3N$: C, 73·82; H, 7·12; N, 4·30%.

*Preparative irradiation of **1b**.* A solution of the β-oxo ester **1b** (638 mg) in 100 cm^3 of benzene was irradiated for 62 h with a 450 W high-pressure mercury lamp under nitrogen. After removal of the solvent the residue was chromatographed on silica-gel column. Elution with benzene–ethyl acetate (2 : 1), v/v gave the starting ketone (30 mg), **2b** (96 mg, 16%) and **2b**′ (70 mg, 12%).

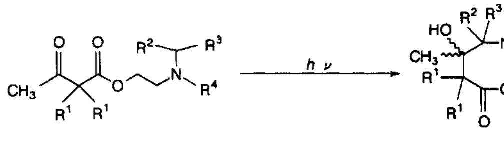
1-Methyl-7-hydroxy-7-methyl-8-phenyl-1-aza-4-oxacyclooctan-5-one (**2b**): m.p. 145–146 °C; IR (KBr), 3460 and 1680 cm^{-1}; ^1H NMR ($CDCl_3$), δ 1·18 (3H, s, CH_3), 2·14 (3H, s, CH_3), 2·52 (2H, s, CH_2CO), 2·6–3·1 (2H, m, NCH_2), 3·34 (1H, s, CHPh), 3·76 (1H, s, OH), 4·2–4·4 (2H, m, OCH_2) and 7·3–7·6 (5H, m, aromatic); ^{13}C NMR ($CDCl_3$), δ 25·6 (q), 39·9 (q), 45·8 (t), 56·0 (t), 67·5 (t), 71·6 (d), 80·8 (s), 127·8 (d), 128·2 (d, 2C), 130·4 (d, 2C), 136·4 (s) and 172·9 (s). Found: C, 67·63; H, 7·71; N, 5·53%. Calculated for $C_{14}H_{19}O_3N$: C, 67·45; H, 7·68; N, 5·62%.

2b′: m.p. 87–88 °C; IR (KBr), 3360 and 1675 cm^{-1}; ^1H NMR ($CDCl_3$), δ 1·40 (3H, s, CH_3), 2·51 (1H, s, OH), 2·53 (3H, s, NCH_3), 2·67 (2H, t, $J = 5·3$ Hz, NCH_2), 2·77 (2H, ABq, $J = 12·3$ Hz, CH_2CO), 3·89 (1H, s, CHPh), 4·19 (2H, t, $J = 5·3$ Hz, OCH_2) and 7·2–7·4 (5H, m, aromatic); ^{13}C NMR ($CDCl_3$), δ 26·1 (q), 45·3 (q), 47·0 (t), 56·3 (t), 68·5 (t), 75·8 (d), 80·0 (s), 128·2 (d), 128·9 (d, 2C), 131·3 (d, 2C), 137·6 (s) and 173·9 (s). Found: C, 67·67; H, 7·57; N, 5·39%. Calculated for $C_{14}H_{19}O_3N$: C, 67·45; H, 7·68; N, 5·62%.

Quantum yield determination and quenching experiment. The β-oxo ester **1a** was dissolved in purified benzene (*ca.* 0·05 mol dm^{-3}) and placed in 150 × 15 mm Pyrex tubes. In quenching experiments, the solution also contained appropriate concentration of 2,5-dimethyl-hexa-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. The potassium chromate filter solution was used to isolate the 313 nm line.[9] Product analyses were performed using a Gasukuro Kogyo 570B high-performance liquid chromatograph with a Model 511 single-wavelength UV detector (254 nm). An Inertsil ODS-2 column (150 × 4·6 mm) was used with acetonitrile–water (7 : 3), v/v as the mobile phase at a flow rate of 8 $cm^3 min^{-1}$. Phenanthrene was used as a calibrant for the analyses. Valerophenone was used as an actinometer.[10]

RESULTS AND DISCUSSION

Irradiation of a benzene solution of 2-(dibenzylamino)ethyl acetoacetate (**1a**) under nitrogen with a



1

2

	R^1	R^2	R^3	R^4	Yield of 2 (%)[a]
a	H	H	Ph	CH_2Ph	64 (36 / 28)
b	H	H	Ph	CH_3	28 (16 / 12)
c	H	CH_3	CH_3	$CH(CH_3)_2$	0
d	H	H	H	CH_3	0
e	CH_3	H	Ph	CH_2Ph	0

a: conversion yield; values in parentheses show yields of isomers.

Scheme 1

450 W high-pressure mercury lamp through a Pyrex filter gave two isomers of azalactones **2a** (m.p. 121–121·5 °C) and **2a**′ (b.p. 143–148 °C/3 mm Hg) in 36 and 28% yield, respectively (Scheme 1). The IR spectra of **2a** and **2a**′ showed the characteristic peaks due to the hydroxyl group at 3420 and 3460 cm^{-1}, respectively, and peaks due to the lactone carbonyl group at 1720 and 1705 cm^{-1}, respectively. In the ^{13}C NMR spectra of **2a** and **2a**, the doublet signals due to C-8 were observed at δ 76·1 and 64·6, respectively. The isomers **2a** and **2a**′ are probably *trans* and *cis* isomers with respect to 7-hydroxyl and 8-phenyl groups. Irradiation of the ester **1b** under the same conditions also gave two isomers of azalactones **2b** (m.p. 145–146 °C) and **2b**′ (m.p. 87–88 °C) in 16 and 12% yield, respectively. These azalactones showed the characteristic hydroxyl and lactone carbonyl absorptions in their IR spectra (**2b**: 3460 and 1680 cm^{-1}; **2b**′: 3360 and 1675 cm^{-1}) and a singlet ^1H NMR signal attributable to the *N*-methyl hydrogen at δ 2·14 (**2b**) and 2·53 (**2b**′). The lactones **2b** and **2b**′ are the products arising from benzylic hydrogen transfer to the acetyl carbonyl oxygen. No azalactones resulting from methyl hydrogen transfer could be detected. On the other hand, only polymeric materials were formed when the (diisopropylamino)- and (dimethylamino)ethyl esters **1c** and **1d** were irradiated.

The isomeric pairs **2a**/**2a**′ and **2b**/**2b** are probably *trans* and *cis* isomers with respect to the 7-hydroxyl and 8-phenyl groups. The configuration of the isomers is determined in recombination of radical centres of intermediate biradicals. The stereochemistry of the isomeric pair may be determined from the substantial differences in the chemical shifts of C-7 methyl and hydroxyl protons in the ^1H NMR spectra. However, the stereochemistry of the isomers has not yet been clarified because the most stable conformation could not be determined. Medium-sized cyclic aminoketones, such as 1-azacyclooctan-5-ones, show a transannular electronic interaction between the carbonyl group and amine nitrogen, and show the C=O stretching absorptions at lower wavenumbers than normal ketones.[11] The azalactones **2a**, **2a**′, **2b** and **2b**′ also showed the transannular interaction. The interaction increases in the order **2a**, **2a**′, **2b**, and **2b**′, so that the distance between carbonyl carbon and nitrogen must decrease in this order and the ring conformation of these azalactones must be slightly different.

Formation of the azalactones from **1a** and **1b** can be explained in terms of photocyclization via an η-benzylic hydrogen transfer to the acetyl carbonyl oxygen. We have already reported that photocyclization via remote hydrogen transfer took place either through direct hydrogen atom abstraction by the excited carbonyl oxygen[4] or through proton migration to the carbonyl oxygen from a charge-transfer state.[5] The process involving direct hydrogen atom abstraction in **1a** and **1a** can be excluded because 93% of the starting material was recovered when 2-benzyloxyethyl acetoacetate was irradiated under the same conditions. The η-proton transfer in **1** probably occurs from the charge-transfer state. Methyl hydrogen is known to be more reactive than benzylic hydrogen in photoreactions of ketones with amines[12] and anodic oxidation of amines.[13] The lack of azalactones derived from methyl hydrogen transfer can be explained in terms of instability of the *N*-methyl radical centre in the biradical intermediate produced through the methyl proton transfer from the charge transfer state. The benzylic radical centre is expected to have a sufficient lifetime to change the conformation of the biradical into a suitable conformation for cyclization.[4a,5c,d]

Introduction of a methyl group on C-2 in 2-benzoylacetates increases the photoreactivity because of an increase in the percentage of keto forms.[4b] However, the C-2 methyl group in the acetoacetate system resulted in a complicated photoreaction. Irradiation of the 2,2-dimethyl derivative **1e** under the same conditions gave an intractable mixture. The presence of the C-2 methyl group in some β-dicarbonyl compounds facilitates the α-cleavage.[14] Competition of the α-cleavage might cause the complex photoreaction of **1e**.

The quantum yields for the formation of **2a** and **2a**′ from **1a** at 313 nm were determined to be 0·043 and 0·033, respectively. Since the enol form of β-dicarbonyl compounds can act as internal filters[15–17] the normal Stern–Volmer quenching kinetics cannot be applied to such a photoreaction system.[16] Despite the possible keto–enol tautomerism of the β-oxo ester, **1a** exists almost completely in the keto form in benzene, chloroform and carbontetrachloride. Therefore, the internal filtering effect by the enol form can be neglected.[17]

The quantum yields for the formation of **2a** in the photoreaction of **1a** in the presence of various concentrations of 2,5-dimethylhexa-2,4-diene as a quencher were measured. Figure 1 shows a plot of the ϕ^0/ϕ

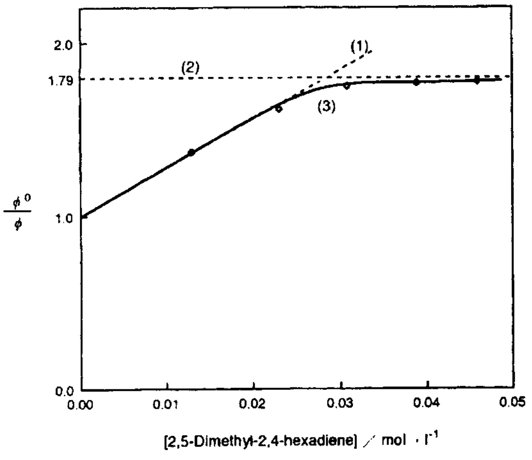


Figure 1. Quantum yields for the formation of **2a** as a function of quencher concentration. The conversion in all runs was less than 15%. Slope of the dotted line 1 = 27. Curve 3 was obtained from equation (9) by using $a = 33{\cdot}9$ and $b = 79.5$

values against quencher concentration. At low concentrations of the quencher the plot was approximately linear but in each case the quenching effect levelled off and a limiting quantum yield ($\phi = 0{\cdot}024$) was reached at high concentrations of the quencher. The results indicate that the photoproducts are formed from two reactive excited states of **1a**, quenchable and unquenchable states.[18] Such a quenching curve is familiar in the photochemistry of aliphatic ketones.[7] Since dienes have relatively low triplet state energies and are very efficient acceptors for the energy of excited triplet states of ketones, but do not quench their excited singlet states,[19] it is apparent that the excited singlet state of **1a** is the reactive unquenchable state. If the triplet reaction is completely quenched ($\phi_T = 0$), the quenching curve tends to approach a horizontal asymptote.

$$\frac{\phi^0}{\phi} = \frac{\phi_S^0 + \phi_T^0}{\phi_S^0 + \phi_T} \tag{1}$$

$$= 1 + \frac{\phi_T^0}{\phi_S^0} \quad (\text{when } \phi_T = 0) \tag{2}$$

where ϕ_T^0 and ϕ_T are the triplet quantum yields in the absence and presence of the quencher, respectively, and ϕ_S^0 is the singlet quantum yield. The equations are widely used for the analysis of the photoreaction of aliphatic ketones which react from both excited singlet and triplet states.[7] The value of ϕ_T^0/ϕ_S^0 might be determined from graphical analysis of the Stern–Volmer quenching curve.[7a–d] In the case of the photoreaction of **1a** the ϕ_T^0/ϕ_S^0 value was determined to be 0·79. This means 56% of the reaction should occur from the singlet excited state of **1a**. The ϕ_T^0/ϕ_T^0 ratio can be calculated from the following equation:

$$\frac{\phi_T^0}{\phi_T} = \frac{\dfrac{\phi_T^0}{\phi_S^0} \cdot \dfrac{\phi^0}{\phi}}{1 + \dfrac{\phi_T^0}{\phi_S^0} - \dfrac{\phi^0}{\phi}} \tag{3}$$

The familiar Stern–Volmer expression represented by the equation

$$\frac{\phi_T^0}{\phi_T} = 1 + kq\tau_T[\mathrm{Q}] \tag{4}$$

shows the linear relationship between ϕ_T^0/ϕ_T and quencher concentration. However, the plots of the calculated ϕ_T^0/ϕ_T ratios for the formation of azalactone **2a** against quencher concentration did not show a linear relationship (Figure 2). This must be caused by inaccuracy in the graphical estimation of ϕ_T^0/ϕ_S^0 using a horizontal asymptote. The scatter in the experimental data often makes graphical analysis impossible.[7c] We then used the curve-fitting method for the determination of the $kq\tau_T$ value directly from the non-linear relationship between the ϕ^0/ϕ values and the quencher concentrations.

A simple scheme for the photoreaction of **1** is shown in Figure 3. The Stern–Volmer equation can be derived as equation (9) by applying the steady-state hypothesis to the system.

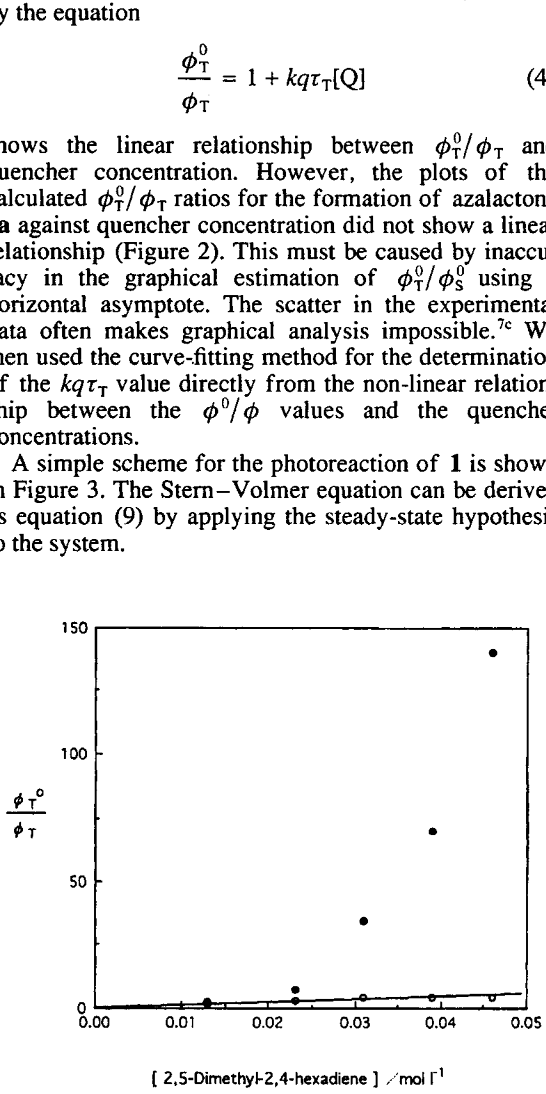


Figure 2. Triplet quantum yields as a function of quencher concentration ϕ_T^0/ϕ_T values were estimated from equation (3); (●) $\phi_T^0/\phi_S^0 = 0{\cdot}79$; (o) $\phi_T^0/\phi_S^0 = 1{\cdot}345$; slope of the line $(kq\tau) = 79{\cdot}5$

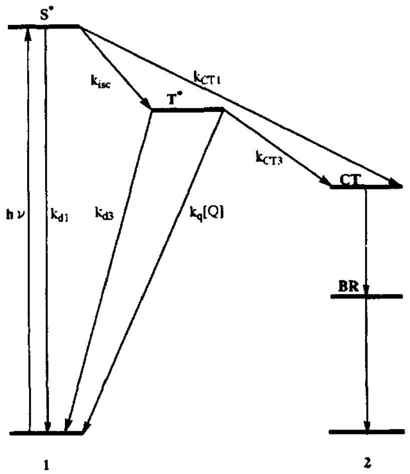


Figure 3. Simple scheme for photoreaction of **1**

$$\phi^0 = \frac{k_{CT1}}{k_{ISC}+k_{d1}+k_{CT1}} + \frac{k_{ISC}}{k_{ISC}+k_{d1}+k_{CT1}}\cdot\frac{k_{CT3}}{k_{d3}+k_{CT3}} \qquad (5)$$

$$\phi = \frac{k_{CT1}}{k_{ISC}+k_{d1}+k_{CT1}} + \frac{k_{ISC}}{k_{ISC}+k_{d1}+k_{CT1}}\cdot\frac{k_{CT3}}{k_{d3}+k_{CT3}+kq[Q]} \qquad (6)$$

$$\frac{\phi^0}{\phi} = \frac{[k_{CT1}(k_{d3}+k_{CT3})+k_{ISC}k_{CT3}](k_{d3}+k_{CT3}+kq[Q])}{\{k_{CT1}(k_{d3}+k_{CT3}+kq[Q])+k_{ISC}k_{CT3}\}(k_{d3}+k_{CT3})} \qquad (7)$$

$$= \frac{1+b[Q]}{1+a[Q]} \qquad (8)$$

$$= 1 + \frac{(b-a)[Q]}{1+a[Q]} \qquad (9)$$

where

$$a = \frac{k_{CT1}kq}{k_{CT1}(k_{d3}+k_{CT3})+k_{ISC}k_{CT3}}$$

and

$$b = \frac{kq}{k_{d3}+k_{CT3}} = kq\tau_T$$

Equation (9) has a horizontal asymptote. The limiting value is $1 + (b-a)/a$, where $(b-a)/a$ gives the ratio of ϕ_T^0/ϕ_S^0.

The curve fitting was performed by a non-linear least-squares method using equation (9). The experimentally obtained data in Figure 1 fit a curve obtained with $a = 33{\cdot}9$ and $b = 79{\cdot}5$ (line 3). From these values, the ratio of ϕ_T^0/ϕ_S^0 can be estimated to be 1·345. Therefore, 43% of the photoreaction of **1a** occurs through the charge-transfer state arising from the singlet excited state. Since the value of b corresponds to the $kq\tau_T$ value, the triplet lifetime can be determined to be 16×10^{-9} s assuming a diffusion-controlled rate for kq (5×10^9 mol^{-1} dm^3 s^{-1} in benzene).[20] This value is 2·5 times larger than that for 2-(*N*,*N*-dibenzylamino)ethyl 2,2-dimethylbenzoylacetate ($6{\cdot}4 \times 10^{-9}$ s)[5b] and suggests that the electron transfer process from the excited triplet state of the acetoacetate **1a** is as efficient as that in the corresponding benzoylacetate. The triplet lifetime of the oxo ester **1a** is comparable to those of pentan-2-one (5×10^{-9} s) and hexan-2-one (1×10^{-9} s),[7c] although the oxo ester undergoes photoreaction via electron transfer and the alkanones undergo Type II photoreactions via γ-hydrogen atom abstraction.

Electron transfer is a consequence of the overlap of the half-vacant carbonyl n orbital and the nitrogen sp^3 orbital,[20] and occurs efficiently in aminoketones where the carbonyl and the amino groups are linked by a short flexible chain.[21] The process competing with the bimolecular quenching by the diene in the photoreaction of **1a** must be a change in its conformation to that suitable for electron transfer from remote nitrogen to the excited ketone carbonyl because the rate of the elementary step of electron transfer itself in a suitable conformer is much more higher than that of the bimolecular quenching.[22] Hence, conformational flexibility is an important factor for photoreaction via the remote proton transfer in the aliphatic ketone system **1**.

CONCLUSION

The acetoacetates **1a** and **1b** underwent photocyclization via remote proton transfer from their charge-transfer states with nearly same efficiency as benzoylacetates. Electron transfer occurred from both singlet and triplet excited states. The contribution of the singlet excited state to the photoreaction of **1a** was 43%. The triplet state lifetime of **1a** was $1{\cdot}6 \times 10^{-8}$ s which is comparable to those of the corresponding benzoylacetate, pentan-2-one and hexan-2-one. Conformational flexibility is an important factor for the photoreaction of **1** via remote proton transfer because conformational transformation in the excited state **1** determines the rate of the charge transfer process.

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