

Photochemistry of Substituted 2-Benzoylcyclohexanones

Tadashi HASEGAWA,* Yiming YANG, and Michikazu YOSHIOKA†

Department of Chemistry, Tokyo Gakugei University,
Nukuikitamachi, Koganei, Tokyo 184† Department of Chemistry, Saitama University,
Shimo-okubo, Urawa, Saitama 338

(Received June 28, 1991)

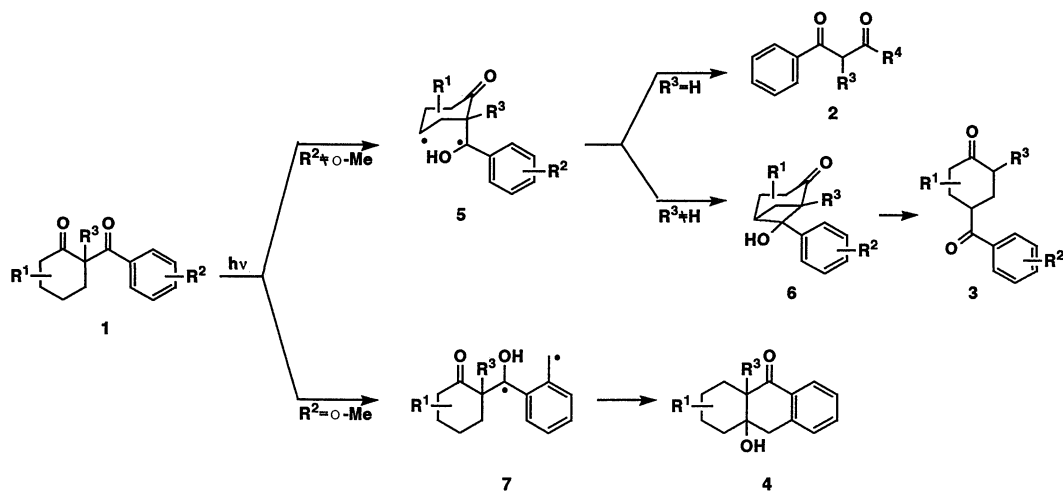
Synopsis. The photoreactivities of substituted 2-benzoylcyclohexanones were distinguished as three different types; 1) the exclusive Norrish Type II cleavage when there were no alkyl groups on the 2- nor on the ortho-position, 2) the benzoyl group shift from the 2- to the 4-position when an alkyl group was present on the 2- and not on the ortho-position, and 3) 1,2,3,4,4a,9a-hexahydro-9(10*H*)-anthracenone derivative formation when an ortho-methyl group was present.

The Norrish Type II photoreactions of alkyl phenyl ketones have been investigated extensively.¹⁾ In the Type II reaction, the cleavage generally competes with the cyclization. We have reported that 2-benzoylcyclohexanone (**1a**) underwent an exclusive Type II cleavage reaction to give **2a** and that the enol from of **2a** acted as an effective internal filter.²⁾ A 1-phenyl-1,3-alkanedione has been utilized to prevent the coloration of polymers, and ability and efficiency as a preventer are known to be affected by the alkyl chain length of the diketone and alkyl substituents on the chain.³⁾ Compound **2a** may be utilized as a good preventer with a C=C double bond at the end of the alkyl chain. The Type II cleavage reaction of substituted 2-benzoylcyclohexanones **1** is expected to be a useful method for the preparation of substituted 1-phenyl-6-heptene-1,3-diones **2**. The ratio of the cleavage to the cyclization in the Type II reaction was reported to be affected by α - and β -substituents.⁴⁾ We recently found that the introduction of a methyl group to the 2-position of **1a** resulted in a remarkable changeover in the reaction course.⁵⁾ We report here a substituent effect on the product distribution in the Type II reaction of substituted 2-benzoylcyclohexanones.

The substituted 2-benzoylcyclohexanones **1c**, **d**, **f**, and **g** have no 2- nor ortho-alkyl substituents. Irradiation of these compounds in benzene under nitrogen with a 450 W high-pressure mercury lamp through a Pyrex filter gave the corresponding Type II cleavage products in high yields as in the case of **1a**.²⁾ The photoreactions are applicable to the synthesis of **2** because of high product yields.

On the other hand, irradiation of **1i** and **1j**, both of which have 2-methyl groups, gave a pair of isomers of the 1,4-aroyl shift products **3i** and **3j**, respectively. Irradiation of **1k**, which has a 4-methyl group in addition to the 2-methyl group, gave an intractable mixture. Formation of **3** can be explained in terms of the Type II cyclization followed by the cyclobutanol ring opening as reported in the case of **1b**.⁵⁾ The enhanced cyclization caused by the 2-methyl group can be explained in terms of the presence of an unfavourable nonbonding interaction in the transition state during the elimination.⁶⁾ The 4-methyl group may prevent the recombination of the radical centers in the 1,4-biradical intermediate **5k** because of steric repulsion so as to reduce the yield of the Type II product **3k**. Two isomers of **3**, cis and trans isomers with respect to the C4-aroyl and C2-methyl groups, might be produced in the process of the cyclobutanol ring opening.⁵⁾ The major isomer seems to be the more stable trans isomer.

Compound **1l** has two γ -hydrogens, one on the ethyl group and one on the cyclohexanone ring. However, only the γ -hydrogen on the ring was abstracted by the excited benzoyl oxygen. Irradiation of **1l** gave **3l** in a



Scheme 1.

Table 1. Product Yields in the Type II Reaction of 1

Ketone	R ¹	R ²	R ³	R ⁴	Yield/%			Ref.
					2	3 ^{a)}	4	
a	H	H	H	CH ₂ CH ₂ CH=CH ₂	82	0	—	2)
b	H	H	Me		0	79/11	—	5)
c	4-Me	H	H	CH ₂ CH ₂ CMe=CH	68	0	—	
d	6-Me	H	H	CHMeCH ₂ CH=CH ₂	72	0	—	
e	H	<i>o</i> -Me	H		0	0	57	7)
f	H	<i>m</i> -Me	H	CH ₂ CH ₂ CH=CH ₂	97	0	—	
g	H	<i>p</i> -Me	H	CH ₂ CH ₂ CH=CH ₂	99	0	—	
h	H	<i>o</i> -Me	Me		0	0	93	
i	H	<i>m</i> -Me	Me		0	78/20	—	
j	H	<i>p</i> -Me	Me		0	70/17	—	
k	4-Me	H	Me	CH ₂ CH ₂ CMe=CH ₂	x	x	x ^{b)}	
l	H	H	Et		0	75/16	—	

a) Two isomers with respect to C4-aroyl and C2-alkyl groups were isolated. b) An intractable mixture was formed.

91% yield. No products derived from ethyl hydrogen abstraction were detected. The axial hydrogen at the 4-position seemed to be more favored for abstraction by the benzoyl carbonyl group than γ -hydrogen on the ethyl group because of geometrical preference.

The excited aroyl oxygen in **1** could abstract a γ -hydrogen on the ortho-methyl group when the group was present.^{7,8)} Hornback *et al.* reported that photolysis of **1e** gave **4e** in a 57% yield via intramolecular hydrogen abstraction from the ortho-methyl group.⁷⁾ Compound **1h** had a methyl group on C2 as well as the ortho-position. The presence of the 2-methyl group was expected to affect the direction of hydrogen abstraction. However, irradiation of **1h** gave only the product via the ortho-methyl hydrogen abstraction in a 93% yield. No products arising from abstraction of the C4-hydrogen could be detected. Formation of **4** may be explained in terms of trapping of the benzyl radical center by the cyclohexanone carbonyl.⁷⁾ The 2-methyl group seemed to promote the trapping process.

Experimental

The IR spectra were recorded with a JASCO A-3 spectrometer, ¹H and ¹³C NMR spectra were measured with a JEOL FX90Q spectrometer using tetramethylsilane as an internal standard. An Ushio 450 W high-pressure mercury lamp was used as an irradiation source. The substituted 2-benzoylcyclohexanones without a 2-methyl group were prepared from the corresponding morpholinocyclohexanone and aroyl chloride⁹⁾ and 2-methylation was performed using a phase-transfer catalyst.⁵⁾

General Procedure for Irradiation of 1. A solution of the substituted 2-benzoylcyclohexanone **1** (ca. 2 mmol) in 50 cm³ of benzene was irradiated under nitrogen with a 450 W high-pressure mercury lamp through a Pyrex filter. After removing the solvent the residue was chromatographed on a silica-gel column. Elution with a mixture of benzene and ethyl acetate gave **2**, **3**, or **4**.

4-Benzoyl-2-methylcyclohexanone (3b): Major isomer: 79%⁵⁾ yield. Minor isomer: 11% yield; bp 120–121 °C/3 mmHg (1 mmHg=133.322 Pa); IR (neat) 1680 and 1710 cm⁻¹; ¹H NMR (CDCl₃) δ =1.09 (3H, d, *J*=6.7 Hz, CH₃), 1.7–2.9 (7H, m, CH and CH₂), 3.81 (1H, quint, *J*=5.1 Hz, CHCOPh), 7.4–7.7 (3H, m, aromatic), and 7.9–8.1 (2H, m, aromatic); ¹³C NMR (CDCl₃) δ =15.2 (q), 28.4 (t), 36.2 (t), 38.0 (t), 39.7 (d),

41.6 (d), 128.4 (d, 2C), 128.8 (d, 2C), 132.8 (d), 135.9 (s), 202.5 (s), and 212.9 (s). Found: C, 77.65; H, 7.61%. Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46%.

6-Methyl-1-phenyl-6-heptene-1,3-dione (2c): 68% yield; bp 112–115 °C/2 mmHg; IR (neat) 1600 cm⁻¹; ¹H NMR (CDCl₃) δ =1.79 (3H, s, CH₃), 2.3–2.8 (4H, m, CH₂), 4.11 (0.14H, s, CH₂), 4.78 (2H, s, olefinic), 6.22 (0.93H, s, olefinic), 7.3–7.6 (3H, m, aromatic), 7.8–8.0 (2H, m, aromatic), and 16.23 (0.93H, bs, OH). Found: C, 77.69; H, 7.39%. Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46%.

4-Methyl-1-phenyl-6-heptene-1,3-dione (2d): 72% yield; bp 110–113 °C/2 mmHg; IR (neat) 1600 cm⁻¹; ¹H NMR (CDCl₃) δ =1.21 (3H, d, *J*=6.6 Hz, CH₃), 2.1–2.7 (3H, m, CH and CH₂), 4.11 (0.14H, s, CH₂), 5.01 (1H, d, *J*=1.3 Hz, olefinic), 5.12 (1H, d, *J*=5.3 Hz, olefinic), 5.6–6.0 (1H, m, olefinic), 6.16 (0.93H, s, olefinic), 7.4–7.6 (3H, m, aromatic), 7.8–8.0 (2H, m, aromatic), and 16.31 (0.93H, bs, OH). Found: C, 77.49; H, 7.69%. Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46%.

1-(3-Methylphenyl)-6-heptene-1,3-dione (2f): 97% yield; bp 115–120 °C/2 mmHg; IR (neat) 1600 cm⁻¹; ¹H NMR (CDCl₃) δ =2.3–2.8 (4H, m, CH₂), 2.36 (3H, s, CH₃), 4.02 (0.18H, s, CH₂), 4.94 (1H, d, *J*=1.4 Hz, olefinic), 5.10 (1H, d, *J*=7.5 Hz, olefinic), 5.7–6.1 (1H, m, olefinic), 6.13 (0.91H, s, olefinic), 7.3–7.5 (2H, m, aromatic), 7.6–7.8 (2H, m, aromatic), and 16.33 (0.91, s, OH). Found: C, 77.73; H, 7.59%. Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46%.

1-(4-Methylphenyl)-6-heptene-1,3-dione (2g): 99% yield; bp 115–120 °C/2 mmHg; IR (neat) 1580 cm⁻¹; ¹H NMR (CDCl₃) δ =2.3–2.6 (4H, m, CH₂), 2.34 (3H, s, CH₃), 3.99 (0.2H, s, CH₂), 4.93 (1H, bs, olefinic), 5.08 (1H, d, *J*=8.5 Hz, olefinic), 5.7–6.1 (1H, m, olefinic), 6.10 (0.9H, s, olefinic), 7.17 (2H, d, *J*=8.4 Hz, aromatic), 7.73 (2H, d, *J*=8.4 Hz, aromatic), and 16.29 (0.9H, bs, OH). Found: C, 77.76; H, 7.30%. Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46%.

4a-Hydroxy-9a-methyl-1,2,3,4,4a,9a-hexahydro-9(10H)-anthracenone (4h): 93% yield; mp 127.5–135 °C; IR (KBr) 1670, 1685, 3480, and 3520 cm⁻¹; ¹H NMR (CDCl₃) δ =1.13 (3H, s, CH₃), 1.3–2.1 (8H, m, CH₂), 1.19 (1H, s, OH), 2.93 (2H, ABq, *J*=17.6 Hz, CH₂), 7.0–7.6 (3H, m, aromatic), and 7.95 (1H, d, *J*=5.8 Hz, aromatic); ¹³C NMR (CDCl₃) δ =19.8 (t), 20.7 (t), 20.8 (q), 27.6 (t), 34.3 (t), 40.5 (t), 49.3 (s), 75.0 (s), 126.6 (d), 127.5 (d), 129.2 (d), 131.7 (s), 133.0 (d), 138.6 (s), and 202.1 (s). Found: C, 78.32; H, 7.74%. Calcd for C₁₅H₁₈O₂: C, 78.23; H, 7.88%.

4-(3-Methylbenzoyl)-2-methylcyclohexanone (3i): Major isomer: 78% yield; bp 130–135 °C/2 mmHg; IR (neat) 1680 and 1710 cm⁻¹; ¹H NMR (CDCl₃) δ =1.07 (3H, d, *J*=6.2 Hz, CH₃), 1.4–2.8 (7H, m, CH and CH₂), 2.43 (3H, s, CH₃), 3.82 (1H, tt,

$J=3.9$ and 11.5 Hz, CHCOPh), $7.3-7.5$ (2H, m, aromatic), and $7.7-7.9$ (2H, m, aromatic); ^{13}C NMR (CDCl_3) $\delta=14.4$ (q), 21.3 (q), 30.0 (t), 38.1 (t), 40.3 (t), 43.9 (d), 44.5 (d), 125.3 (d), 128.7 (d), 128.8 (d), 133.9 (d), 136.0 (s), 138.5 (s), 201.3 (s), and 210.6 (s). Found: C, 78.16; H, 7.88%. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88%.

Minor isomer: 20% yield; bp $120-125^\circ\text{C}/2$ mmHg; IR (neat) 1680 and 1710 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.08$ (3H, d, $J=6.7$ Hz, CH_3), $1.6-2.9$ (7H, m, CH and CH_2), 2.43 (3H, s, CH_3), 3.77 (1H, quint, $J=4.8$ Hz, CHCOPh), $7.4-7.5$ (2H, m, aromatic), and $7.7-7.9$ (2H, m, aromatic); ^{13}C NMR (CDCl_3) $\delta=15.3$ (q), 21.3 (q), 28.3 (t), 36.1 (t), 37.9 (t), 40.0 (d), 41.6 (d), 125.5 (d), 128.7 (d), 128.9 (d), 133.7 (d), 136.5 (s), 138.6 (s), 202.4 (s), and 211.8 (s). Found: C, 78.24; H, 7.81%. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88%.

4-(4-Methylbenzoyl)-2-methylcyclohexanone (3j): Major isomer: 70% yield; mp $74-74.5^\circ\text{C}$; IR (KBr) 1675 and 1710 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.08$ (3H, d, $J=5.9$ Hz, CH_3), $1.4-2.7$ (7H, m, CH and CH_2), 2.45 (3H, s, CH_3), 3.83 (1H, tt, $J=7.2$ and 11.7 Hz, CHCOPh), 7.37 (2H, d, $J=8.7$ Hz, aromatic), and 7.94 (2H, d, $J=8.7$ Hz, aromatic); ^{13}C NMR (CDCl_3) $\delta=13.9$ (q), 21.0 (q), 29.6 (t), 37.8 (t), 39.8 (t), 43.4 (d), 43.8 (d), 127.9 (d, 2C), 129.0 (d, 2C), 133.4 (s), 143.4 (s), 200.2 (s), and 209.7 (s). Found: C, 78.21; H, 7.81%. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88%.

Monor isomer: 17% yield; bp $120-123^\circ\text{C}/2$ mmHg; IR (neat) 1670 and 1710 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.08$ (3H, d, $J=6.7$ Hz, CH_3), $1.6-3.0$ (7H, m, CH and CH_2), 2.45 (3H, s, CH_3), 4.93 (1H, quint, $J=5.1$ Hz, CHCOPh), 7.29 (2H, d, $J=8.7$ Hz, aromatic), and 7.90 (2H, d, $J=8.7$ Hz, aromatic); ^{13}C NMR (CDCl_3) $\delta=15.1$ (q), 21.4 (q), 28.3 (t), 36.2 (t), 37.9 (t), 39.7 (d), 41.6 (d), 128.4 (d, 2C), 129.4 (d, 2C), 133.9 (s), 143.7 (s), 201.8 (s), and 211.9 (s). Found: C, 78.25; H, 7.80%. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88%.

4-Benzoyl-2-ethylcyclohexanone (3l): Major isomer: 75% yield; bp $125-128^\circ\text{C}/2$ mmHg; IR (neat) 1680 and 1710 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.91$ (3H, t, $J=7.2$ Hz, CH_3),

$1.1-2.6$ (9H, m, CH and CH_2), 3.83 (1H, tt, $J=7.2$ and 11.6 Hz, CHCOPh), $7.4-7.7$ (3H, m, aromatic), and $8.0-8.2$ (2H, m, aromatic); ^{13}C NMR (CDCl_3) $\delta=11.5$ (q), 22.2 (t), 30.0 (t), 35.5 (t), 40.6 (t), 44.5 (d), 50.7 (d), 128.2 (d, 2C), 128.8 (d, 2C), 133.0 (d), 136.5 (s), 201.3 (s), and 210.6 (s). Found: C, 77.97; H, 7.83%. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88%.

Minor isomer could not be separated completely from the major isomer. 16% yield (based on the ^1H NMR analysis); ^1H NMR (CDCl_3) $\delta=0.91$ (3H, t, $J=7.2$ Hz, CH_3), $1.2-2.6$ (9H, m, CH and CH_2), 3.83 (1H, quint, $J=5.8$ Hz, CHCOPh), $7.4-7.7$ (3H, m, aromatic), and $7.9-8.1$ (2H, m, aromatic); ^{13}C NMR (CDCl_3) $\delta=11.5$ (q), 23.4 (t), 28.4 (t), 33.7 (t), 38.1 (t), 39.8 (d), 49.1 (d), 128.2 (d, 2C), 128.8 (d, 2C), 133.0 (d), 136.5 (s), 202.5 (s), and 212.8 (s).

References

- 1) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971); "Rearrangements in Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), Vol. 3, p. 381.
- 2) T. Hasegawa, M. Nishimura, and M. Yoshioka, *J. Phys. Org. Chem.*, **3**, 230 (1990).
- 3) N. Kamiya, *Enkabirinu to Porima*, **25**, 7 (1985).
- 4) For instance, F. D. Lewis, and T. A. Hillard, *J. Am. Chem. Soc.*, **92**, 6672 (1970); *ibid.*, **94**, 3852 (1972).
- 5) T. Hasegawa, M. Nishimura, Y. Kodama, and M. Yoshioka, *Bull. Chem. Soc. Jpn.*, **63**, 935 (1990); we have not been able to assign the structure of the minor isomer of **3b**.
- 6) F. D. Lewis, R. W. Johnson, and R. A. Ruden, *J. Am. Chem. Soc.*, **94**, 4292 (1972).
- 7) J. M. Hornback, M. L. Poundstone, B. Vadlamani, S. M. Graham, J. Gabay, and S. T. Patton, *J. Org. Chem.*, **53**, 5597 (1988).
- 8) M. Yoshioka, K. Nishizawa, M. Arai, and T. Hasegawa, *J. Chem. Soc., Perkin Trans. 1*, **1991**, 541.
- 9) R. S. Monson, "Advanced Organic Synthesis," Academic Press, New York (1971), p. 81.