Type II Photoreaction of 2-Benzoylcycloalkanones: Conformational Control in the Biradical Formation and in the Behavior of Biradicals

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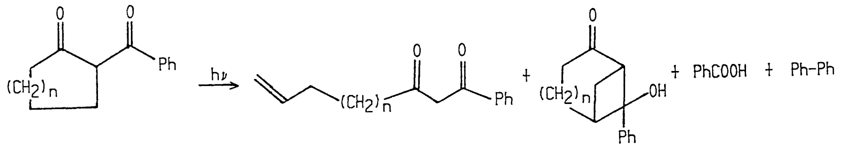
Synopsis. The photoreactivities of 2-benzoylcycloalkanones were shown to be controlled by their ring conformation; 2-benzoylcycloalkanones underwent the Type II elimination and/or cyclization, and/or the α-cleavage reaction.

The Type II photoelimination and cyclization of alkyl aryl ketones have been investigated extensively.[1] These reactions are now well known to involve 1,4-biradical intermediates formed through γ-hydrogen abstraction by the excited carbonyl group.[2] The behavior of the biradical intermediate is affected by α-substitution; an α-methyl substituent increases the ratios of cyclization/elimination and Type I reaction/Type II reaction.[3] Aryl cycloalkyl ketones also undergo the Type II photoreaction.[3b,4] Benzoylcyclohexane undergoes the Type II elimination with a very low quantum yield,[3b] while the Type II cyclization is not observed. In contrast to benzoylcyclohexane, 2-benzoylcyclohexanone (**1a**) shows an efficient Type II photoreactivity.[5] The Introduction of a methyl group to the 2-position of **1a** produces a remarkable change in the behavior of the 1,4-biradical intermediate; exclusive Type II cyclization occurs in 2-benzoyl-2-methylcyclohexanone.[6] We report here on the photoreaction of 2-benzoylcycloalkanones **1a**—**c**, where the photoreactivities are controlled by a ring conformation.

The irradiation of 2-benzoylcycloheptanone (**1b**) in benzene under nitrogen with a 450-W high-pressure mercury lamp through a Pyrex filter gave the Type II elimination and cyclization products **2b** and **3b**, in 41 and 40% yield, respectively. Their structures were elucidated from their spectral data and elemental analyses. The IR spectrum of **3b** showed the characteristic absorptions of the carbonyl and hydroxyl groups at 1705 and 3490 cm^{-1}, respectively. The ^{13}C NMR showed four triplets at δ=28.3, 29.7, 40.2, and 41.0 attributable to four methylene groups, doublets at δ=42.2 and 59.3 attributable to two methine groups, and singlets at δ=80.9 and 207.7 attributable to quaternary carbon and carbonyl carbon, respectively. The photochemical behavior of **1b** was quite different from that of **1a**. The diketone **1a** has been reported to undergo the Type II photoelimination.[5,7] No cyclization products have been observed.[5,7] The remarkable difference in the product distribution between **1a** and **1b** can be explained in terms of a difference in the conformation of the 1,4-biradical intermediates, **6a**

Table 1. Product Yields in Photoreaction of 2-Benzoylcycloalkanones **1**

Compound	Yield/%				
	n	**2**	**3**	**4**	**5**
1a	1	82	0	0	0
1b	2	41	40	0	0
1c	3	29	trace	9	14



(**1**) (**2**) (**3**) (**4**) (**5**)

Fig. 1. a: *n*=1, b: *n*=2, c: *n*=3

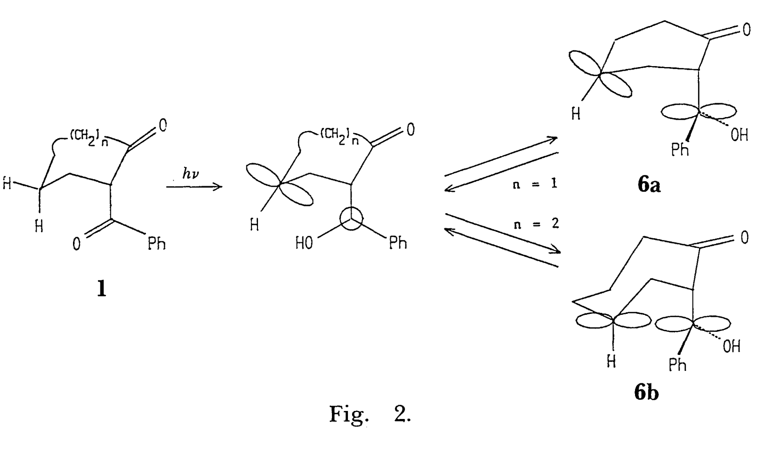


Fig. 2.

and **6b**. Analysis using Dreiding molecular models indicated that **6b** can take a favorable conformation for cyclization in which the two *p*-orbitals on both radical sites are nearly on the line with a C–C distance of ca. 2.3 Å. On the other hand, the two *p*-orbitals in **6a** are oriented with a 120° angle and the C–C distance between them is ca. 2.7 Å. Efficient cyclization is a consequence of an efficient orbital overlap. Cyclization requires a limited C–C distance as well as a limited orientation of the orbitals. The angle and the distance in **6a** are presumed to still meet the distance and orientation demands for cyclization, since 2-benzoyl-2-methylcyclohexanone undergoes the Type II cyclization efficiently.[6] Cyclization probability must be affected by both the rate of recombination of the radical centers and that of the conformational change to more stable conformers unfavorable for cyclization. The recombination rate should be higher in **6b** than that in **6a**, since the former can take a more favorable conformation for cyclization than the latter. On the basis of these considerations, cyclization is expected to compete with the elimination in **6b**; this elimination occurs predominantly in **6a**. No detectable α-cleavage reactions were observed in the photoreaction of the cyclohexanone **1a** and the cycloheptanone **1b**. On the other hand, a comparable α-cleavage competed with the Type II reaction in the case of the cyclooctanone **1c**.

Irradiation of **1c** under the same conditions gave **2c**, benzoic acid (**4**), and biphenyl (**5**) in 29, 9, and 14% yield,[8] respectively. A trace of **3c** was also detected. The formation of **4** can be rationalized in terms of the oxidation of benzaldehyde formed via the α-cleavage, though that of **5** can not yet be explained.[8] Benzaldehyde could be detected by GLC analysis of the reaction mixture from **1c**. The low yield of the Type II product from **1c** can be explained in terms of the difficulty in taking a favorable conformation to γ-hydrogen abstraction, due to a nonbonding interaction between the hydrogens on the ring. The low cyclization/elimination ratio presumably indicates that the rate of conformational change into a conformation unfavorable for cyclization is accelerated by the nonbonding interaction; the rate is much higher than that for the recombination of radical centers.

The ring conformation in the 2-benzoylcycloalkanones **1** is an important factor in the biradical formation and in determining the behavior of the biradical.

Experimental

The IR spectra were recorded with a JASCO A-3 spectrometer and the ^{1}H and ^{13}C NMR spectra were measured with a JEOL FX90Q spectrometer using tetramethylsilane as an internal standard. An Ushio 100-W or 450-W high-pressure mercury lamp was used as the irradiation source. The 2-benzoylcycloalkanones, **1a—c**, were prepared according to a method described in the literature.[9]

Photoreaction of 1b. A solution of **1b** (500 mg, 2.31 mmol) in 50 cm^3 of benzene was placed in a 30×200 mm Pyrex tube and irradiated with a 450-W high-pressure mercury lamp under nitrogen through a Pyrex filter for 58 h. After removing the solvent, the residue was chromatographed on a silica-gel column. Elution with a mixture of benzene–ethyl acetate (v/v=30/1) gave the unreacted diketone **1b** (200 mg), 1-phenyl-7-octene-1,3-dione (**2b**) (123 mg, 41%), and 7-hydroxy-7-phenylbicyclo[4.1.1]octan-2-one (**3b**) (120 mg, 40%) **2b**: bp 140 °C/3 mmHg (bath temperature, 1 mmHg=133.322 Pa); IR (neat) 1605 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.77 (2H, quintet, 5-CH$_2$), 2.13 (2H, q, 6-CH$_2$), 2.43 (2H, t, 4-CH$_2$), 4.05 (0.2H, s, 2-CH$_2$ in the keto form), 4.93 (1H, s, 8-CH$_2$), 5.08 (1H, d, *J*=5.4 Hz, 8-CH$_2$), 5.4—6.1 (1H, m, 7-CH), 6.15 (0.9H, s, CH in the enol form), 7.3—7.7 (5H, m, aromatic), and 16.27 (0.9H, bs, OH in the enol form); ^{13}C NMR (CDCl$_3$) δ=25.1 (t), 33.2 (t), 38.6 (t), 96.2 (d), 115.3 (t), 127.1 (d, 2C), 128.6 (d, 2C), 132.1 (d), 133.6 (s), 137.8 (d), 183.5 (s), and 196.5 (s). Found: C, 77.65; H, 7.43%. Calcd for $\mathrm{C_{14}H_{16}O_2}$: C, 77.75; H, 7.46 %. **3b**: mp 93—93.5 °C (from a mixture of benzene–hexane); IR (KBr) 1705 and 3500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.6—2.5 (8H, m, CH$_2$), 2.8—3.0 (2H, m, 2×CH), 3.22 (1H, s, OH), and 7.2—7.4 (5H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ=28.3 (t), 29.9 (t), 40.2 (t), 41.0 (t), 42.2 (d), 59.3 (d), 80.9 (s), 125.0 (d, 2C), 127.5 (d), 128.4 (d, 2C), 145.1 (s), and 207.7 (s). Found: C, 77.76; H, 7.67%. Calcd for $\mathrm{C_{14}H_{16}O_2}$: C, 77.75; H, 7.46%.

Photoreaction of 1c. A solution of **1c** (1.00 g, 4.35 mmol) in 100 cm^3 of benzene was placed in a flask for immersion irradiation and irradiated with a 100-W high-pressure mercury lamp under nitrogen for 72 h. After removing the solvent, the residue was chromatographed on a silica-gel column. Elution with benzene gave the unreacted diketone **1c** (170 mg), 1-phenyl-8-nonene-1,3-dione (**2c**) (240 mg, 29%), biphenyl (16 mg, 14%), and benzoic acid (75 mg, 9%). Though a trace amount of **3c** was also detected, however, complete purification could not be achieved. **2c**: bp 140 °C/3 mmHg (bath temperature); IR (neat) 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.3—1.9 (4H, m, 5- and 6-CH$_2$), 2.14 (2H, q, *J*=6.9 Hz, 7-CH$_2$), 2.42 (2H, t, *J*=6.7 Hz, 4-CH$_2$), 4.08 (0.1H, s, 2-CH$_2$ in the keto form), 4.90 (1H, s, 9-CH$_2$), 5.05 (1H, d, *J*=6.2 Hz, 9-CH$_2$), 5.6—6.1 (1H, m, 8-CH), 6.14 (0.95H, s, 2-CH in the enol form), 7.3—7.8 (3H, m, aromatic), 7.8—8.3 (2H, m, aromatic), and 16.3 (0.95H, bs, OH in the enol form); ^{13}C NMR (CDCl$_3$) δ=25.2 (t), 28.6 (t), 33.4 (t), 39.0 (t), 96.0 (d), 114.7 (t), 127.0 (d, 2C), 128.5 (d, 2C), 132.1 (d), 135.2 (s), 138.3 (d), 183.4 (s), and 196.6 (s). Found: C, 77.89; H, 7.91%. Calcd for $\mathrm{C_{15}H_{18}O_2}$: C, 78.23; H, 7.88%. **3c**: IR (neat) 1690 and 3470 cm^{-1}.

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8) Formation of **5** may be explained in terms of coupling of phenyl radicals produced via hydrogen abstraction by the benzoyl radical from benzene. The yield was calculated assuming that two moles of **1c** gave one mole of biphenyl.

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