

Photochemistry of 4-Aryl-4-Methyl-2-Cyclohexenone: Solvent Effect on the Excited States

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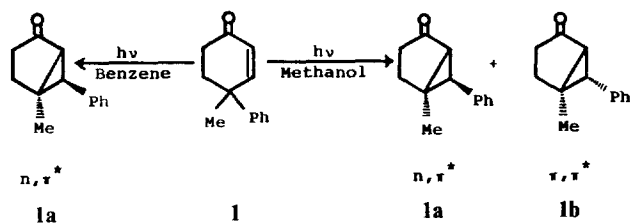
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Irradiation of 4-biphenyl-4-methyl-2-cyclohexenone (**5**) in benzene or methanol produced *trans*-6-biphenyl-5-methylbicyclo[3,1,0]hexan-2-one (**5a**) and 3-biphenyl-4-methylcyclohex-2-enone (**5b**). Electronic configurations of the excited states for **5a** and **5b** were assigned as n, π^* and π, π^* triplet states respectively. Irradiation of 4-methyl-4(β -naphthyl)-2-cyclohexenone in benzene or methanol gave 4-methyl-3-(β -naphthyl)-2-cyclohexenone (**6a**), which is thought to arise from π, π^* triplet state.

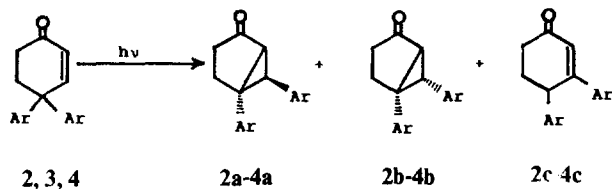
Introduction

Photochemistry of 4,4-disubstituted cyclohexenones¹⁻⁵ are well known, and the mechanism involving solvent effect on the excited states of the enones were proposed in Dauben's earlier publication.⁴

Irradiation of the enone **1** in a nonpolar solvent, benzene, gave product arising from n, π^* triplet states, while in a polar solvent, methanol, gave products arising from the both of n, π^* and π, π^* triplet states.



Recently Zimmerman^{1,2} and his co-workers investigated the photochemical behavior of the excited states of bichromophoric enones, 4,4-biphenyl-2-cyclohexenone (**3**) and 4,4-di(β -naphthyl)-2-cyclohexenone (**4**).



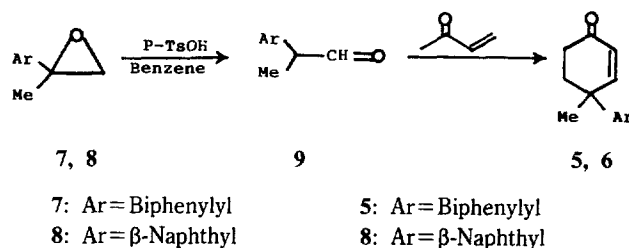
2: Ar=Phenyl, 3: Ar=Biphenyl, 4: Ar= β -Naphthyl

Since biphenyl and β -naphthyl groups on the C-4 of the enone moiety produce the same type of photoproducts as 4,4-diphenylcyclohexenone (**2**) photochemistry,⁶ 4-biphenyl-4-methyl-2-cyclohexenone (**5**) and 4-methyl-4(β -naphthyl)-2-cyclohexenone (**6**) were synthesized, and the solvent effects on the excited states involving the relative energy levels of n, π^* and π, π^* triplet states were investigated.

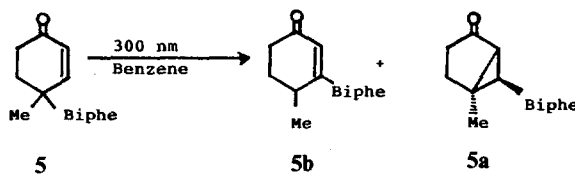
Results and Discussion

The synthesis of the requisite enones **5** and **6** began with the 1,1-disubstituted oxiranes **7** and **8**. These syntheses are

outlined below.



Direct irradiation of the enone **5** in benzene led to two photoproducts. The first had infrared and NMR spectra reminiscent of that of the *trans*-phenyl bicyclic ketone **1a** encountered as the major product of irradiation of the enone **1**, and an assignment as *trans*-6-biphenyl-5-methylbicyclo[3,1,0]hexan-2-one (**5a**) seemed reasonable.



In cyclopropyl ring of the product **5a**, the *cis* coupling constant in the *trans* bicyclic ketone is *ca.* 9.5 Hz at 2.6 ppm. This is in agreement with the observation of Graham and Rogers⁷ who reported a series of *cis*- and *trans*-cyclopropane coupling constants to average 5.7 Hz for *trans* and 8.4 Hz for *cis*. The second photoproduct was thought on similar spectral bases to be 3-biphenyl-4-methylcyclohex-2-enone (**5b**).

Direct irradiation of the enone **6** in benzene or methanol produced 4-methyl-3-(β -naphthyl)-2-cyclohexenone (**6a**) only.

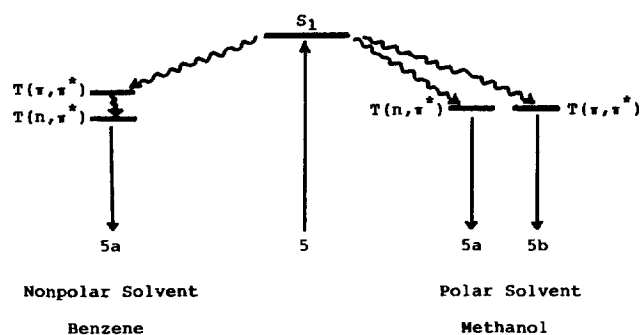
When a polar solvent such as methanol was used for the irradiation of **5** and **6**, relative amount of the product **5b** and the yield of **6a** were greatly increased (Table 1).

Sensitized irradiations of the enone **5** and **6** with acetophenone produced the same products as those from direct irradiation. According to Dauben's⁴ works on the solvent effects, the enone **5a** in benzene is thought to arise from n, π^* triplet state while the enone **5b** in methanol is thought to arise from π, π^* triplet state.

But this solvent effect only becomes important when the

Table 1. Product Distribution on the Irradiation of **5** and **6** in Different Solvent Polarity

Solvent	Quantum Yields			Yields (%)			Relative Amounts (%)		
	5	5a	5b	5a	5b	6a	5a	5b	6a
Benzene	— ^a	— ^a	— ^a	13	~0.3	~0.2	98	~2	20
Methanol	0.0070	0.0033	0.0007	15	~3.3	~1.0	82	~18	100

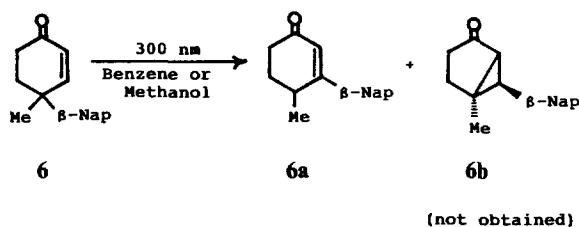
^a not determined¹³.**Scheme 1.** Solvent effect on the excited states of the enone **5**.

n, π^* and π, π^* states are very close in energy.

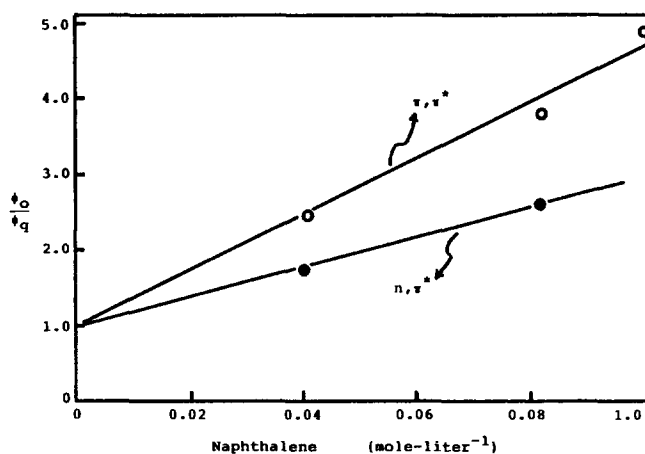
Since the n, π^* and π, π^* triplet states are thought to be nearly degenerated, the possibility exist that the solvent has an effect on the ordering of these two states (Scheme 1).

Stern-Volmer type analysis for the products, **5a** and **5b**, possibly representative of the reactions from different triplet states, were undertaken in methanol using naphthalene ($E_T = 60.9$ Kcal) as a quencher (Figure 1). The difference observed in the slopes for the quenching is indicative of the involvement of two excited states of different lifetimes.^{4,8,9} It seems reasonable that there be a quantitative correlation between the lifetimes of these excited state: n, π^* triplet states have shorter lifetimes than π, π^* triplets. If this would be the case, then the plots in Figure 1 further demonstrate the n, π^* character of the triplet involved in the formation of **5a** and the π, π^* character of the triplet involved in the formation of the enone **5b**.

Photochemistry of the enone **6** is quite different from that of the enone **5**. As mentioned above, irradiation of the enone **6** in benzene produced photoproduct **6a**, however, bicyclic ketone **6b** which was expected to arise from n, π^* triplet was not observed for some reasons. Irradiation of the enone **6** in methanol produced also the enone **6a** only.



These unusual photochemical behavior of the enone **6** could not be explained clearly at present, however, the n, π^* and π, π^* triplet states of the enone **6** are thought to be completely degenerated in nonpolar solvent and the relative

**Figure 1.** Stern-Volmer plot of triplet quenching of formation of **5a** (●) and **5b** (○) in methanol.

energy levels of these two states could be reversed⁴ in polar solvent; If this be the case, the electronic configuration of the lowest triplet state of the enone **6** in methanol is π, π^* which is responsible for the product **6b**.

Experimental

Gas chromatographic analysis were performed on a Varian Aerograph Model 2800 and Mass spectra were obtained on a Shimadzu LKB-9000, a Hewlett-Packard 5985A GC-MASS System EI method. Microanalyses were performed on a Yanco Model MTT2. The following spectrophotometers were used: NMR, Varian EM-360, Varian XL-100A and Varian FT-80A; IR, Unicam PS1000; UV Varian Techtron Model 635; Emission, Aminco-Bowman and Varian Spectrophotometer. Irradiations were performed using medium-pressure Hg-Arc lamps and Merry-go-round Rayonet Photoreactor.

4-Biphenyl-4-methyl-2-cyclohexenone (5) and 4-Methyl-4-(β -naphthyl)-2-cyclohexenone (6). Slight modification of the method of Zimmerman, Swenton¹⁰ and Schuster¹¹ gave a 16% yield of the enone **5**, mp. 83-84°C and 5% yield for the enone **6**. Spectral data for the enone **5**, NMR (CDCl₃) δ 7.50 (m, 4H), 7.00 (d, 1H), 6.2 (d, 1H), 2.3 (m, 4H), 1.6 (s, 3H); IR (KBR) 3100, 2900, 1690 cm⁻¹ UV λ_{max} (CCl₄) 355 nm (ϵ 226), 330 (ϵ 261), 255 (ϵ 41071); MASS, m/e (rel. abund) 262 (100), 247 (30), 220 (29), 219 (49), 205 (49), 165 (21); Anal. Calcd. for C₁₉H₁₈O: C, 86.99; H, 6.92. Found C, 86.76; H, 6.79. Spectral data for the enone **6**, NMR (CDCl₃) δ 7.4-7.8 (m, 7H), 6.95 (d, 1H), 6.13 (d, 1H), 2.1-2.4 (m, 4H), 1.6 (s, 3H); IR (KBr) 3050, 2900, 1690 cm⁻¹ UV λ_{max} (CCl₄) 355 nm (ϵ 200), 340 (ϵ 220), 255 (ϵ 30601); MASS, m/e (rel. abund) 236 (100), 179 (70), 165 (55), 193

(45), 89 (40); Anal. Calcd. for $C_{17}H_{16}O$: C, 84.40; H, 6.82. Found C, 86.27; H, 6.33.

Direct Irradiation of 4-Biphenyl-4-methyl-2-cyclohexenone (5). A solution of 380 mg of the enone, **5** in 10 mL of benzene was degassed with purified nitrogen and irradiated with 12 RPR-3000 Å lamps for 104 hours in pyrex tube. The solvent was then evaporated *in vacuo* to give solid material, which was recrystallized from ethanol to obtain 30 mg of bicyclic ketone **5a**. The spectral data for the ketone **5a**, NMR ($CDCl_3$) δ 7.2-7.8 (m, 9H), 2.6-2.8 (d, 1H), 2.1-2.2 (d, 1H), 1.7-2.2 (m, 3H), 1.0-1.4 (m, 1H), 1.5 (s, 3H); IR (neat) 3100, 2900, 1715 cm^{-1} ; MASS, m/e (rel. abund) 262 (57), 221 (17), 220 (100), 219 (78), 205 (68), 204 (23), 203 (27); Anal. Calcd. for $C_{17}H_{16}O$: C, 86.99; H, 6.92. Found C, 87.24; H, 6.85, mp. 96-97°C.

Direct Irradiation of 4-Methyl-4-(β -naphthyl)-2-cyclohexenone (6). A solution of 380 mg of the enone, **6** in 20 mL of benzene was degassed with purified nitrogen and irradiated with 12 RPR-3000 Å lamps for 96 hours in pyrex tube. The evaporated residue was analyzed by column chromatography and HPLC to obtain 5 mg of the enone **6a**. The spectral data for the ketone **6a**, NMR ($CDCl_3$) δ 7.4-7.9 (m, 7H), 6.3 (s, 1H), 3.2-3.3 (m, 1H), 1.8-2.7 (m, 4H), 1.2 (d, 3H); IR (neat) 3050, 2900, 1680 cm^{-1} ; MASS, m/e (rel. abund) 236 (100), 208 (80), 165 (38), 179 (35), 152 (20), 194 (18).

Direct Irradiation of the enone 5 and 6 in Methanol. The ketones **5** and **6** in methanol was irradiated as above to obtain the enone **5b** and **6a**. The spectral data for **5b**, NMR ($CDCl_3$) δ 7.2-7.8 (m, 7H), 6.18 (s, 1H), 3.75 (s, 1H), 2.1-2.5 (m, 4H), 1.9 (s, 3H); IR (neat) 3050, 2900, 1680 cm^{-1} ; MASS, m/e (rel. abund) 236 (100), 208 (35), 179 (50), 165 (40), 194 (38).

Sensitized Irradiation of the enone 5 and 6. A solution of 15 mg of the ketone and 120 mg of acetophenone in 15 mL of benzene was degassed with purified nitrogen and irradiated with 14 RPR-3500 Å lamps for 44 hours. GC and MASS analysis revealed that the photoproduct was same as in direct irradiation. Acetophenone or benzophenone sensitized irradiation of the enone **6** was performed as above. The photoproduct of sensitized irradiation was same as direct irradiation.

Quantitative Investigation. Quantum Yield Determinations. Quantum yield determinations were performed by the following general procedures. A solution of 100 mg of ketones in 10 mL methanol or benzene in pyrex tubes were

degassed with purified nitrogen. Irradiations were carried out with 12-15 RPR-3000 Å lamps. Light out-put was monitored by potassium ferrioxalate¹² actinometry according to the method of Hatchard and Parker. After irradiation with several intervals, the solutions were analyzed directly by GC using 1-undecanol as an internal standard.

Quenching Experiments. Several solutions of 80 mg of ketones and various concentration of naphthalene in 10 mL of benzene were degassed with purified nitrogen and irradiated with 12 RPR-3000 Å lamps. The irradiated mixtures were analyzed (internal standard, 1-undecanol) by gas chromatography.

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13. Quantum yields for **5** and **6** in benzene were not determined since the reactions were reversible at room temperature.