March, 1990] © *1990 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 63, 935—937 (1990)*

Photochemical Reaction of 1,3-Diketones. Transformation of 2-Benzoyl-2-methylcyclohexanones to 4-Benzoyl-2-methylcyclohexanones

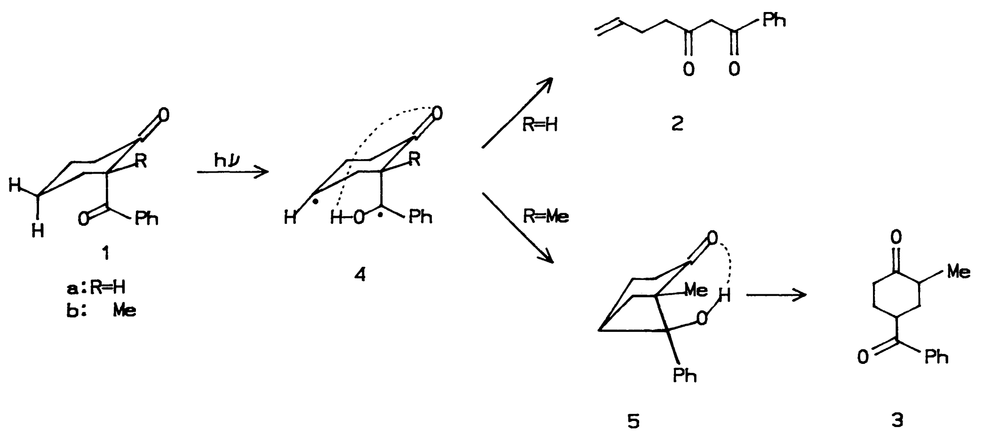
Tadashi HASEGAWA,* Michiko NISHIMURA, Yukio KODAMA,† and Michikazu YOSHIOKA*,†
Department of Chemistry, Tokyo Gakugei University, Nukuikitamachi, Koganei, Tokyo 184
†Department of Chemistry, Saitama University, Shimo-okubo, Urawa, Saitama 338
(Received September 12, 1989)

Synopsis. Upon irradiation, 2-benzoyl-2-methylcyclohexanone gave 4-benzoyl-2-methylcyclohexanone via Type II cyclization and a subsequent ring opening in 79% yield, whereas 2-benzoylcyclohexanone gave only the Type II elimination product. 2-Benzoyl-2-methyl-1-tetralone also underwent phototransformation to 4-benzoyl-2-methyl-1-tetralone.

Type II photoelimination and cyclization reactions of alkyl aryl ketones have been extensively investigated.[1] These reactions involve a 1,4-biradical intermediate, formed through γ-hydrogen abstraction by the excited carbonyl group.[2,3] Aryl cycloalkyl ketones also undergo Type II reactions, though the quantum yields are not high.[4] The introduction of a carbonyl group to the α-position of the cycloalkane ring in the aryl cycloalkyl ketones increases the photoreactivity of the ketones. The quantum yield of Type II elimination for 2-benzoylcyclohexanone (**1a**)[5] is ca. 34-times higher than that for benzoylcyclohexane.[4e] A methyl group on the α-carbon of aryl cycloalkyl ketones favors the Type II cyclization over elimination, along with an enhancement of the the α-cleavage.[4c,e] We report here on the photoreaction of 2-benzoylcyclohexanones in which a remarkable changeover in the reaction course was produced by introducing a methyl group on the 2-position.

Previously, the photoreaction of **1a** was reported to give only a Type II elimination product, 1-phenyl-6-heptene-1,3-dione (**2**), in 71—82% yield.[5,6] No evidence for the formation of the cyclization product has been observed.[5—7] On the other hand, irradiation of **1b** gave **3** in 79% yield. The structure of **3** was elucidated from spectral data and elemental analysis. The ^{1}H NMR spectrum of **3** showed a doublet methyl signal (δ 1.08) and a C$_4$-hydrogen signal being coupled to four hydrogens (δ 3.93). Neither the Type II elimination product nor α-cleavage products could be isolated. On the contrary, the photoreaction of **1a** yielded no 4-benzoylcyclohexanone, corresponding to a photorearrangement. Similarly, a photorearrangement of 2-benzoyl-2-methyl-1-tetralone (**6**) in benzene gave a rearranged product, **8**, in 36% yield,[8] while 2-benzoyl-1-tetralone, which exists almost completely in the enol form, did not show any photoreactivity. The ^{1}H NMR of **8** showed a methyl doublet (δ 1.31) and a C$_4$-methine hydrogen coupled with two hydrogens (δ 5.09).

The formation of the 4-benzoylcyclohexanone **3** and the 4-benzoyltetralone **8** can be explained in terms of a retro-aldol type ring opening of Type II cyclization products **5** and **7**, respectively. The undetectability of the bicyclic alcohol, both **5** and **7**, is not surprising in view of their thermal instability. We have already reported a similar rearrangement, ethyl 2-benzoylvalerates rearranged to ethyl 4-benzoylvalerates via cyclobutanols,[9] though the chemical and the quantum yield were low. In that case, the main reaction course was Type II elimination.[9] The rearrangement of **1b** was very efficient. The quantum yields for the



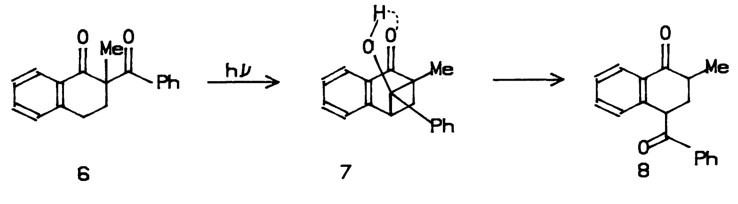


Table 1. Quantum Yields and Kinetic Data

Ketone	ϕ_{cy}[a]	ϕ_{el}[b]	ϕ_{α}[c]	$k_q\tau$[d] M^{-1}	τ 10^{-9} s	$1/\tau$ 10^{8} s^{-1}	Ref.
Benzoylcyclohexane	—[e]	0.024	—	0.74	0.15	68	4e
1-Methylbenzoylcyclohexane	0.045[f]	—	0.20[f]	29	5.8	1.7	4e
1a	—	0.82	—	9.1	1.8	5.5	5
1b	0.79	—	—	56	11.2	0.9	

a) Quantum yield for Type II cyclization product formation in benzene. b) Quantum yield for Type II elimination product formation in benzene. c) Quantum yield for α-cleavage product formation. d) Slope of Stern–Volmer plots for quenching of Type II product. e) Not detected. f) In 0.01 M dodecanethiol–benzene.

formation of the 4-benzoylcyclohexanone, **3**, and the disappearance of the starting ketone, **1b**, were 0.79 and unity, respectively. These values indicate the absence of the reverse hydrogen-transfer process from the 1,4-biradical intermediate, **4b**, to the starting material, **1b**, because of intramolecular hydrogen bonding between the hydroxyl and the cycloalkanone carbonyl groups. The hydrogen bonding between the hydroxyl group and the cyclohexanone carbonyl group also possible in the cyclobutanol, **5** and so the ring opening occurs easily.[9] The changeover from exclusive Type II elimination to exclusive Type II cyclization upon α-methyl substitution has rarely been observed. In a rigid bicycloalkyl phenyl ketone system, a 2-benzoylbicyclo[2.2.2]octane and 2-benzoyl-2-methylbicyclo-[2.2.2]octane pair, this changeover has been reported.[4c] However, in a flexible monocycloalkyl phenyl ketone system, the main competing process is the α-cleavage reaction; 1-benzoyl-1-methylcyclohexane mainly gave an α-cleavage product, together with Type II cyclization product.[4e] The enhanced formation of a Type II cyclization product caused by the α-methyl group can be explained analogously to a similar behavior in acyclic and cyclic alkyl aryl ketones with the α-methyl group, in terms of the presence of unfavourable nonbonding interactions in the transition states for elimination.[4c,10]

The photoreaction of **1b** was quenched by 2,5-dimethyl-2,4-hexadiene with a linear Stern–Volmer plots. The kinetic data are summarized in Table 1. The $k_q\tau$ value was determined to be 56 M^{-1}. The lifetime (τ) and $1/\tau$ values were calculated to be 11.2×10^{-9} s and 0.9×10^{8} s^{-1} respectively, assuming k_q to be the diffusion-controlled rate constant (5×10^{9} M^{-1} s^{-1} in benzene). The lifetime (τ) of **1b** is twice that of 1-methylbenzoylcyclohexane. The rate constant for the γ-hydrogen abstraction (k_r) can be defined as $k_r=\phi_{\mathrm{Type\ II}}/\tau$. Therefore, the k_r value for **1b** can be calculated to be 0.71×10^{8} s^{-1}. This value is ca. 9-times larger than that for 1-methylbenzoylcyclohexane.[4e] These results reflect the fact that the Type II reaction is the main reaction course in **1b**, whereas α-cleavage is the main course in the 1-methylcyclohexane. This might be due to an increase in the population of favorable conformers for the γ-hydrogen abstraction because of a decrease in the ring flexibility by the introduction of a carbonyl group in the cycloalkane ring or a nonbonding carbonyl-carbonyl repulsive interaction.

Experimental

The IR spectra were recorded with a JASCO A-3 spectrometer, ^{1}H and ^{13}C NMR spectra were measured with a JEOL FX90Q or a Bruker AM400 spectrometer using tetramethylsilane as an internal standard, and the mass spectra were recorded with a JEOL JMS-O1SG-2 spectrometer. An Ushio 100 W or 450 W high-pressure mercury lamp was used as irradiation source.

Preparation of 2-Benzoyl-2-methylcyclohexanone (1b). A solution of tetrabutylammonium bromide (1.48 g, 4.6 mmol) and sodium hydroxide (0.38 g, 9.5 mmol) in 5 cm^3 water was added to a stirred solution of **1a** (0.92 g, 4.6 mmol) and methyl iodide (3.24 g, 2.3 mmol) in 5 cm^3 chloroform. The mixture was stirred overnight at room temperature and then extracted with 10 cm^3 of chloroform. The chloroform solution was washed with water and then dried over calcium chloride. After filtration the solvent was evaporated in vacuo. To the residue was added 10 cm^3 of benzene. An insoluble material in benzene was filtered off. The residue was chromatographed on silica-gel column (Merck Kieselgel 60). Elution with benzene gave **1b** (0.77 g, 3.6 mmol, 78%): bp 116 °C/3 mmHg (1 mmHg=133.222 Pa); IR (neat) 1670 and 1710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.17—2.97 (8H, m, CH$_2$), 1.47 (3H, s, CH$_3$), 7.14—7.63 (3H, m, aromatic), and 7.8—8.0 (2H, m, aromatic). Found: C, 77.51; H, 7.49%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

Preparation of 2-Benzoyl-2-methyl-1-tetralone (6). The diketone **6** was prepared according to a similar procedure previously reported by us.[11] Condensation of 1-tetralone (2.92 g, 20 mmol) and benzaldehyde (2.12 g, 20 mmol) using *N*-methylanilinomagnesium bromide (prepared from 20 mmol of ethylmagnesium bromide and 20 mmol of *N*-methylaniline) as a condensing agent followed by oxidation with Jones reagent gave 2-benzoyl-1-tetralone (2.00 g, 8.0 mol, 40%): mp 68 °C (from hexane); IR (CHCl$_3$) 1615 and 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.66—2.88 (4H, m, CH$_2$-CH$_2$), 7.05—7.75 (7H, m, aromatic), 7.80—8.15 (2H, m, aromatic), and 16.90 (1H, s, OH).[12] Found: C, 81.65; H, 5.71%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%. The 2-benzoyl-1-tetralone was methylated by methyl iodide (1.20 g, 8.5 mmol) and sodium hydride (0.34 g, 8.5 mmol) in benzene-DMF (2/1 (v/v), 20 cm^3) according to a method in the literature.[13] Column chromatography on silica gel eluted with hexane-ethyl acetate (6:1) and recrystallization from hexane gave **6** (1.3 g, 5.0 mmol, 63%): mp 102 °C; IR (CHCl$_3$) 1690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=4.59 (3H, s, CH$_3$), 1.75—2.36 (1H, m, 5-H), 2.58—3.35 (3H, m, 4-H$_2$ and 5-H), and 7.08—8.15 (9H, m, aromatic). Found: C, 81.86; H, 6.18%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

Photoreaction of 1b. A solution of **1b** (201 mg, 0.93 mmol) in 50 cm^3 of benzene was irradiated with a 450 W high-pressure mercury lamp through a Pyrex filter for

20 min. After removing the solvent the residue was chromatographed on a silica-gel column. Elution with benzene gave the unreacted starting ketone, **1b** (92 mg), and **3** (86 mg, 79%). **3**: mp 87—88 °C (from a mixture of benzene–hexane); IR (KBr) 1680 and 1720 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.08 (3H, d, J=6.5 Hz, $\mathrm{CH_3}$), 1.70 (1H, ddd, J=12.0, 12.0, and 12.0 Hz, 3-H), 1.97 (1H, ddd, J=6.5, 12.0, and 12.0 Hz, 5-H), 2.24—2.29 (2H, m, 3-H and 5-H), 2.47—2.82 (3H, m, 2-H and 6-$\mathrm{H_2}$), 3.93, (1H, dddd, J=3.3, 3.3, 12.0, and 12.0 Hz, 4-H), 7.49—7.62 (3H, m, aromatic), and 7.94—8.00 (2H, m, aromatic); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=14.3 (q), 29.7 (t), 37.9 (t), 40.3 (t), 43.8 (d), 44.1 (d), 128.1 (d, 2C), 128.7 (d, 2C), 133.2 (d), 135.7 (s), 201.3 (s), and 211.1 (s); MS m/z 216 ($\mathrm{M^+}$). Found: C, 77.74; H, 7.39%. Calcd for $\mathrm{C_{14}H_{16}O_2}$: C, 77.75; H, 7.41%.

Photoreaction of 6. A solution of **6** (599 mg, 2.274mmol) in 120 $\mathrm{cm^3}$ of benzene was irradiated with a 100 W high-pressure mercury lamp through a Pyrex filter for 2.5 h. After removing the solvent the residue was chromatographed on a silica-gel column. Elution with hexane–ethyl acetate (6:1) gave the unreacted starting ketone, **6** (353 mg), and the rearranged product, **8** (88 mg, 36%).[8] **8**: mp 78 °C (from cyclohexane); IR ($\mathrm{CHCl_3}$) 1690 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.31 (3H, d, J=6.5 Hz, $\mathrm{CH_3}$), 2.26 (1H, ddd, J=13.5, 13.5, and 13.5 Hz, 5-H), 2.36 (1H, ddd, J=4.5, 4.5, and 13.5 Hz, 5-H), 2.74 (1H, ddq, J=4.5, 13.5, and 6.5 Hz, 6-H), 5.09 (1H, dd, J=4.5 and 13.5 Hz, 4-H), 7.04 (1H, d, J=7.5 Hz), 7.39 (1H, t, J=7.5 Hz), 7.43 (1H, t, J=7.5 Hz), 7.52 (2H, t, J=7.5 Hz), 7.62 (1H, t, J=7.5 Hz), 8.03 (2H, d, J=7.5 Hz), and 8.12 (1H, d, J=7.5 Hz) (aromatic); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=15.3 (q), 35.6 (t), 41.9 (d), 47.6 (d), 127.4 (d), 127.8 (d), 128.6 (d), 128.8 (d, 2C), 128.9 (d, 2C), 132.7 (s), 133.4 (d), 133.6 (d), 136.7 (s), 142.2 (s), 199.1 (s), and 201.2 (s). Found: C, 81.61; H, 6.09%. Calcd for $\mathrm{C_{18}H_{16}O_2}$: C, 81.79; H, 6.10%.

Quantum Yields and Rate Constant Determination: Benzene solutions of **1b** (ca. 0.05 mol $\mathrm{l^{-1}}$) containing a known concentration of eicosane (ca. 0.001 mol $\mathrm{l^{-1}}$) as a caliburant, were placed in 15×150 mm Pyrex culture tubes. In quenching experiments, the solutions also contain appropriate concentrations of 2,5-dimethyl-2,4-hexadiene. The tubes were degassed with three freeze-pump-thaw cycles and then sealed. Irradiation was performed on a "merry-go-round" apparatus with a 450 W high-pressure mercury lamp. A potassium chromate filter solution was used to isolate the 313 nm line.[14] Analyses were performed on a Shimazu GC-4B gas chromatograph equipped with a flame ionization detector using a 2 m column containing OV-1. Quantum yields were determined by the use of a valerophenone actinometer.[2b]

References

1) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971); "Rearrangements in Ground and Excited States," ed by P. de Mayo, Vol. 3, Academic Press, New York (1980), p. 381.

2) a) P. J. Wagner and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 287 (1972); b) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *ibid.*, **94**, 7480 (1972); c) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, *ibid.*, **94**, 7506 (1972).

3) J. C. Scaiano, *Acc. Chem. Res.*, **15**, 252 (1982).

4) a)A. Padwa, E. Alexander, and M. Niemcyzk, *J. Am. Chem. Soc.*, **91**, 456 (1969); b) A. Padwa and D. Eastman, *ibid.*, **91**, 462 (1969); c) F. D. Lewis, R. W. Johnson, and R. A. Ruden, *ibid.*, **94**, 4292 (1972); d) A. Padwa and W. Eisenberg, *ibid.*, **94**, 5852 (1972); *ibid.*, **94**, 5859 (1972); e) F. D. Lewis, R. W. Johnson, and D. E. Johnson, *ibid.*, **96**, 6090 (1974); f) F. D. Lewis, R. W. Johnson, and D. R, Kory, *ibid.*, **96**, 6100 (1974); g) P. J. Wagner and B. J. Scheve, *ibid.*, **99**, 1858 (1977) and references cited therein.

5) T. Hasegawa, M. Nishimura, and M. Yoshioka, *J. Phys. Org. Chem.*, in press.

6) C. L. McIntosh, *Can. J. Chem.*, **45**, 2267 (1967).

7) M. F. Gorodetsky and Y. Mazur, *Tetrahedron Lett.*, **1963**, 369.

8) On silica-gel TLC, the R_f-value of the product **8** was close to that of the starting ketone **6**. Therefore, the complete separation of **8** required repeated chromatography, which caused the relatively low isolated yield of **8**. The GC analysis of the iradiation mixture revealed that the yield of **6** was 70% at 60% conversion.

9) T. Hasegawa, Y. Arata, M. Endoh, and M. Yoshioka, *Tetrahedron*, **41**, 1667 (1985).

10) F. D. Lewis and T. H. Hiward, *J. Am. Chem. Soc.*, **94**, 3852 (1974).

11) M. Yoshioka, M. Saitoh, H. Arai, K. Ichikawa, and T. Hasegawa, *Tetrahedron*, **43**, 5237 (1987).

12) These data indicates that 2-benzoyl-1-tetralone exists completely in the enol form in solution.

13) J. C. Shivers, M. L. Dilion, and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 119 (1947).

14) S. L. Murov, "Handbook of Photochemistry," Mercel Dekker, New York (1973), p. 99.