Photochemistry of Substituted 2-Benzoylcyclohexanones

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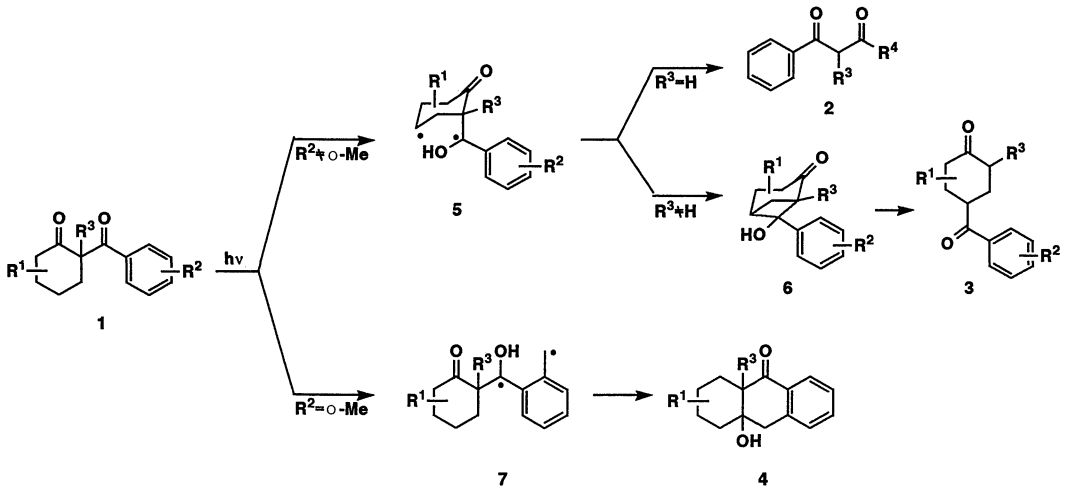
Synopsis. The photoreactivities of substituted 2-benzoylcyclohexanones were distinguished as three different types; 1) the exclusive Norrish Type II cleavage when there were no alkyl groups on the 2- nor on the ortho-position, 2) the benzoyl group shift from the 2- to the 4-position when an alkyl group 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 **11** 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 **11** gave **31** 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	$CH_2CH_2CH=CH_2$	82	0	—	2)
b	H	H	Me		0	79/11	—	5)
c	4-Me	H	H	$CH_2CH_2CMe=CH$	68	0	—	
d	6-Me	H	H	$CHMeCH_2CH=CH_2$	72	0	—	
e	H	*o*-Me	H		0	0	57	7)
f	H	*m*-Me	H	$CH_2CH_2CH=CH_2$	97	0	—	
g	H	*p*-Me	H	$CH_2CH_2CH=CH_2$	99	0	—	
h	H	*o*-Me	Me		0	0	93	
i	H	*m*-Me	Me		0	78/20	—	
j	H	*p*-Me	Me		0	70/17	—	
k	4-Me	H	Me	$CH_2CH_2CMe=CH_2$	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 geometical 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 ^{13}C 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 chloride[9] 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 cm^3 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 ($CDCl_3$) δ= 1.09 (3H, d, J=6.7 Hz, CH_3), 1.7—2.9 (7H, m, CH and CH_2), 3.81 (1H, quint, J=5.1 Hz, CHCOPh), 7.4—7.7 (3H, m, aromatic), and 7.9—8.1 (2H, m, aromatic); ^{13}C NMR ($CDCl_3$) 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 $C_{14}H_{16}O_2$: 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 ($CDCl_3$) δ=1.79 (3H, s, CH_3), 2.3—2.8 (4H, m, CH_2), 4.11 (0.14H, s, CH_2), 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 $C_{14}H_{16}O_2$: 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 ($CDCl_3$) δ=1.21 (3H, d, J=6.6 Hz, CH_3), 2.1—2.7 (3H, m, CH and CH_2), 4.11 (0.14H, s, CH_2), 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 $C_{14}H_{16}O_2$: 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 ($CDCl_3$) δ=2.3—2.8 (4H, m, CH_2), 2.36 (3H, s, CH_3), 4.02 (0.18H, s, CH_2), 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 $C_{14}H_{16}O_2$: 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 ($CDCl_3$) δ=2.3—2.6 (4H, m, CH_2), 2.34 (3H, s, CH_3), 3.99 (0.2H, s, CH_2), 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 $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

4a-Hydroxy-9a-methyl-1,2,3,4,4a,9a-hexahydro-9(10*H*)-anthracenone (4h): 93% yield; mp 127.5—135 °C; IR (KBr) 1670, 1685, 3480, and 3520 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.13 (3H, s, CH_3), 1.3—2.1 (8H, m, CH_2), 1.19 (1H, s, OH), 2.93 (2H, ABq, J=17.6 Hz, CH_2), 7.0—7.6 (3H, m, aromatic), and 7.95 (1H, d, J=5.8 Hz, aromatic); ^{13}C NMR ($CDCl_3$) 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 $C_{15}H_{18}O_2$: 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 ($CDCl_3$) δ=1.07 (3H, d, J=6.2 Hz, CH_3), 1.4—2.8 (7H,m, CH and CH_2), 2.43 (3H, s, CH_3), 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 ($CDCl_3$) δ=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 $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

Minor isomer: 20% yield; bp 120—125 °C/2 mmHg; IR (neat) 1680 and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=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 ($CDCl_3$) δ=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 $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

4-(4-Methylbenzoyl)-2-methylcyclohexanone (3j): Major isomer: 70% yield; mp 74—74.5 °C; IR (KBr) 1675 and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=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 ($CDCl_3$) δ=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 $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

Monor isomer: 17% yield; bp 120—123 °C/2 mmHg; IR (neat) 1670 and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=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 ($CDCl_3$) δ=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 $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

4-Benzoyl-2-ethylcyclohexanone (31): Major isomer: 75% yield; bp 125—128 °C/2 mmHg; IR (neat) 1680 and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=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 ($CDCl_3$) δ=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 $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

Minor isomer could not be separated completely from the major isomer. 16% yield (based on the ^{1}H NMR analysis); ^{1}H NMR ($CDCl_3$) δ=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 ($CDCl_3$) δ=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).

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