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TYPE I AND TYPE II PHOTOCHEMICAL REACTION OF ω-ISOBUTYRYL-ω-METHYL-2,3-BENZOCYCLOALK-2-EN-1-ONES.

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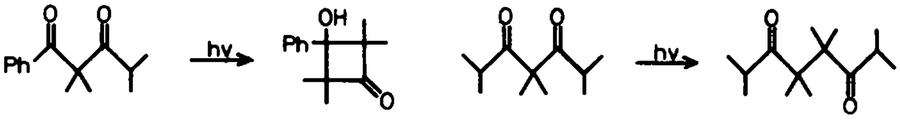
Abstract - ω-Isobutyryl-ω-methyl-2,3-benzocycloalk-2-en-1-ones (6a-c) undergo both type I and type II photoreactions. The type I/type II product ratio depends on the ring size; the six-membered ketone 6a is subject to type II reaction and the eight-membered ketone 6c is subject to type I reaction predominantly. The cyclization/elimination ratio of the type II reaction of 6 also depends on the ring size; the ratio decreases with increasing ring size.

The two major photochemical processes of ketones, Norrish type I and Norrish type II, have been widely studied.[1] The ketones with γ-hydrogens and α-substituents in the alkyl chain undergo competitive type I and type II reactions.[2] The cyclic ketones with γ-hydrogens also undergo both reactions.[3] The reactivity of the type II reaction increases with decreasing γC-H bond strength and decreases with the electron-withdrawing groups on γ carbon.[4] The reactivity of the type I reaction increases with α substituents.[2] In the case of aliphatic 1,3-diketones, no example of type II reaction where an α-hydrogen to one carbonyl group undergoes 1,5-shift to another carbonyl oxygen has been found. The non-enolizable aliphatic 1,3-diketones undergo type I reaction.[5] We have previously found that the non-enolizable 1-aryl-1,3-diketone bearing tertiary hydrogen on γ carbon, 2,2,4-trimethyl-1-phenylpentane-1,3-dione (1), undergoes type II cyclization to give 3-hydroxycyclobutanone (2) in good yield.[6] On the contrary, the aliphatic 1,3-diketone analogous to 1 such as 2,4,4,6-tetramethylheptane-3,5-dione (3) undergoes only type I fragmentation.††



1 2 3

Thus, the non-enolizable 1-aryl-1,3-diketones bearing tertiary hydrogen on C_4 may be subject to type II reaction preferentially, and the analogous aliphatic 1,3-diketones are subject to type I reaction. On these considerations in mind, we have studied the photochemistry of ω-isobutyryl-ω-methyl-2,3-benzocycloalk-2-en-1-ones (6a-c) in

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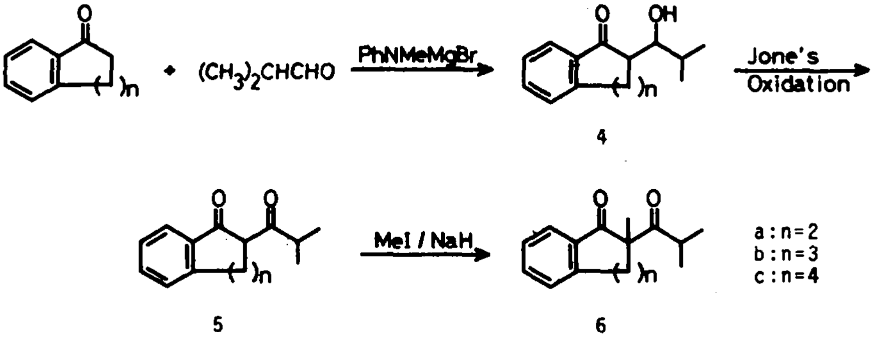
††Photolysis of 3 gave 2,4,4,5,5,7-hexamethyloctane-3,6-dione and 2,4,4,5-tetramethylhexan-3-one as two major products. No sign for the formation of type II products was obtained on the ir and nmr analyses of the mixture.

which the p-orbital overlap of the C_1-carbonyl with the benzene ring is maximum in the cyclohexenone **6a** and minimum in the cyclooctenone **6c** owing to steric factors, suggesting that the nature of the 1,3-diketone **6** changes from aryl to alkyl ketone character with increasing ring size. We now report that **6** undergoes competitive type I and type II reactions and that the type I/type II product ratio depends on the ring size. We also report that the cyclization/elimination ratio of the type II reaction of **6** depends on the ring size.

The ω-isobutyryl-ω-methyl-2,3-benzocycloalk-2-en-1-ones (**6a-c**) were prepared in 30-50 % overall yields by the condensation of the corresponding 2,3-benzocycloalkenones with isobutyraldehyde using methylanilinomagnesium bromide as the condensing agent[7] and the subsequent oxidation of the ketols with Jone's reagent and methylation by methyl iodide, and characterized by spectroscopic methods. The uv



spectra of **6a-c** in ethanol are shown in Figure 1. In the absorption curves of **6a** and **6b**, the phenyl ketone band occurred at 253 and 250 nm, respectively. The six-membered ketone **6a** showed substantially normal intensity (ε 12,800) for the conjugated phenyl ketone and the seven-membered ketone **6b** showed reduced intensity (ε 9,200). This result reveals that the carbonyl group is fixed in the plane of the benzene ring in **6a** and is twisted out-of-plane in **6b**. It is known that the carbonyl group is fixed in the plane of the benzene ring in 2,3-benzocyclohex-2-en-1-one and is twisted out-of-plane with the torsion angle of 29° in 2,3-benzocyclohept-2-en-1-one.[8] The spectrum of **6c** showed no maximum at about 250 nm. The uv spectrum of 2,3-benzocyclooct-2-en-1-one shows the maximum at 245 nm (ε 7,200), though the carbonyl group is twisted out-of-plane with the torsion angle of 37° which is greater than that in the corresponding seven-membered ketone.[8] The absence of the maximum in the spectrum of **6c** is explained in terms of the increased angle of twist caused by the presence of ω-substituents. These results indicate that the C_1-carbonyl of **6c** is virtually alkyl ketone in nature, while that of **6a** is aryl ketone. The molecular models of **6a-c** reveal that, in the conformation where p-orbitals of the benzene

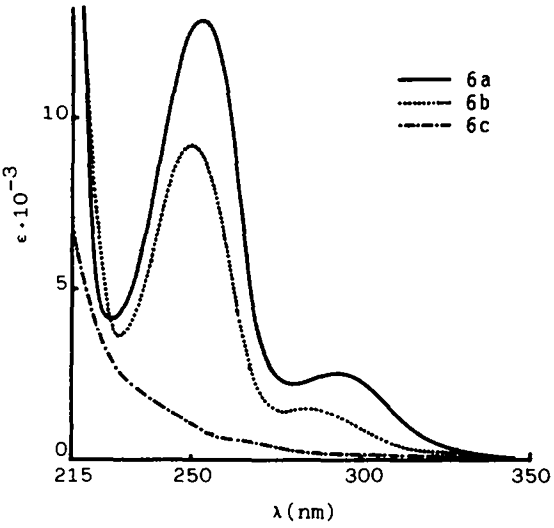
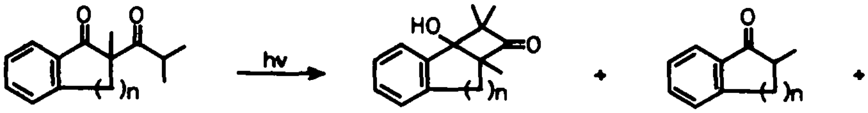


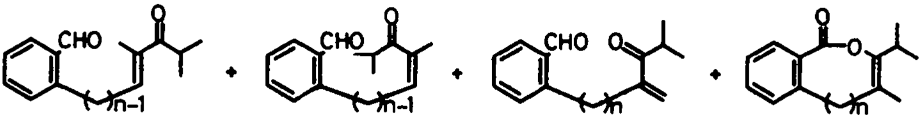
Figure 1. Absorption spectra of **6a-c** in ethanol.

ring are parallel to those of the C$_1$-carbonyl group, there is very severe steric interaction between the C$_\omega$-methyl group or C$_\omega$-isobutyryl group and one of the C$_4$-methylene protons in 6c. The interaction between them is less severe in 6b than in 6c and not significant in 6a, suggesting that the degree of p-orbital overlap of the C$_1$-carbonyl with the benzene ring decreases with increasing ring size.

The 1,3-diketones (6a-c) were irradiated with Pyrex-filtered light in a variety of solvents. In the case of 6a, photolysis resulted in the formation of the type II cyclization product (7a) in good yield along with trace of 8a, the type II elimination product. No evidence for the formation of type I products (9, 10, 11, and 12) could be obtained on nmr analysis. In contrast, the photolysis of 6b and 6c resulted in the formation of enals (9, 10, and 11) and the enol lactone (12) along with the cyclobutanone (7) in yields given in table 1. The structures of the photoproducts were assigned on the spectral data. The ir spectrum of 7 in chloroform showed the characteristic absorptions for the four-membered carbonyl group and the hydroxyl group at 1770-1780 and 3600 cm^{-1}, respectively. The nmr spectra of 9b and 10b showed a singlet due to the aldehydic proton at δ 10.14 and 10.17, and a triplet due to the olefinic proton at δ 6.61 and 5.61, respectively. The geometry of these enals were readily assigned from the chemical shift of the olefinic proton. It is well established that *cis*-β-protons are less shielded than *trans*-β-protons in α,β-unsaturated carbonyl compounds. The nmr spectrum of 11b showed a singlet due to the aldehydic proton at δ 10.17 and two singlets due to the exo-methylene group at δ 5.73 and 5.96. The product 12b showed a lactone carbonyl band at 1745 cm^{-1} in its ir spectrum, a lactone carbonyl carbon at δ 170.71 in its ^{13}C nmr spectrum, and a singlet due to the allylic methyl group at δ 1.62 in its ^{1}H nmr spectrum. On the basis of these spectral data, we could not precrude another possible structure 13 which is the coupling product of radicals resulting from cleavage between C$_7$ and the isobutyryl group. We have synthesized the enol ester 13 by the reaction of 7-methyl-2,3-benzocyclohept-2-en-1-one with isobutyryl chloride in the presence of sodium amide. Acylation of ketone-sodium amide system with acid chloride is known to give mixtures of enol esters and 1,3-diketones.[9] The nmr spectrum of 13 resembled that of 12b except for aromatic protons. The aromatic protons of 13 appeared as a singlet at δ 7.12, whereas those of 12b appeared as a set of multiplets at δ 7.04-7.46 (3H) and 7.54-7.70 (1H). Consequently, we could assign the photoproduct 12b to a nine-membered lactone. The spectra of 9c, 10c,



6a:n=2 7a:n=2 8a:n=2
6b:n=3 7b:n=3 8b:n=3
6c:n=4 7c:n=4 8c:n=4



9b:n=3 10b:n=3 11b:n=3 12b:n=3
9c:n=4 10c:n=4 11c:n=4 12c:n=4

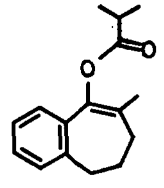


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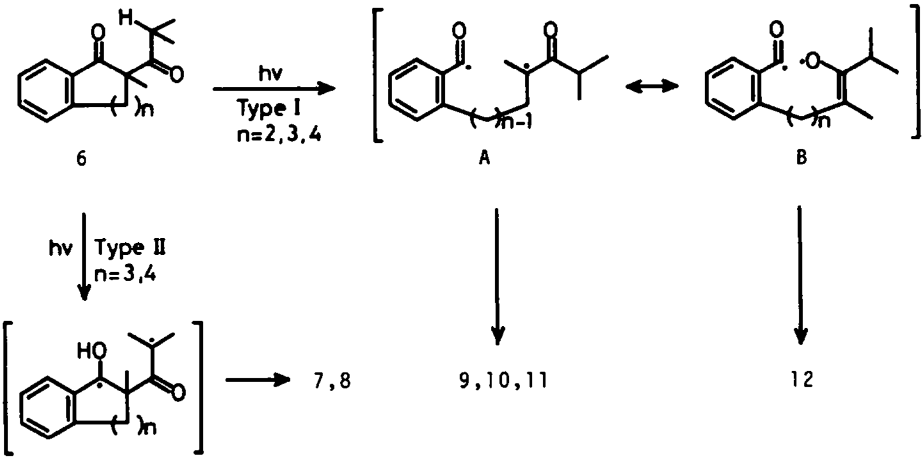
Table 1. Photolysis of 6 in Various Solvents.

Solvent	Diketone	Conversion (%)	Yield (%)[a]						Type I/Type II Ratio	%Cy / Type II
			Type II		Type I					
			7	8[b]	9	10	11	12		
Benzene	6a	83	65	trace	-	-	-	-	0	~100
	6b	79	47	4	4	4	4	3	0.3	92
	6c	73	7	10	11	13	19	8	3.0	41
Hexane	6a	77	64	trace	-	-	-	-	0	~100
	6b	77	55	3	-	-	-	5	0.1	95
	6c	78	12	9	9	10	15	9	2.0	57
iso-PrOH	6a	56	77	trace	-	-	-	-	0	~100
	6b	78	37	7	7	4	-	6	0.4	84
	6c	61	3	11	22	9	-	7	2.7	21

[a] Isolated Yield. [b] The compound 8 can be taken as type II elimination product because we could not detect other products resulting from type I cleavage between C_ω and the isobutyryl group.

11c, and 12c closely resembled those of 9b, 10b, 11b, and 12b, respectively.

The formation of the 3-hydroxycyclobutanone 7 and the ω-methyl-2,3-benzocycloalk-2-en-1-one 8 can be explained in terms of type II cyclization and elimination. The formation of enals 9-11 and the enol lactone 12 can be explained in terms of type I cleavage of the C_1-C_ω bond to produce the 1,ω-biradical A which is resonant with the O-radical B. The 1,ω-biradical A and the O-radical B undergo disproportionation and cyclization, respectively, to give the enals 9-11 and the enol lactone 12. The type I biradical generated from cycloalkanones is known to produce enals by disproportionation.[3,10] It is also known that type I radicals from 1,3-diketones produce enol esters by recombination.[5,6]



As shown in table 1, photolysis of 6a gave type II product, whereas that of 6c gave type I products predominantly. The photolysis of 6b gave both type I and type II products with the greater yield of type II products. Thus, the type I/type II product ratio observed in the reaction of 6 correlates to the ring size. As mentioned before, 6c is a aliphatic 1,3-diketone in nature, while 6a is a arylic 1,3-diketone. This means that the aliphatic 1,3-diketones might be subject to type I reaction instead of type II reaction even though the rather weak γ-hydrogen such as tertiary hydrogen exists in the molecule and the arylic 1,3-diketones might be subject to type II reaction when the rather weak γ-hydrogen such as tertiary hydrogen exists in the molecule.† It is noteworthy that the cyclization/elimination product ratio of the type II reaction of 6 decreases as the ring size increases (table 1). In the biradical generated from 6a, the p-orbital at C_1 is parallel to those of the benzene ring and almost perpendicular to the C_6-C(C=O) σ bond, indicating the inefficient cleavage of the C_6-C(C=O) bond. However, in the biradical from 6c, the p-orbital at C_1 is twisted out of the benzene plane owing to the steric repulsion between the C_8-methyl and C_4-hydrogen and almost parallel to the C_8-C(C=O) σ bond so as to enhance cleavage. The efficient cleavage requires maximum overlap of p-orbitals at C_1 and C_4 with the C_2-C_3 σ bond in the type II biradical intermediate.[11]

Both type I and type II reactions of 6a and 6b could be quenched by 1,3-pentadiene and a plot of Φ_0/Φ vs. the concentration of the quencher (Stern-Volmer) was linear with a slope of 33 M^{-1} for 6a and 45 M^{-1} for 6b. In contrast, the formation of enals from 6c was not quenched by 1,3-pentadiene. These results suggest that the reaction of 6a and 6b takes place from the triplet excited state, and that of 6c takes place from the singlet excited state. The triplet excited state of 6b gave type I products as well as type II products, whereas that of 6a gave type II products and no type I products. The reason of this is probably ascribed to the reduced arylic 1,3-diketone nature of 6b. In general, dialkyl ketones undergo type I cleavage much faster than analogous aryl alkyl ketones.[12]

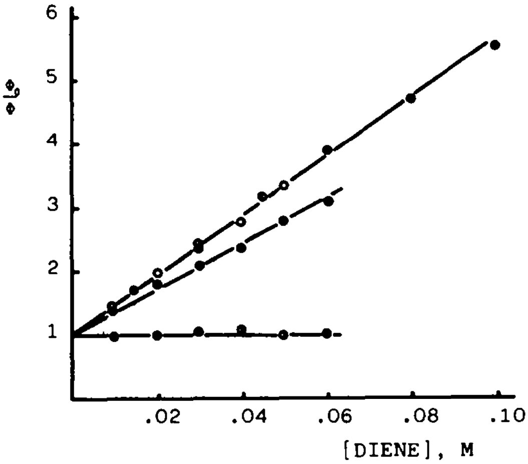
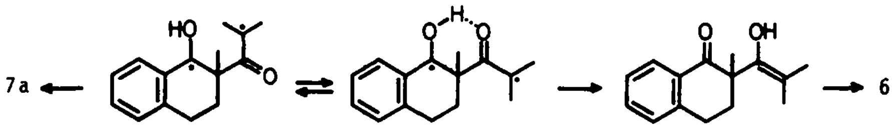


Figure 2. Stern-Volmer plots for 1,3-pentadiene quenching in benzene. ●,formation of 7a; ○,formation of 7b; ◐,formation of 9b; ⊙,formation of 9c

The quantum yield for the formation of 7a from 6a was nearly equal (*ca.* 0.25) in benzene and a 1:1 mixture of benzene and tert-butyl alcohol. The quantum yields for type II reactions of simple phenyl alkyl ketones are known to be enhanced in polar solvents.[13] Although we can not provide a conclusive answer regarding the insensitivity of the type II reaction of 6a towards solvent, a possible intramolecular hydrogen bonding in the biradical intermediate seems to be responsible for the insensitivity. The intramolecular hydrogen bonding provides a path for the regeneration of 6a. The similar type of regeneration of the parent ketone was proposed in the reaction of type II biradical from 1,5-diphenyl-1,5-diketones.[14]



In conclusion, ω-isobutyryl-ω-methyl-2,3-benzocycloalk-2-en-1-ones undergo both type I and type II photoreactions. The type I/type II product ratio depends on the ring size. The six-membered ketone 6a which is the aryl ketone in nature is subject to type II reaction, while the eight-membered ketone 6c which is the alkyl

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†The photolysis of 2,2-dimethyl-1-phenyl-1,3-butanedione gives only type I products (see Reference 6).

ketone in nature is subject to type I reaction predominantly. The cyclization/elimination product ratio of the type II reaction of **6** also depends on the ring size; the ratio decreases with increasing ring size because the overlap of the p-orbital at C_1 with the C_ω-C(C=O) σ bond in the biradical intermediate increases with increasing ring size. The quantum yield for the formation of the type II product is independent of the solvent polarity.

EXPERIMENTAL

Melting points were uncorrected. Uv spectra were recorded on a Hitachi 340 spectrometer. Ir spectra were recorded on a Hitachi 270-50 spectrometer. ^{1}H nmr spectra were recorded on a JEOL FX-90Q spectrometer using tetramethylsilane as an internal standard. ^{13}C nmr spectra were recorded on a JEOL FX-90Q spectrometer in deuterochloroform. High pressure liquid chromatography (HPLC) was carried out on a JASCO LCP-150 apparatus with a uv detector (254 nm). A JASCO Finepak SIL column was used and a 2:1 mixture of hexane and ether was used as a moving phase. Irradiations were carried out with an Ushio 100 W or 450 W high-pressure mercury lamp.

Materials. 1,3-Diketones **6a-c** were prepared by the condensation of the corresponding 2,3-benzocycloalk-2-en-1-ones with isobutyraldehyde, followed by Jone's oxidation and methylation. By the same procedure as that reported by Nielsen,[7] ketols **4** were prepared in 60-85 % yields. These ketols were purified by column chromatography on silica gel. To a solution of ketol **4** (33 mmol) in acetone (45 cm^3) was added slowly with cooling and stirring a solution of Jone's reagent (10 cm^3) which was prepared by dissolving chromium(VI) oxide (26.72 g) in 98 % sulfulic acid (23 cm^3) diluted with water to a volume of 100 cm^3. The mixture was stirred for several hours under cooling with ice and worked up by general procedure. Chromatography of the mixture on silica gel eluted with hexane-ethyl acetate gave **5** in about 70 % yield. To a suspension of sodium hydride (60 % in oil, 22 mmol) in benzene-DMF (2:1, 20 cm^3) was added with stirring a solution of diketone **5** (20 mmol) in benzene-DMF (2:1, 65 cm^3). After stirring at room temperature for 1 hour, methyl iodide (25 mmol) was added. The mixture was heated under reflux for 3 hours and extracted with ether. The ethereal solution was worked up in the usual way. Column chromatography on silica gel using a hexane-ethyl acetate mixture gave **6** in about 85 % yield.

6-Isobutyryl-6-methyl-2,3-benzocyclohex-2-en-1-one (**6a**): bp 110 °C (bath)/0.7 mmHg; ir(CCl_4) 1725 and 1695 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 0.79 (3H, d, J=7.2 Hz), 1.07 (3H, d, J=7.2 Hz), 1.40 (3H, s), 1.73-2.09 (1H, m), 2.47-3.11 (4H, m), 7.07-7.55 (3H, m), and 7.91-8.07 (1H, m); ^{13}C nmr δ 19.97 (2q), 20.68 (q), 25.69 (t), 32.33 (t), 36.16 (d), 60.29 (s), 126.49 (d), 127.33 (d), 128.63 (d), 131.89 (s), 133.38 (d), 143.33 (s), 197.83 (s), and 212.59 (s); uv λmax(EtOH) 253 nm (ε 12,800). Found: C, 77.98; H, 7.92 %. Calcd for $C_{15}H_{18}O_2$: C, 78.22; H, 7.87 %.

7-Isobutyryl-7-methyl-2,3-benzocyclohept-2-en-1-one (**6b**): mp 61 °C (from pentane); ir(CCl_4) 1730 and 1690 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 0.72 (3H, d, J=6.5 Hz), 1.04 (3H, d, J=6.5 Hz), 1.42 (3H, s), 1.48-2.50 (4H, m), 2.52-2.92 (3H, m), and 7.00-7.56 (4H, m); ^{13}C nmr δ 19.77 (q), 20.62 (2q), 20.81 (t), 22.96 (t), 31.54 (t), 32.26 (d), 64.64 (s), 126.55 (d), 128.44 (d), 129.15 (d), 131.63 (d), 139.04 (s), 140.02 (s), 207.19 (s), and 212.78 (s); uv λmax(EtOH) 250 nm (ε 9,200). Found: C, 78.61; H, 8.27 %. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25 %.

8-Isobutyryl-8-methyl-2,3-benzocyclooct-2-en-1-one (**6c**): bp 135 °C (bath)/0.5 mmHg; ir(CCl_4) 1730 and 1700 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.03 (3H, d, J=7.2 Hz), 1.11 (3H, d, J=7.2 Hz), 1.27 (3H, s), 1.51-1.95 (5H, m), 2.00-2.31 (1H, m), 2.63-2.85 (2H, m), 3.05 (1H, sep, J=7.2 Hz), and 6.79-7.35 (4H, m); ^{13}C nmr δ 18.60 (q), 19.58 (q), 19.77 (q), 22.57 (t), 26.60 (t), 31.28 (t), 32.26 (t), 35.71 (d), 66.60 (s), 124.60 (d), 125.90 (d), 128.37 (d), 128.76 (d), 137.48 (s), 139.43 (s), 209.66 (s), and 212.91 (s). Found: C, 78.99; H, 8.65 %. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58 %.

Photolysis of **6**. A typical procedure is described. A solution of *ca.* 2.5 mmol of **6** in 120 cm^3 of a variety of solvents was irradiated for 40 minutes under nitrogen using a 100 W high-pressure mercury lamp and a Pyrex filter. The photoproducts were isolated by column chromatography on silica gel eluted with a mixture of hexane and ethyl acetate. The yields were given in table 1.

1-Hydroxy-6,8,8-trimethyl-2,3-benzobicyclo[4,2,0]oct-2-en-7-one (**7a**): mp 110-111 °C (from hexane); ir($CHCl_3$) 3600, 3500, and 1780 cm^{-1}; ^{1}H nmr(C_6D_6) δ 0.49 (3H, s), 1.14 (3H, s), 1.32 (3H, s), 0.72-1.08 (1H, m), 1.50 (1H, s, OH), 1.76-2.04 (1H, m), 2.16-2.40 (2H, m), 6.68-7.08 (3H, m), and 7.28-7.48 (1H, m); ^{13}C nmr δ 18.14 (q), 19.51 (q), 19.84 (q), 28.29 (t), 29.53 (t), 64.19 (s), 64.97 (s), 73.94 (s), 126.55 (d), 127.07 (d), 128.11 (2d), 137.02 (s), 139.56 (s), and 222.93 (s). Found: C, 78.25; H, 7.99 %. Calcd for $C_{15}H_{18}O_2$: C, 78.22; H, 7.87 %.

1-Hydroxy-7,9,9-trimethyl-2,3-benzobicyclo[5,2,0]non-2-en-8-one (**7b**): mp 163 °C (from ether); ir($CHCl_3$) 3600, 3480, and 1780 cm^{-1}; ^{1}H nmr(C_6D_6) δ 1.15 (3H, s), 1,27 (3H, s), 1.33 (3H, s), 1.41 (1H, s, OH), 1.43-1.67 (4H, m), 2.03-2.35 (1H, m), 2.43-2.87 (1H, m), and 6.75-7.07 (4H, m); ^{13}C nmr δ 12.36 (q), 18.99 (q), 21.46 (t), 25.69 (q), 29.27 (t), 30.96 (t), 64.38 (s), 64.77 (s), 80.77 (s), 126.23 (d), 128.24

(d), 129.28 (d), 130.52 (d), 138.58 (s), 141.71 (s). and 222.28 (s). Found: C, 78.61; H, 8.29 %. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25 %.

1-Hydroxy-8,10,10-trimethyl-2,3-benzobicyclo[6,2,0]dec-2-en-9-one (7c): mp 138-139 °C (from hexane); ir($CHCl_3$) 3600, 3450, and 1770 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.26 (3H, s), 1.29 (3H, s), 1.31 (3H, s), 1.38-2.14 (6H, m), 1.74 (1H, s, OH), 2.44-2.66 (2H, m), and 6.94-7.14 (4H, m); ^{13}C nmr δ 15.87 (q), 18.41 (q), 23.22 (t), 25.17 (q), 30.24 (t), 31.54 (t), 33.43 (t), 65.10 (s), 67.05 (s), 81.75 (s), 125.58 (d), 128.50 (d), 129.55 (d), 131.89 (d), 140.54 (s), 143.14 (s), and 223.32 (s). Found: C, 79.16; H, 8.44 %. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58 %.

(E)-7-(o-formylphenyl)-2,4-dimethylhept-4-en-3-one (9b): bp 110 °C (bath)/0.5 mmHg; ir(CCl_4) 2750, 1715, and 1680 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.04 (6H, d, J=6.0 Hz), 1.68 (3H, d, J=1.6 Hz), 2.54 (2H, q, J=7.5 Hz), 3.08-3.48 (3H, m), 6.61 (1H, td, J= 7.5 and 1.6 Hz), 7.16-7.60 (3H, m), 7.70-7.83 (1H, m), and 10.14 (1H, s); ^{13}C nmr δ 11.45 (q), 19.45 (2q), 30.76 (t), 31.61 (t), 33.76 (d), 126.88 (d), 131.11 (d), 133.64 (2d), 133.84 (s), 136.83 (s), 139.49 (d), 143.46 (s), 192.37 (d), and 205.89 (s). Found: C, 78.61; H, 8.39 %. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25 %.

(Z)-7-(o-formylphenyl)-2,4-dimethylhept-4-en-3-one (10b)†: ir(CCl_4) 2750 and 1715 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.02 (6H, d, J=6.8 Hz), 1.90 (3H, d, J=1.2 Hz), 2.41 (2H, q, J=8.0 Hz), 2.79 (1H, sep, J=6.8 Hz), 3.10 (2H, t, J=8.0 Hz), 5.61 (1H, td, J=8.0 and 1.2 Hz), 7.15-7.60 (3H, m), 7.66-7.82 (1H, m), and 10.17 (1H, s).

7-(o-Formylphenyl)-2-methyl-4-methyleneheptan-3-one (11b): bp 110 °C (bath)/ 0.5 mmHg; ir(CCl_4) 2750, 1720, and 1695 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.08 (6H, d, J=7.2 Hz), 1.51-1.95 (2H, m), 2.37 (2H, t, J=8.0 Hz), 3.02 (2H, t, J=8.0 Hz), 3.28 (1H, sep, J=7.2 Hz), 5.73 (1H, s), 5.96 (1H, s), 7.07-7.51 (3H, m), 7.69-7.96 (1H, m), and 10.17 (1H, s). Found: C, 78.46; H, 8.39 %. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25 %.

(E)-8-(o-formylphenyl)-2,4-dimethyloct-4-en-3-one (9c): bp 130 °C (bath)/0.6 mmHg; ir(CCl_4) 2750, 1715, and 1680 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.07 (6H, d, J=6.5 Hz), 1.76 (3H, s), 1.56-2.00 (2H, m), 2.33 (2H, q, J=7.2 Hz), 3.07 (2H, t, J=8.0 Hz), 3.29 (1H, sep, J=6.5 Hz), 6.58 (1H, t, J=7.2 Hz), 7.11-7.56 (3H, m), 7.69-7.84 (1H, m), and 10.13 (1H, s); ^{13}C nmr δ 11.65 (q), 19.51 (2q), 28.75 (t), 30.76 (t), 32.46 (t), 33.69 (d), 126.62 (d), 130.98 (d), 132.99 (d), 133.59 (s+d), 136.44 (s), 140.67 (d), 144.41 (s), 192.37 (s), and 205.96 (s). Found: C, 78.78; H, 8.58 %. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58 %.

(Z)-8-(o-formylphenyl)-2,4-dimethyloct-4-en-3-one (10c)†: ir(CCl_4) 2750, 1720, and 1710 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.06 (6H, d, J=7.0 Hz), 1.91 (3H, d with fine coupling), 1.48-1.90 (2H, m), 2.04-2.40 (2H, m), 2.66-3.11 (3H, m), 5.55 (1H, t, J=8.0 Hz), 7.11-7.60 (3H, m), 7.69-7.83 (1H, m), and 10.17 (1H, s).

8-(o-Formylphenyl)-2-methyl-4-methyleneoctan-3-one (11c): bp 125 °C (bath)/0.6 mmHg; ir(CCl_4) 2750, 1715, and 1690 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.06 (6H, d, J=7.2 Hz), 1.33-1.82 (4H, m), 2.28 (2H, t, J=8.0 Hz), 3.02 (2H, t, J=8.0 Hz), 3.17 (1H, sep, J=7.2 Hz), 5.64 (1H, s), 5.89 (1H, s), 7.11-7.56 (3H, m), 7.64-7.82 (1H, m), and 10.17 (1H, s). Found: C, 78.85; H, 8.72 %. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58 %.

9-Isopropyl-8-methyl-3,4-benzoxacyclonona-3,8-dien-2-one (12b): bp 100 °C (bath)/0.5 mmHg; ir(CCl_4) 1745 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.06 (6H, d, J=7.0 Hz), 1.62 (3H, s), 1.70-2.12 (4H, m), 2.80 (1H, sep, J=7.0 Hz), 2.90-3.10 (2H, m), 7.06-7.46 (3H, m), and 7.54-7.70 (1H, m); ^{13}C nmr δ 18.82 (q), 20.23 (2q), 29.01 (t), 29.27 (d), 31.87 (t), 35.38 (t), 118.75 (s), 126.16 (d), 129.02 (d), 131.04 (d), 131,82 (d), 132.67 (s), 142.10 (s), 152.57 (s), and 170.71 (s). Found: C, 78.62; H, 8.31 %. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25 %.

10-Isopropyl-9-methyl-3,4-benzoxacyclodeca-3,9-dien-2-one (12c): bp 120 °C (bath)/0.6 mmHg; ir(CCl_4) 1760 and 1740 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.10 (6H, d, J=6.5 Hz), 1.76 (3H, s), 1.40-1.72 (4H, m), 1.96-2.20 (2H, m), 2.72-3.12 (3H, m), 7.05-7.36 (3H, m), and 7.36-7.56 (1H, m); ^{13}C nmr δ 19.25 (q), 19.90 (2q), 23.35 (t), 29.53 (d), 30.37 (t), 30.57 (t), 30.76 (t), 120.44 (s), 125.77 (d), 127.14 (d), 130.39 (d), 130.78 (d), 133.97 (s), 140.99 (s), 148.73 (s), and 168.69 (s). Found: C, 79.01; H, 8.64 %. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58 %.

Synthesis of 3-isobutyryloxy-4-methyl-1,2-benzocyclohepta-1,3-diene (13). To a suspension of sodium amide (135 mg) in dry ether (5 cm^3) was added a solution of 7-methyl-2,3-benzocyclohept-2-en-1-one (600 mg) in dry ether (10 cm^3). The mixture was heated under reflux for 20 minutes. To this was added slowly a solution of isobutyryl chloride (735 mg) in dry ether (10 cm^3). After heating under reflux for 6 hours, the mixture was poured into ice-water. The organic phase was separated and worked up. Chromatography on silica gel eluted with a mixture of hexane and ether (10:1) gave the enol ester 13 (320 mg): bp 95 °C (bath)/0.2 mmHg; ir(CCl_4) 1760 and 1150 cm^{-1}; ^{1}H nmr($CDCl_3$) δ 1.26 (6H, d, J=7.2 Hz), 1.81 (3H, s), 1.86-2.34 (4H, m), 2.46-2.70 (3H, m), and 7.12 (4H, s); ^{13}C nmr δ 17.43 (q), 18.86 (2q), 30.24

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†Analytically pure samples of these enals could not be obtained because they were unstable on distillation.

(t), 32.13 (t), 33.43 (t), 33.82 (d), 125.12 (d), 125.58 (s), 125.77 (d), 127.40 (d), 128.76 (d), 136.57 (s), 140.28 (s), 141.12 (s), and 175.00 (s). Found: C, 78.79; H, 8.34 %. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25 %.

Determination of Quantum Yields. The sealed Pyrex tubes containing 3 cm^3 of degassed 0.05 M solution of samples were irradiated on a merry-go-round apparatus using a 450 W high-pressure mercury lamp and a potassium chromate filter solution to isolate 313 nm light. The determination of product yield was carried out by HPLC analysis with constant volume. The yield was based on the average of three analyses. The type II reaction of valerophenone was used as chemical actinometer.

REFERENCES

1. N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, Acc. Chem. Res., 5, 92 (1972).
2. F. D. Lewis and T. A. Hilliard, J. Am. Chem. Soc., 94, 3852 (1972).
3. J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, J. Am. Chem. Soc., 93, 7213 (1971).
4. P. J. Wagner and A. E. Kemppainen, J. Am. Chem. Soc., 94, 7495 (1972).
5. H. Nozaki, Z. Yamaguti, T. Okada, R. Noyori, and M. Kawanisi, Tetrahedron, 23, 3993 (1967).
6. M. Yoshioka, T. Suzuki, and M. Oka, Bull. Chem. Soc. Jpn., 57, 1604 (1984).
7. A. T. Nielsen, C. Gibbons, and C. A. Zimmerman, J. Am. Chem. Soc., 73, 4696 (1951).
8. R. Huisgen, I. Ugi, E. Rauenbusch, V. Vossius, and H. Oertel, Chem. Ber., 90, 1946 (1957).
9. W. M. Muir, P. D. Pitchie, and D. J. Lyman, J. Org. Chem., 31, 3790 (1966).
10. X-G. Lei, C. E. Doubleday, Jr., M. B. Zimmt, and N. J. Turro, J. Am. Chem. Soc., 108, 2444 (1986).
11. P. J. Wagner and A. E. Kemppainen, J. Am. Chem. Soc., 90, 5896 (1968).
12. F. D. Lewis and J. G. Magyar, J. Org. Chem., 37, 2102 (1972); N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, J. Am. Chem. Soc., 92, 6974 (1970).
13. P. J. Wagner, J. Am. Chem. Soc., 89, 5898 (1967).
14. J. P. Bays, M. V. Encinas, R. D. Small, Jr., and J. C. Scaiano, J. Am. Chem. Soc., 102, 727 (1980).