Type II photoreaction of benzoyl- and (benzoylmethyl)cyclohexanones: cyclohexanone ring inversion and other factors determining their photoreactivities

Tadashi Hasegawa,* Yiming Yang, Shuichi Kikuchi, Takayuki Nakamura and Yutaka Maeda

Department of Chemistry, Tokyo Gakugei University, Nukuikitamachi, Koganei, Tokyo 184-8501, Japan

ABSTRACT: X-ray crystallographic structure analysis showed that a molecule of 2-benzoylcyclohexanone (**2**), which undergoes an efficient Type II reaction in solution but not in the crystalline state, is in a keto and chair form with an equatorial benzoyl group. Irradiation of 3-benzoylcyclohexanone (**3**) gives 7-phenylhepten-4,7-dione (**4**, 61%) and a mixture of cyclization products **5** (25%). High photoreactivity of **2** and **3** is caused by the efficient cyclohexanone ring inversion. Upon irradiation, 2-(benzoylmethyl)cyclohexanone (**6**) gives acetophenone (**7**), 2-cyclohexenone (**8**) and the cyclobutanol **9** in 59, 59 and 35% yield, respectively, and 1-phenyl-3-propylpentan-1,4-dione (**10**) gives **7** and the cyclobutanol **11** in 73 and 4% yield, respectively. The quantum yields for the disappearance of **6** and **10** are 0.68 and 0.67, respectively. Irradiation of 2-(benzoylmethyl)-2-ethoxycarbonylcyclohexanone (**12**) gives **7** and the cyclobutanol **13** in 46 and 51% yield, respectively. The quantum yield for the disappearance of **12** is 1.00, so that reverse hydrogen transfer is suppressed by intramolecular hydrogen bonding in the 1,4-biradical intermediate. When **6** is irradiated on a dry silica gel surface, the Type II reaction occurs to give **7**, **8** and **9** in 38, 38 and 43% yield, respectively. The cyclization in the photoreaction of (benzoylmethyl)cyclohexane also increases from 68% in benzene to 81% on a dry silica gel surface. Restriction of conformational change in the 1,4-biradical is an important factor for the cyclization. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: Type II reaction; phenyl ketones; photoreaction in solution; surface photoreaction; hydrogen abstraction; ring inversion; conformational flexibility; reverse hydrogen transfer

INTRODUCTION

The Norrish Type II photoreaction of alkyl aryl ketones having a γ-hydrogen has been extensively studied. Intervention of a 1,4-biradical intermediate, which undergoes elimination and cyclization, is now well established.[1] The length of the alkyl chain hardly affects the cyclization percentage in the Type II reaction of simple alkyl aryl ketones, *e.g.* 12, 18, 20 and 20% in butyro-, valero-, capro- and octyrophenone, respectively.[2] (Aroylmethyl)-cyclohexanes also undergo the Type II reaction.[3] The photoreactivity of the cyclohexanes is almost the same as that of the simple ketones[2,4] in solution. Although the cyclohexanes undergo the Type II reaction even in the solid state[3c,d] and in the polymer-bound form,[3a] benzoylcyclohexane (**1**) shows fairly low photoreactivity.[5] Introduction of an isopropyl group on the 1-position of **1** increases the Type II reactivity and allows the compound to cyclize in

solution and even in the solid state.[6] As γ-hydrogen abstraction in **1** occurs only from the conformer having an axial benzoyl group, cyclohexane ring inversion must be an important factor determining the photoreactivity.[5] Upon irradiation, 2-benzoylcyclohexanone (**2**) undergoes only Type II elimination[7,8] with a 'true' quantum yield of unity for the disappearance of the keto form of **2**; the enol forms of **2** and the Type II elimination product act as internal filters, so that the observed quantum yields for the disappearance of **2** are less than unity and depend on the reaction time.[8] Introduction of a methyl group on the 2-position of **2** provides a remarkable changeover in the reaction course; 2-methyl-2-benzoylcyclohexanone undergoes Type II cyclization exclusively.[9] We report here the factors determining photochemical behavior of phenyl ketones having the cyclohexanone chromophore.

RESULTS AND DISCUSSION

Ground state molecular conformations influence photochemical behavior in cases where excited state reactions
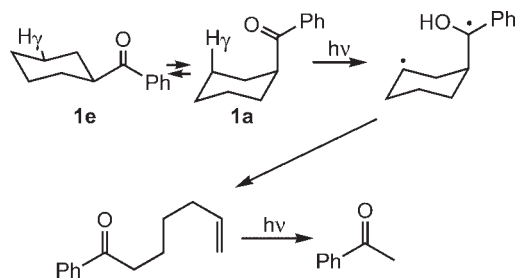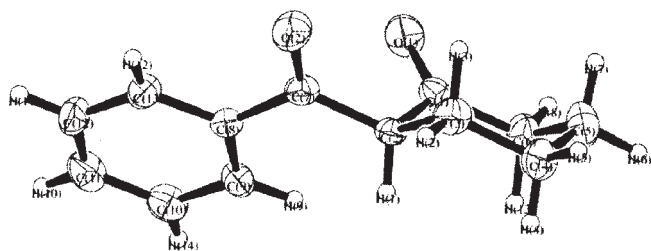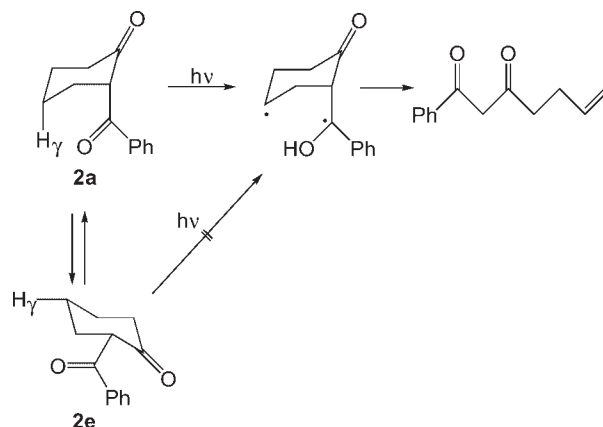
Scheme 1

Scheme 2

are more rapid than conformational transformation.[10] High ground state population of the unreactive conformer having an equatorial benzoyl group and fast radiationless decay processes competing with ring inversion from the equatorial to the photoreactive axial conformer should result in low photoreactivity of **1** (Scheme 1).[5c] The high photoreactivity of **2** may arise from a distorted chair conformation which may be the most stable conformer and allow the excited benzoyl carbonyl access to γ-hydrogen. If that is the case, the cyclohexanone **2** should show high Type II photoreactivity in the crystalline state. However, when crystals of **2** were irradiated with a 450 W high-pressure mercury lamp, no reactions were observed. This might suggest that the most stable conformer of **2** is the equatorial conformer and the ring inversion is suppressed in the crystalline state. Therefore, an x-ray crystallographic structure analysis of **2** was performed.

The x-ray analysis showed that a molecule of **2** is in a keto and chair form having an equatorial benzoyl group as shown in Fig. 1. The distance between the migrating hydrogen and carbonyl oxygen has been considered to be the most important parameter for intramolecular hydrogen migration and the theoretically ideal value is ≤ 2.7 Å.[11] The distances between benzoyl carbonyl oxygen and γ-hydrogens in the crystals of **2** were 4.68 Å [H(4) in Fig. 1] and 4.81 Å (H5). These values deviated greatly from the theoretical ideal value. These results and the high quantum yield for the disappearance of **2**[8] strongly suggest that high photoreactivity of **2** results from rapid cyclohexanone ring inversion (Scheme 2). The inversion should be much more faster than the γ-hydrogen abstraction by the excited benzoyl carbonyl. The difference between the photoreactivities of **1** and **2** can be reasonably explained in terms of the difference between the efficiency of the ring inversion in the cyclohexane and

cyclohexanone ring system. The activation energy for ring inversion of cyclohexanone is known to be lower than that of cyclohexane; the substitution of a methylene group in cyclohexane to a carbonyl group leads to the elimination of torsional strain during the ring inversion.[12] The idea of the rapid cyclohexanone ring inversion as a factor determining the photoreactivity of **2** is also supported by the following experiment.

Irradiation of a benzene solution of 3-benzoylcyclohexanone (**3**) under nitrogen gave the Type II elimination product, 7-phenylhepten-4,7-dione (**4**, 61%), and a mixture of cyclization products **5** (25%) (Scheme 3). The mixture could not be separated into its components. The IR spectrum of the mixture showed the characteristic absorption of the cyclohexanone carbonyl and hydroxyl groups at 1740 and 3440 cm^{-1}, respectively. Its mass spectrum showed a molecular ion signal at m/z 202. These results support the structure of 6-hydroxy-6-phenylbicyclo[3.1.1]heptan-3-one. However, the ^{1}H NMR spectrum was complex and the ^{13}C NMR spectrum showed four signals attributable to carbonyl groups at δ 197.3, 199.4, 200.2 and 210.1. As there are at least four possible isomers for the Type II cyclization products,[3] we deduced that the mixture consists of four 6-hydroxy-6-phenylbicyclo[3.1.1]heptan-3-one isomers. The Type II reaction should occur from the axial conformer **3a**. The
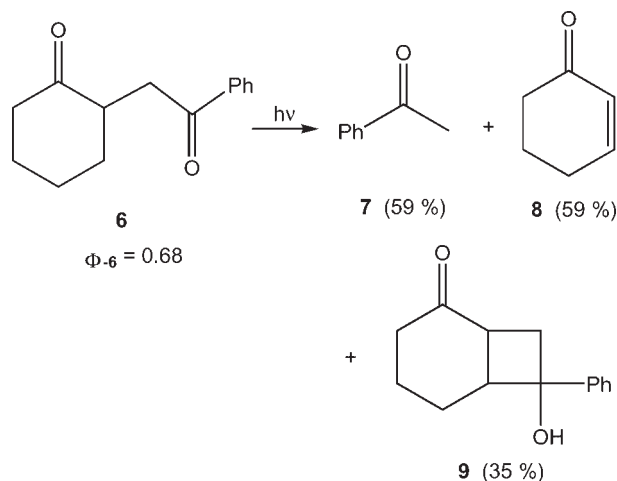

Figure 1. Structure of 2-benzoylcyclohexanone (**2**)
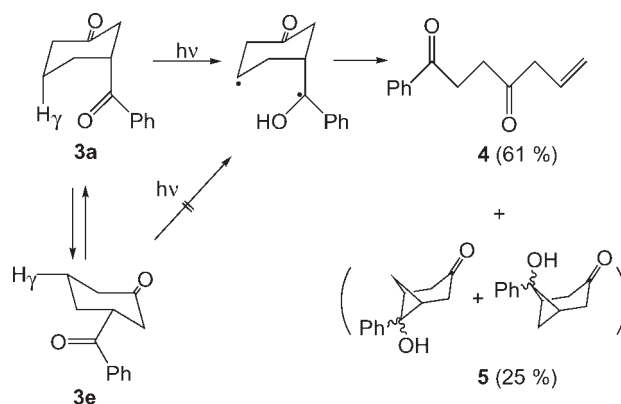
Scheme 3

quantum yields for the disappearance of **3** and the formation of **4** were determined as 0.36 and 0.22, respectively. Although the cyclization products could not be isolated but were obtained as a mixture of four isomers, the Type II reactivity of **3** is obviously much higher than that of **1** ($\phi < 0.005$).[5a] This strongly supports the idea of the rapid ring inversion as the factor. The quantum yield for the disappearance of **3** was lower than the 'true' quantum yield of the keto form of **2**, which shows keto—enol tautomerization. This indicates the absence of intramolecular hydrogen bonding causing suppression of reverse hydrogen transfer[2,8] in the 1,4-biradical intermediate from **3**.

Insertion of a methylene group between the cyclohexane ring and the benzoyl group of **1** has been reported to increase the Type II reactivity[3] compared with **1** and the cyclization percentage compared with that in the Type II reaction of the simple alkyl aryl ketones.[13] Therefore, we studied the photochemical behavior of 2-(benzoylmethyl)cyclohexanone (**6**) in order to compare it with that of **2** and clarify the effect of the inserted methylene group.

Irradiation of a benzene solution of **6** gave acetophenone (**7**), 2-cyclohexenone (**8**) and the cyclobutanol **9** in 59, 59 and 35% yield, respectively. The quantum yields for the disappearance of **6** and for production of **7** and **9** were 0.68, 0.40 and 0.24, respectively (Scheme 4). The quantum yield for the disappearance of **6** is lower than that of the keto form of **2**. This indicates that the insertion of the methyl group prevents the formation of the intramolecular hydrogen bonding which causes increase of the Type II reactivity because of suppression of reverse hydrogen transfer reproducing the starting ketone from the biradical intermediate.[2,8]

On the other hand, the quantum yield of **6** is high compared with those of alkyl phenyl ketones such as butyrophenone (**BP**, 0.40),[14,15] valerophenone (**VP**, 0.42)[14,15] and β-methylbutyrophenone (0.30).[15] This may be explained in terms of a decrease in conformational flexibility owing to the presence of the cyclohexanone ring. However, this idea is probably excluded for the following reasons. The quantum yields of the phenyl ketones increase to nearly unity in polar solvents and the reproduction of the ground state ketone from the excited phenyl ketones in benzene occurs only via reverse hydrogen transfer from the 1,4-biradical intermediates.[4] These indicate that conformational flexibility is not the factor determining the quantum yield for the disappearance of the starting ketones in the phenyl ketones and so the decrease in the conformational flexibility in **6** is not the reason for its higher quantum yield compared with that of the phenyl ketones.

Although the intramolecular hydrogen bond producing a seven-membered ring in the 1,4-biradical intermediate from **3** must be formed much less efficiently than that producing a six-membered ring in the biradical from **2**, the hydrogen bonding in the former may cause the high Type II reactivity of **6**. The photoreaction of 1-phenyl-3-propylpentan-1,4-dione (**10**) was studied in order to clarify this possibility.

Irradiation of a benzene solution of **10** gave **7** and the cyclobutanol **11** in 73 and 4% yield, respectively (Scheme 5). The quantum yields for the disappearance of **10** and formation of **7** were 0.67 and 0.49, respectively. The quantum yield for the disappearance of **10** is nearly equal to that of the cyclohexanone **6** (Table 1). Therefore, the decrease in conformational flexibility due to the presence of the cyclohexanone ring is not an important reason for the more efficient Type II reaction of **6** than the simple alkyl phenyl ketones. However, the presence of the ring increases the cyclization percentage in the Type II reaction, the values for **6** and **10** being 37 and 5%, respectively. In order for efficient cleavage to occur, the radical-containing p-orbitals are required to be parallel to the carbon–carbon bond undergoing scission (0,0 geometry).[1,3d,15] The 1,4-biradical from **6** is very unlikely to rotate to the 0,0 geometry because of ring constraints,[3d] so the probability of cyclization from the biradical would be increased. That is, the increase in cyclization may be due to the decrease in the conformational flexibility. As the quantum yields for the Type II reaction of **6** and **10** were high, the presence of the carbonyl group on the β-carbon of alkyl phenyl ketones seems to increase the Type II photoreactivity. Therefore, the photoreaction of 2-(benzoylmethyl)-2-ethoxycarbonylcyclohexanone (**12**) was studied.
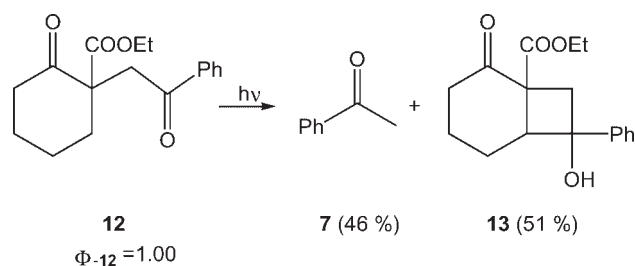
6
$\Phi_{-6} = 0.68$

7 (59 %)   **8** (59 %)

9 (35 %)

Scheme 4

10
$\Phi_{-10} = 0.67$

7 (73 %)   **11** (4 %)
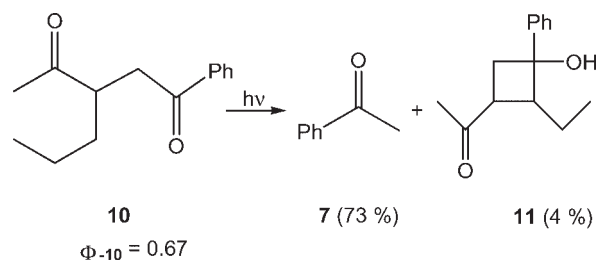
Scheme 5

Table 1. Quantum and chemical yields in the Type II photoreactions

| Ketone	Irradiation conditions	$\phi_{-\text{ketone}}$	ϕ_{elim}	ϕ_{cy}	Cyclization (%)
6	In benzene	0.68	0.40	0.24	37
10		0.67	0.49	0.03	5
12		1.00	0.46	0.51	53
14		0.27	0.056	0.12	68 (67)[a]
BP[b]		0.40	0.36	0.042	12
VP[b]		0.42	0.33	0.091	18
6	On SiO$_2$	—	38[c]	43[c]	53
14		—	13[c]	55[c]	81

[a] Ref. 13.
[b] Ref. 15.
[c] Chemical yield (%).

Irradiation of a benzene solution of **12** gave **7** and the cyclobutanol **13** in 46 and 51% yield, respectively (Scheme 6). The quantum yield for the disappearance of **12** was 1.00. Although β, β-dimethyl substitution in **BP** has been known to decrease both the Type II photoreactivity and cyclization percentage because of steric effect in the 1,4-biradical intermediate,[15] introduction of the 2-ethoxycarbonyl group into the (benzoylmethyl)cyclohexanone **6** obviously increases the Type II photoreactivity and the cyclization percentage. The percentage in the Type II reaction of **12** (54%) is higher than those of **6** (37%) and simple alkyl phenyl ketones having no α-substituents (ca 10–25%).[2,15] The effect of the 2-ethoxycarbonyl group on the Type II photoreactivity can be reasonably explained in terms of suppression of reverse hydrogen transfer by intramolecular hydrogen bonding between the hydroxyl and carbonyl groups in the 1,4-biradical.[2,8] The reverse hydrogen transfer in the 1,4-biradical produced from **6** cannot be suppressed completely because the quantum yield for the disappearance of the starting ketone increased from 0.68 in **6** to 1.00 in **10**. The increase of the cyclization percentage might be also explained in terms of the hydrogen bonding in the biradical that causes a decrease in conformational flexibility and in the possibility of rotation to the 0,0 geometry.

Conformational transformation may be restricted on a silica gel surface[16] and this restriction may facilitate the cyclization of **6**. When **6** was irradiated on a dry silica gel surface, the Type II reaction occurred as in solution to give **7**, **8** and **9** in 38, 38 and 43% yield, respectively, with 53% cyclization. The latter value is 1.4 times larger than that in the photoreaction of **6** in benzene. Similarly, the cyclization in the photoreaction of (benzoylmethyl)cyclohexane (**14**) increased from 68% in benzene to 81% on a dry silica gel surface. Restriction of conformational change in the 1,4-biradical must be an important factor for the cyclization.

The absolute quantum yields for the Type II reaction on the surface are difficult to determine because of scattering of irradiated light. Therefore, the relative quantum yield for the disappearance of **6** with respect to that of **VP** ($\phi_{-6}/\phi_{-\text{VP}}$) was determined. The ratio was found to be 1.67, which is smaller than that in benzene (1.73). The difference is not very large, but probably suggests a decrease in the photoreactivity of **6** on the surface. This decrease in reactivity may be due to the high polarity of the surface. It is well known that energy levels of the electric configuration of ketones depend on solvent polarity and their lowest triplet states may change from the n, π^* to the π, π^* configuration in polar solvents.[17] Weis *et al.* reported that the polarity of silica gel is higher than that of methanol.[18] When **6** was irradiated in acetonitrile, ethanol or methanol, the Type II reaction products were also formed almost quantitatively as in benzene. The ratios of the Type II cyclization to elimination were nearly constant, although the ratio of the Type II cyclization to elimination in a polar solvent is slightly smaller than that in a non-polar solvent [$(\phi_9/\phi_9)_{\text{MeOH}}/(\phi_9/\phi_7)_{\text{PhH}} = 0.88$], as known in the Type II reaction of phenyl ketones.[2] Hence the quantum yields for the formation of **7** from **6** in different solvents were determined in order to examine the solvent effect on the Type II reaction of **6**. The relationship between reactivity and solvent polarity, defined as the Z-value,[19] is shown in Fig. 2. The results indicate that the photoreactivity of **6** decreases with increase in solvent polarity.

Scheme 6
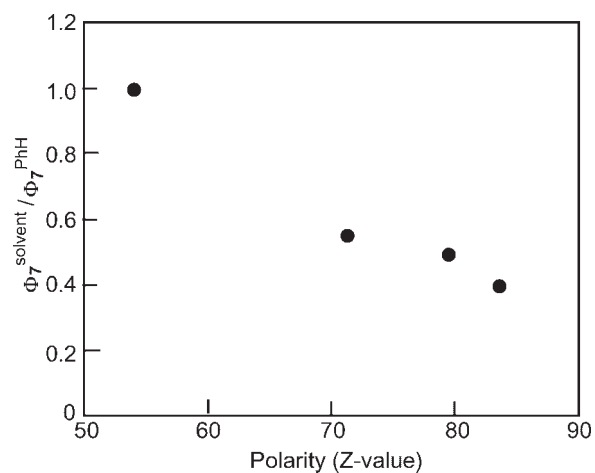
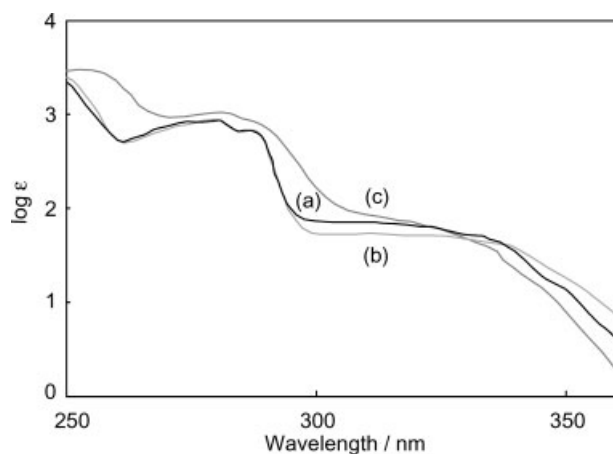**Figure 2.** Relationship between reactivity and polarity of solvent

Figure 3. UV absorption spectra of **6** in (a) hexane, (b) cyclohexane, and (c) EtOH

Figure 3 shows the UV absorption spectra of **6**. The broad absorption peak at around 320 nm in hexane underwent the blue shift and moved into the π, π* end absorption in ethanol. The lifetimes and triplet energies of **6** in cyclohexane and EPA were determined as 1.9 and 88 ms and 74.4 and 73.9 kcal mol^{-1}, respectively, from its phosphorescence spectra (Table 2). These results indicate that the lowest triplet state of **6** in non-polar solvents is the n,π* state and that in polar solvents is the π, π* state. The decrease in the photoreactivity of **6** with increase in solvent polarity can be rationalized to the increase in the π, π* character in its excited state. The decrease in the photoreactivity of **6** on the silica gel surface can also be explained in terms of the increase in the π, π* character by the highly polar surface.

In conclusion, the much higher photoreactivity of **2** than **1** can be reasonably explained in terms of rapid ring inversion. Insertion of a methylene group between the benzoyl group and the cyclohexanone ring of **2** increases the Type II reactivity; the quantum yield for the disappearance of **6** is higher than those of simple alkyl phenyl ketones. Reverse hydrogen transfer should be partially suppressed by intramolecular hydrogen bonding between the cyclohexanone carbonyl and hydroxyl hydrogen in the 1,4-biradical intermediate from **6**. Although the decrease in conformational flexibility due to the presence of the cyclohexanone ring is not an important reason for the efficient Type II reaction of **6**, the presence of the ring increases the cyclization percentage in the reaction.

Table 2. Lifetimes (τ), triplet energies (E_T) and electronic configurations of the lowest triplet state of 6

Solvent	τ (ms)	E_T (kcal mol^{-1})[a]	Electronic configuration
Cyclohexane	1.9	74.4	n,π*
EPA	88	73.9	π,π*

[a] 0–0 band of phosphorescence.

Introduction of the ethoxycarbonyl group to the 2-position of **6** increases the Type II photoreactivity because of possible intramolecular hydrogen bonding in the 1,4-biradical intermediate. A silica gel surface provides a polar media increasing the π, π* character in the excited state of ketones. The surface also restricts conformational change of the 1,4-biradical and increases the cyclization percentage in the Type II reaction.

EXPERIMENTAL

IR, UV, mass and phosphorescence spectra were recorded with a JASCO IR Report-100, Shimadzu UV-3150, Varian SATURN 2000R and Hitachi F-4500 spectrometer, respectively. ^{1}H and ^{13}C NMR spectra were measured with a JEOL FX-90Q and Bruker AVANCE 300 spectrometer using tetramethylsilane as an internal standard. The diketones were prepared according to reported methods.[8,20–22] Ushio 450 W and Taika 100 W high-pressure mercury lamp were used as the irradiation sources. A potassium chromate filter solution was used for isolation of the 313 nm line.[23] Gas–liquid chromatographic (GLC) analysis was performed with a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector which was connected to a Shimadzu C-R6A Chromatopac integrator, using a 2 m column containing 15% propylene glycol succinate or SE-30 on Uniport B. Hexadecane, octadecane or tetradecanol was used as calibrant for the GLC analysis. Silica gel (Merck Kieselgel 60, Art. 7734) was used as received for surface photoreactions.

X-ray structure determination of 2

A Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation (0.71069 Å) was used. The unit-cell parameters were determined from 25 reflections with $25.09° \leq 2\theta \leq 27.12°$. Intensity data with $2\theta \leq 55.1°$ were collected with the $\omega - 2\theta$ scan technique (scan speed 4.0°/min) at 2864 reflections. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability. No decay correction was applied. The intensities were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by direct methods[24] and expanded using Fourier techniques.[25] The full-matrix least-squares refinement for non-hydrogen atoms was carried out for $\sum w(|F_o| - |F_c|)^2$, where the weight $w = 4F_o^2/\sigma^2(F_o)^2$, for 2594 independent reflections with $I > -10.00 \ \sigma(I)$. The final discrepancy factors were $R = 0.051$ and $Rw = 0.062$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.23 and -0.22 e Å^{-3}, respectively. Neutral atom-scattering factors were taken from Cromer and Waber.[26] Anomalous

dispersion effects were included in F_c;[27] the values for $\Delta f'$ and $\Delta f'$ were those of Creagh and McAuley.[28] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[29] All calculations were performed using the CrystalStructure[30,31] crystallographic software package.

Crystal data for 2

A colorless needle crystal, $C_{13}H_{14}O_2$, $M = 202.25$, monoclinic, $a = 12.577(3)$, $b = 5.567(2)$, $c = 15.618(2)$ Å, $\beta = 100.05(1)°$, $V = 1076.8(5)$ Å^3, $T = 293 \pm 1$ K, space group $P2_1/n$, Z = 4, μ(Mo Kα) = 0.8 cm^{-1}, 2864 reflections measured, 2594 unique ($R_{int} = 0.052$).

General procedure for determination of quantum yields in solution

A solution of a ketone (ca 0.05 mol dm^{-3}) containing an appropriate amount of a calibrant was placed in 150×15 mm Pyrex tubes. 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. A potassium chromate filter solution was used to isolate the 313 nm line. Analyses of products and the unreacted starting ketone were performed with a gas chromatograph. Valerophenone was used as an actinometer.[15]

General procedure for preparative irradiation in solution

A solution of a ketone (ca 0.05 mol dm^{-3}) was irradiated with the 450 W high-pressure mercury lamp. After removal of the solvent, the residue was chromatographed on a silica gel column with hexane—ethyl acetate as eluent.

7-Phenylhepten-4,7-dione (4). 61%; ν_{max}(neat) 1685 and 1720 cm^{-1}; δ_H (CDCl$_3$) 2.78 (2H, t, J 6.6, CH$_2$), 3.17 (2H, t, J 6.6, CH$_2$COPh), 3.20 (2H, d, J 6.9, CH$_2$C═C), 5.08 (1H, dd, J 17.1 and 1.6, olefinic), 5.10 (1H, dd, J 10.2 and 1.6, olefinic), 5.87 (1H, ddt, J 17.1, 10.2 and 6.9, olefinic), 7.3–7.5 (3H, m, aromatic) and 7.8–7.9 (2H, m, aromatic). Found: C, 77.33; H, 7.13. C$_{13}$H$_{14}$O$_2$ requires C, 77.20; H, 6.98%.

6-Hydroxy-6-phenylbicyclo[3.1.1]heptan-3-ones (5). 25%; ν_{max}(neat) 1740 and 3440 cm^{-1}; δ_H (CDCl$_3$) 1.8–2.9 (8H, m), 7.1–7.7 (5H, m, aromatic); m/z 202 (M$^+$). The isomers of the bicycloheptanones could not be isolated.

2-Hydroxy-2-phenylbicyclo[4.2.0]octan-5-one (9). 35%; m.p. 103.5–105 °C; ν_{max}(KBr) 1690 and 3370 cm^{-1}; δ_H (CDCl$_3$) 1.7–2.1 (2H, m, CH$_2$), 2.19 (1H, s, OH), 2.3–2.6 (3H, m, CH$_2$ + CH), 2.6–2.9 (2H, m, CH$_2$), 3.0–3.3 (1H, m, CH) and 7.3–7.5 (5H, m, aromatic); δ_C (CDCl$_3$) 21.4 (t), 23.2 (t), 38.3 (t), 39.2 (d), 39.7 (t), 47.3 (d), 77.5 (s), 124.9 (d, 2C), 127.4 (d), 128.6 (d, 2C), 146.4 (s) and 213.5 (s). Found: C, 77.90; H, 7.47. C$_{14}$H$_{16}$O$_2$ requires C, 77.75; H, 7.46%.

3-Acetyl-2-ethyl-1-phenylcyclobutanol (11). 4%, ν_{max}(neat) 1700, 1720 and 3450 cm^{-1}; δ_H (CDCl$_3$) 0.73 (3H, t, J 7.0, CH$_3$), 1.3–1.5 (2H, m, CH$_2$), 2.27 (3H, s, COCH$_3$), 2.3–2.7 (2H, m, CH$_2$), 2.94 (1H, q, J 7.8, CH), 3.50 (1H, tt, J 7.9 and 4.0, CH), 4.53 (1H, s, OH) and 7.1–7.5 (5H, m, aromatic). Complete purification of this compound could not be achieved.

4-Ethoxycarbonyl-2-hydroxy-2-phenylbicyclo[4.2.0]octan-5-one (13). 51%; m.p. 100 – 102 °C; ν_{max}(KBr) 1700, 1720 and 3475 cm^{-1}; δ_H (CDCl$_3$) 1.24 (3H, t, J 7.0, CH$_3$), 1.7–2.6 (6H, m, 3 × CH$_2$), 2.19 (1H, s, OH), 2.93 (2H, ABq, J 17.1, CH$_2$), 3.41 (1H, dd, J 3.8 and 7.7, CH), 4.15 (2H, q, J 7.0, CH$_2$) and 7.3–7.5 (5H, m, aromatic); δ_C (CDCl$_3$) 14.1 (q), 20.6 (t), 3.96 (t), 42.7 (t), 52.9 (d), 53.2 (s), 61.7 (t), 76.9 (s), 124.8 (d, 2C), 127.6 (d), 128.6 (d, 2C), 145.5 (s), 171.4 (s) and 209.5 (s). Found: C, 70.90; H, 6.92. C$_{17}$H$_{20}$O$_4$ requires C, 70.81; H, 6.99%.

General procedure for preparative irradiation on silica gel

Five grams of silica gel and ca 1.5 mmol of **6** or **14** in 20 cm^3 of dichloromethane were placed in a 50 cm^3 of round-bottomed flask. The mixture was sonicated for 5 min and then the solvent was evaporated under reduced pressure. The coated silica gel was separated into five nearly equal portions, each of which was placed in a 18×180 mm Pyrex culture tube. The tubes were rotated and irradiated with a 100 W high-pressure mercury lamp. The irradiated silica gel was collected and placed in a 50 cm^3 round-bottomed flask. Acetone (20 cm^3) was added and the mixture was sonicated for 10 min. The silica gel was separated by filtration and washed with 10 cm^3 of acetone. The filtrate and washings were collected and then the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column. Elution with hexane–ethyl acetate gave unreacted starting ketone and photoproducts.

Determination of relative quantum yield for production of 7 on a silica gel surface

Each of a 0.3 mmol amount of **6**, **14** and valerophenone was loaded on 1.0 g of silica gel (the surface coverage was <60%). The coated silica gel was placed in

18×180 mm Pyrex culture tubes. The tubes were rotated and irradiated with 313 nm radiation from a 100 W high-pressure mercury lamp. After the irradiation, $4 \, cm^3$ of acetone containing a known amount of hexadecane as a calibrant were added and the mixture was sonicated for 10 min. The supernatant solutions were analyzed to determine the amounts of **7**.

Acknowledgement

REFERENCES

1. Wagner PJ. *Acc. Chem. Res.* 1971; **4**: 168–177; Wagner PJ. *Acc. Chem. Res.* 1983; **16**: 461–467; Wagner PJ. In *Rearrangements in Ground and Excited States*, vol. 3, de Mayo P (ed). Academic Press: New York, 1980; 381–444; Scaiano JC, Lissi EA, Encina MV. *Rev. Chem. Intermed.* 1978; **2**: 139–196.
2. Wagner PJ, Kelso PA, Kemppainen AE, McGrath JM, Schott HN, Zepp RG. *J. Am. Chem. Soc.* 1972; **94**: 7506–7512.
3. (a) Wamser CC, Wagner WR. *J. Am. Chem. Soc.* 1981; **103**: 7232–7234; (b) Ariel S, Evans S, Omkaram N, Scheffer JR, Trotter J. *J. Chem. Soc., Chem. Com.* 1986; 375–377; (c) Ariel S, Ramamrthy V, Scheffer JR, Trotter J. *J. Am. Chem. Soc.* 1983; **105**: 6959–6960; (d) Ariel S, Evans S, G-Garibay M, Harkness BR, Omkaram N, Scheffer JR, Trotter J. *J. Am. Chem. Soc.* 1988; **110**: 5591–5592.
4. Wagner PJ, Kelso PA, Kemppainen AE, Zepp RG. *J. Am. Chem. Soc.* 1972; **94**: 7500–7506.
5. (a) Padwa A, Eastman D. *J. Am. Chem. Soc.* 1969; **91**: 462–467; (b) Lewis FD, Johnson RW. *Tetrahedron Lett.* 1973; 2557–2560; (c) Lewis FD, Johnson RW, Johnson DE. *J. Am. Chem. Soc.* 1974; **96**: 6090–6099.
6. Xia W, Scheffer JS, Botoshansky M, Kaftory M. *Org. Lett.* 2005; **7**: 1315–1318.
7. McIntosh CL. *Can. J. Chem.* 1967; **45**: 2267–2270.
8. Hasegawa T, Nishimura M, Yoshioka M. *J. Phys. Org. Chem.* 1990; **3**: 230–234.
9. Hasegawa T, Nishimura M, Kodama Y, Yoshioka M. *Bull. Chem. Soc. Jpn.* 1990; **63**: 935–937.
10. Lewis FD, Johnson RW. *J. Am. Chem. Soc.* 1972; **94**: 8914–8916.
11. Scheffer JR, Garibay M, Nalamasu O. In *Organic Photochemistry*, vol. 8, Padwa A (ed). Marcel Dekker: New York, 1988; 249–347.
12. Juaristi E. *Introduction to Stereochemistry and Conformational Analysis.* Wiley: New York, 1991; 255–258.
13. Goswami PC, de Mayo P, Ramhath N, Bernard G, Omkaram N, Scheffer J, Wong YF. *Can. J. Chem.* 1985; **63**: 2719–2725.
14. Wagner PJ. *Tetrahedron Lett.* 1967; 1753–1756.
15. Lewis FD, Hilliard TA *J. Am. Chem. Soc.* 1970; **22**: 6672–6674.
16. Hasegawa T. *Recent Res. Dev. Photochem. Photobiol.* 1997; **1**: 19–39.
17. Wagner PJ, Kemppainen AE, Schott HN. *J. Am. Chem. Soc.* 1972; **95**: 5604–5614.
18. Weis LD, Evans TR, Leermarkers PA. *J. Am. Chem. Soc.* 1968; **90**: 6109–6118.
19. Kosower E.M. *J. Am. Chem. Soc.* 1958; **80**: 3253–3260.
20. Mitani M, Tamada M, Uehara S, Koyama K. *Tetrahedron Lett.* 1984; **25**: 2805–2808.
21. Baumgarten HF, Creger PL, Villars CE. *J. Am. Chem. Soc.* 1958; **80**: 6609–6612.
22. Raffaello R, Trave R. *Gazz. Chim. Ital.* 1950; **80**: 496–501.
23. Murov SL, *Handbook of Photochemistry.* Marcel Dekker: New York, 1973; 99.
24. Altomare Cascarano AG, Giacovazzo C, Guagliardi A, Burla M, Polodori G, Camali M. *J. Appl. Crystallogr.* 1994; **27**: 435–436.
25. Beurskens PT, Admiraal G, Eurskens G, Bosman WP, de Gelder R, Israel R, Smits JMM. *The DIRDIF-99 Program System, Technical Report of the Crystallography Laboratory.* University of Nijmegen: Nijmigen, 1999.
26. Cromer DT, Waber JT. In *International Tables for X-Ray Crystallography*, vol. IV. Ibero JA, Hamiltone WC (eds). Kynoch Press: Birmingham, 1974; Table 2.2A.
27. Ibers JA, Hamilton WC. *Acta Crystallogr.* 1964; **17**: 781–782.
28. Creagh DC, McAuley WJ. In *International Tables for Crystallography*, vol. C. Wilson AJC (ed). Kluwer: Boston, 1992; Table 4.2.6.8, 219–222.
29. Creagh DC, Hubbell JH. In *International Tables for Crystallography*, vol. C. Wilson AJC (ed). Kluwer: Boston, 1992; Table 4.2.4.3, 200–206.
30. *CrystalStructure 2.00.* Rigaku/MSC: The Woodland, TX, 2001.
31. Watkin DJ, Prout CK, Carruthers JR, Betteridge PW. *CRYSTALS*, Issue 10. Chemical Crystallography Laboratory: Oxford, 1996.