

## Formation of 1,5-Diketones from the Photoaddition of 1,3-Diphenyl-1,3-propanedione to *p*-Benzoquinones

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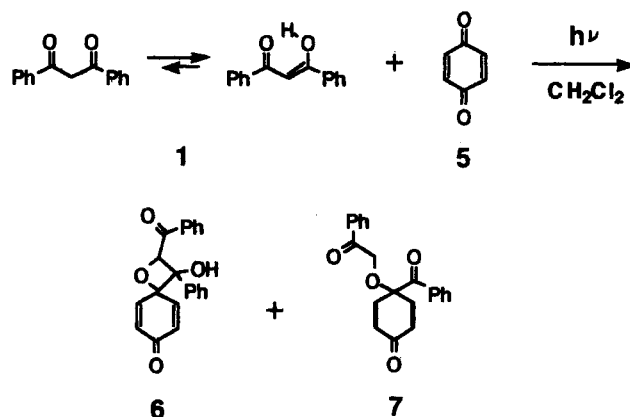
The photochemistry of quinones has been a subject of extensive investigations. It has been known that photocycloaddition of *p*-quinones to olefins generally gives spiro-oxetanes or cyclobutanes, depending upon the substituents.<sup>1,2</sup> For example, the electron-donating methyl groups in duroquinone **2** stabilize diradical intermediate to give cyclobutane. The synthetic significance of the intermolecular enone-alkene photocycloaddition has been extended by irradiating 1,3-diketones and alkenes to yield 1,5-diketones.<sup>3-6</sup> The enolic tautomer of the 1,3-diketone is an intermediate. In a molecule, like 1,3-diphenyl-1,3-propanedione **1**, the enol form is stabilized by internal hydrogen bonding. The enol of the 1,3-diketone adds to an alkene to give a  $\beta$ -hydroxy ketone, which undergoes retroaldolization to the 1,5-diketone.<sup>3-6</sup> Such a tautomerism was also applied to the photochemistry of anthrone to give [4+4]-dimer of anthranol and heptamer of 1,3-cyclohexadiene.<sup>7</sup> The electronic structure of *p*-quinones in the excited state is very similar to that of conjugated enones. It is well known that the photoaddition reaction of *p*-benzoquinone to electron-donor substituted alkenes is an efficient process that leads to spiro-oxetanes as the final products in high yields.<sup>1-2,8</sup>

Our interest in the specific reactivity of excited *p*-quinones has promoted us to investigate the possibility of the formation of 1,5-diketones from 1,3-diketones and *p*-benzoquinones. Photoreactions were conducted in a photo-reactor composed of a water-cooled system and a Pyrex reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208), after purging the mixture with nitrogen gas for 30 min. When a solution of 1,3-diphenyl-1,3-propanedione **1** (337 mg, 1.5 mmol) and tetramethyl-1,4-benzoquinone **2** (164 mg, 1.0 mmol) in dichloromethane (200 mL) was irradiated with 300 nm UV light for 5 days, the major product was found to be a 1,5-diketone **4**, *via* **3**, in 25% yield. The  $\beta$ -hydroxy ketone **3**

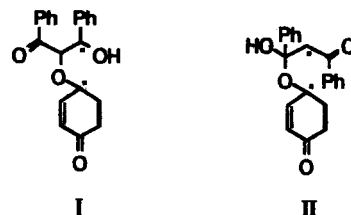
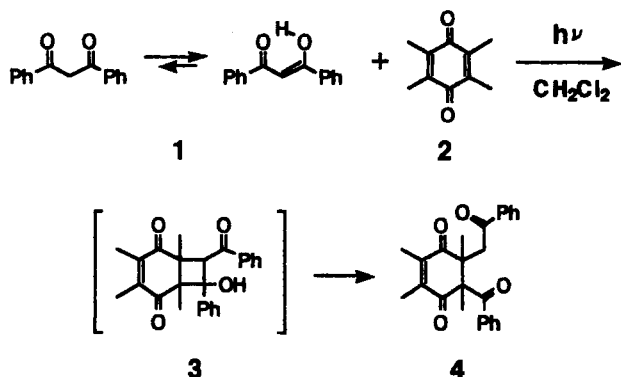
could not be isolated in this photoreaction.

The photoproducts **4** were separated by flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (gradient, 12:1 to 4:1, v/v) as the eluents. Mass spectrum (EI) of **4** showed a molecular ion peak at *m/e* 388. The methylene group was observed at  $\delta$  2.17 and  $\delta$  14.55 in <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra (CDCl<sub>3</sub>), respectively.

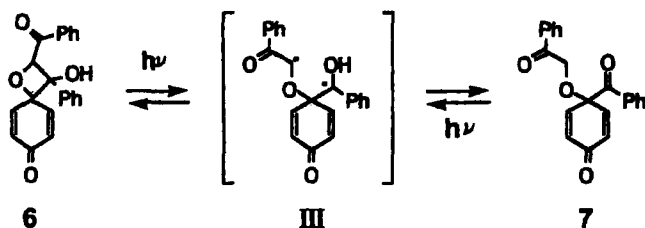
When a solution of 1,3-diphenyl-1,3-propanedione **1** (337 mg, 1.5 mmol) and *p*-benzoquinone **5** (108 mg, 1.0 mmol) in dichloromethane (100 mL) was irradiated with 300 nm UV light for 48 h, the consumption of the starting materials was associated with the formation of two products, spiro-oxetane **6** (25%) and its retroaldolization products **7** (27%).



Although two orientations of addition are possible when the enol form of **1** adds to *p*-benzoquinone **5** to yield the photocycloadducts, only one regioisomer **6** was found and isolated. The spiro-oxetanes **6** may be formed *via* the more stable 1,4-diradical intermediate **I**, followed by the intramolecular cyclization reaction to give oxetane **6**. Consistent with the result, the 1,4-diradical intermediate **I** having ketyl-like tertiary radical is much more stable than **II** having secondary radical. The regiochemistry in the formation of the photoadducts **6** is thus due to the preferential formation of biradical **I**.



In order to investigate the photostability of the  $\beta$ -hydroxy ketone **6**, a solution of **6** (20 mg,  $6.0 \times 10^{-2}$  mmol) in dichloromethane (15 mL) was further irradiated with 300 nm UV light for 12 h to yield retroaldolization products **7** in ca. 20% yield. The starting materials **1** and **5** were not found in this reaction. The formation of **7** would be rationalized by the cleavage of spiro-oxetane **6** at C-C bond containing three substituents, *i.e.*, PhCO, OH and Ph group. The 1,4-diradical **III** would be thought to undergo intramolecular hydrogen atom abstraction to give 1,5-diketone **7**.



Interestingly, irradiation of **7** in dichloromethane with 300 nm UV light also yielded **6**. The photoreversion of 1,5-diketone **7** to  $\beta$ -hydroxy ketone **6** would be explained in terms of Norrish Type II reaction. The 1,5-diketone **7**, which has  $\gamma$  hydrogen atoms, undergoes a characteristic 1,5-hydrogen atom transfer by an intramolecular cyclic process with the formation of ketyl-like 1,4-biradical **III**. The 1,4-diradical may be stabilized by cyclization to form 4-membered ring compound **6**. For this reason, it was found that the prolonged irradiation of a solution of **1** and **5** in dichloromethane does not affect the yield of **6** and **7**.

Extension of the chemical properties of the photoproducts and the reactivity of 1,3-diketones towards various quinonoid compounds will be investigated.

## Experimental Section

**General Procedure for the Photoadditions of 1,3-Diketone to *p*-Quinones.** Preparative photoreactions were conducted in a photochemical reactor composed of a water-cooled system and a Pyrex reaction vessel with 300 nm UV lamp (Rayonet Photochemical Reactor, Model RPR-208). Irradiation was carried out after degassing with dry nitrogen gas for 30 min. The progress of the reactions were analyzed using pre-coated TLC plaes (silica gel, Kieselgel 60 F254, Merck Co.). The residue obtained from the evaporation was chromatographed over silica gel (Kieselgel 60, 230-400 mesh) with *n*-hexane and ethyl acetate as the eluents.

**Irradiation of 1,3-Diphenyl-1,3-propanedione and Tetramethyl-1,4-benzoquinone.** A solution of 1,3-diphenyl-1,3-propanedione **1** (337 mg, 1.5 mmol) and tetramethyl-1,4-benzoquinone **2** (164 mg, 1.0 mmol) in di-

chloromethane (100 mL) was irradiated with 300 nm UV light for 5 days to yield 1,5-diketone **4** in 25% yield. **4**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  8.02-7.42 (10H, m), 2.17 (2H, s,  $\text{CH}_2$ ), 2.14 (6H, s, 2 $\text{CH}_3$ ), 1.99 (3H, s,  $\text{CH}_3$ ), 1.94 (3H, s,  $\text{CH}_3$ );  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ),  $\delta$  200.4 (CO), 199.8 (CO), 195.8 (2CO), 133.6 (2CH), 128.9 (4CH), 128.6 (4CH), 13.30 ( $\text{CH}_2$ ), 12.73 (2 $\text{CH}_3$ ), 12.37 ( $\text{CH}_3$ ), 12.21 ( $\text{CH}_3$ ); UV (MeOH),  $\lambda_{\text{max}}$  342, 243 nm; IR (KBr), 3346, 3340, 2917, 1743, 1693, 1644, 1553, 1518, 1018, 965  $\text{cm}^{-1}$ ; Mass (EI),  $m/e$  388 (M), 105 (100%, PhCO), 77 (Ph).

**Irradiation of 1,3-Diphenyl-1,3-propanedione and *p*-Benzoquinone.** A solution of 1,3-diphenyl-1,3-propanedione **1** (337 mg, 1.5 mmol) and *p*-benzoquinone **5** (108 mg, 1.0 mmol) in dichloromethane was irradiated with 300 nm UV light for 48 h to give spiro-oxetane **6** and its retroaldolization product **7**, in 25% and 27% yield, respectively. **6**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  11.56 (OH, s), 8.19-7.51 (10H, m), 7.06 (2H, dd,  $J=12$  Hz,  $J=8$  Hz), 6.97 (1H, d,  $J=8$  Hz), 6.87 (1H, d,  $J=8$  Hz), 6.71 (1H, s, CH); UV (MeOH),  $\lambda_{\text{max}}$  364, 252, 228, 212, 208 nm; IR (KBr), 3399, 3090, 2919, 1701, 1597, 1482, 1220, 1189  $\text{cm}^{-1}$ ; Mass (EI),  $m/e$  332 (M), 314 (M-18), 105 (100%, PhCO), 77 (Ph). **7**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  7.91-7.36 (10H), 7.05 (2H, d,  $J=8$  Hz), 6.70 (2H, dd,  $J=12$  Hz,  $J=8$  Hz), 6.72 (2H, s,  $\text{CH}_2$ ); UV (MeOH),  $\lambda_{\text{max}}$  334, 289, 250, 212 nm; IR (KBr), 3020, 2952, 1689, 1596, 1448, 1269  $\text{cm}^{-1}$ ; Mass (EI),  $m/e$  332 (M), 105 (100%, PhCO), 77 (Ph).

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