

scope of this reaction for synthesis of natural products, we performed the reaction with (*R*)-glyceraldehyde **6** (Scheme 2). The reaction of **6** with carbanion of **1** furnished products **7** and **8** (5:2) in 87% yield. Compound **7** was converted to the desired diol **9** in 65% yield in three steps.

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- The stereochemistry of ring opening reaction was determined by  $^1\text{H}$  NMR spectral data of acetonides of diols. *Syn-* and *anti-*diols were converted into corresponding *threo-* and *erythro-*isomers of acetonides, respectively.

## Photochemical Formation of 1,5-Diketones from Dibenzoylmethane and *o*-Quinones<sup>†</sup>

Ji Ae Chang, Ae Rhan Kim, and Sung Sik Kim\*

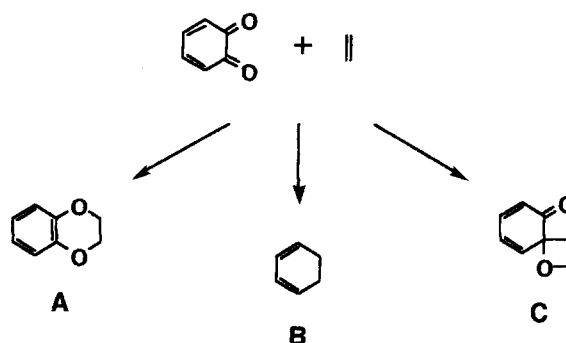
Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea

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Quinones are an important class of compounds in organic synthesis, in industry, and in nature. Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of extensive investigations in many areas.<sup>1,2</sup> It has been known that photoaddition of *o*-quinones to olefins gives mainly three types of products, the 1,4-dioxene (type A), 1,3-cyclohexadiene (type B) and keto-oxetane (type C), as shown in Scheme 1, along with H-abstraction products.<sup>3-9</sup>

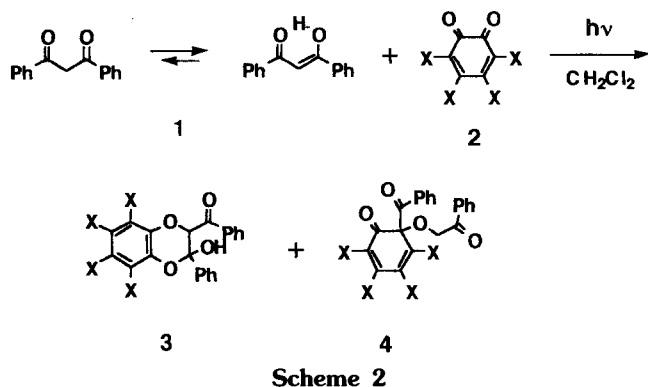
The synthetic significance<sup>10,11</sup> of the intermolecular enone-alkene photocycloaddition was extended by irradiating 1,3-diketones in the presence of quinones to produce 1,5-diketones. The enolic form of the 1,3-diketone, which is restricted in six-membered ring by an intramolecular hydrogen bond, is an intermediate. Photoaddition of an alkene to this enol gives a  $\beta$ -hydroxy ketone, which undergoes retro-aldolization to the 1,5-diketone.

Our interest in the diversity of the reactivity of excited *o*-quinones has promoted us to investigate the type of the photoproducts of *o*-quinones and 1,3-diketones. We report here, for the first time, that irradiation of *o*-quinones to 1,3-diketones leads to 1,4-dioxenes (type A) and/or keto-oxetanes (type C), in which the latter were found to give 1,



Scheme 1

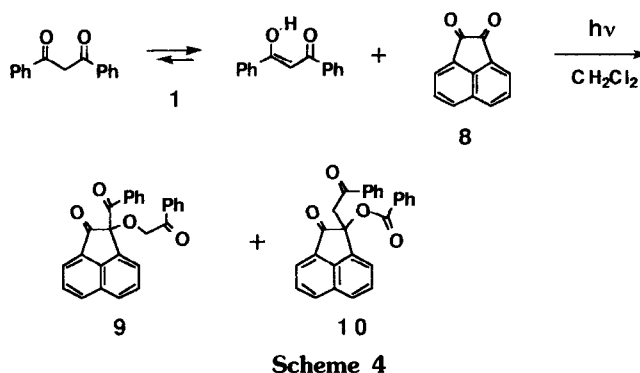
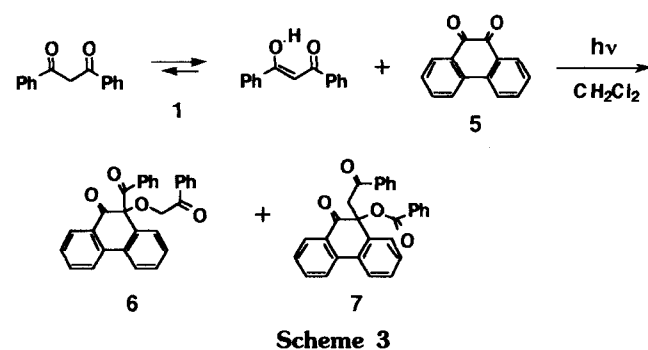
<sup>†</sup>This paper is dedicated to Prof. Sang Chul Shim on the occasion of his 60th birthday.



5-diketones containing dienone moiety. The electronic structure of *o*-quinones in the excited state is very similar to that of conjugated enones. The photoaddition reaction of 1,3-diketone **1** to tetrahalo-1,2-benzoquinones **2** gave not only 1,4-dioxenes **3** but also 1,5-diketones **4**, as shown in Scheme 2, in which the latter were formed from retro-aldolization process of the initially formed keto-oxetanes.<sup>12</sup>

Preparative photoreactions were conducted in a photoreactor composed of a water-cooled system and a Pyrex reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208), after purging with nitrogen gas (purity: 99.9%) for 30 min. When a solution of dibenzoylmethane, *i.e.*, 1,3-diphenyl-1,3-propanedione **1** (135 mg, 0.6 mmol) and tetrachloro-1,2-benzoquinone **2a** (123 mg, 0.5 mmol) in dichloromethane (200 mL) was irradiated with 300 nm UV light for 7 days, the consumption of starting material was associated with the formation of two photoproducts. Separation and isolation of both products were accomplished by flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (10:1, v/v) as the eluents to give 1,4-dioxene **3a** (18%) and 1,5-diketone **4a** (7%).<sup>12</sup> Irradiation of a dichloromethane solution (200 mL) of dibenzoylmethane **1** (135 mg, 0.6 mmol) and tetrabromo-1,2-benzoquinone **2b** (212 mg, 0.5 mmole) with 300 nm UV light for 7 days also afforded **3b** (12%) and **4b** (5%).<sup>12</sup>

In contrast, the photoaddition of 9,10-phenanthrenequinone **5** (or acenaphthenequinone **8**) to **1** led to 1,5-diketones as the major products. 1,4-Dioxenes were not found in these photoreactions. A dichloromethane solution (150 mL) of **1** (449 mg, 2 mmole) and **5** (104 mg, 0.5 mmole) was irradiated with 300 nm UV light for 3 days to give 1,5-diketones **6** (25%) and **7** (3%), as shown in Scheme 3.<sup>13</sup> The keto-oxetanes were not isolated in this

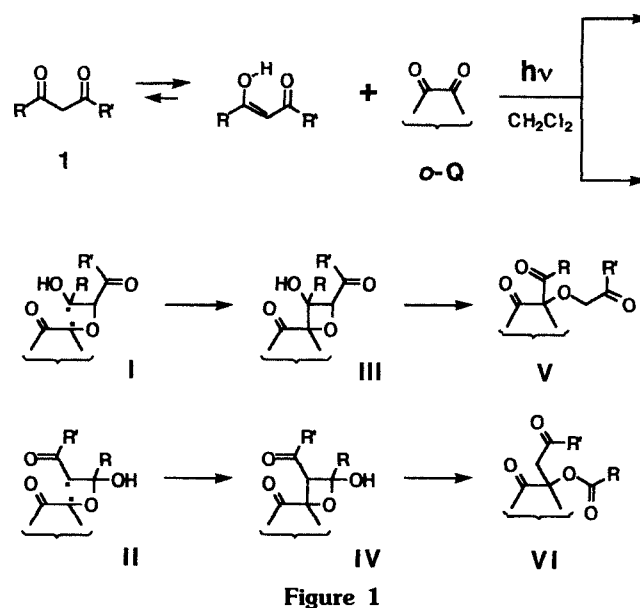


reaction. The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>) of **6** and **7** showed methylene protons at δ 5.43 and δ 4.69, respectively.

Irradiation of **1** (224 mg, 1 mmole) and **8** (91 mg, 0.5 mmole) in dichloromethane (150 mL) with 300 nm UV light for 4 days also led to the same type of photoproducts, **9** and **10**, in 27% and 6% yields, respectively (Scheme 4).<sup>14</sup> The methylene protons of **9** and **10** were observed at δ 5.55 and δ 4.71, respectively, in <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>).

The preferential formation of **6** to **7** (or **9** to **10**) may be rationalized by comparing the two 1,4-diradical intermediates, I and II, as shown in Figure 1. Consistent with the experimental results, the 1,4-diradical intermediate I having ketyl-like tertiary radical is more stable than II having secondary radical. Thus, the 1,5-diketone V may be formed *via* the more stable 1,4-diradical intermediate I, followed by the intramolecular cyclization reaction to give keto-oxetane III, and finally undergoes retro-aldolization to give V, such as **6** and **9**.

In conclusion, we have found that 1,5-diketones can be produced photochemically from *o*-quinones and 1,3-diketone, *via* keto-oxetanes. Extension of the chemical properties of the photoproducts and the photoaddition of *o*-quinones and various kinds of 1,3-diketones will be investigated.



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- (a) **3a**: UV (MeOH)  $\lambda_{\max}$  310, 280, 231, 212 nm; IR (KBr) 3630, 3020, 2922, 1679, 1590, 1287  $\text{cm}^{-1}$ ; 400 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  9.81 (1H, OH, s), 8.20-7.04 (10H, aromatic), 6.24 (1H, s); Mass (EI), m/e 470 (M). (b) **4a**: UV (MeOH)  $\lambda_{\max}$  300, 222 nm; IR (KBr) 3060, 2923, 1703, 1689, 1592, 1451, 1038  $\text{cm}^{-1}$ ; 400 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  8.20-7.51 (10H, aromatic), 5.48 (2H, s); Mass (EI), m/e 470 (M). (c) Dibenzoylmethane were also found to add to *p*-benzoquinone to give 1,5-diketone. For this reaction, see Kim, A. R.; Kim, K. J.; Shim, S. C.; Kim, S. S. *Bull. Korean Chem. Soc.* **1997**, 18(10), 1125.
- (a) **6**: UV (MeOH)  $\lambda_{\max}$  344, 300, 283, 248, 244 nm; IR (KBr) 3020, 2915, 1737, 1253, 1025  $\text{cm}^{-1}$ ; 400 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  8.70-7.30 (18H, aromatic), 5.43 (2H, s); Mass (EI), m/e 432 (M), 327 (M-105), 105. (b) Due to the high reactivity of **5** toward the solvent, the minor product **7** could not be isolated. The molar ratio of **6** to **7** was found to be *ca.* 8.3:1.0 in  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of the mixture, in which methylene protons of **7** were observed at  $\delta$  4.69. (c) Another 1,3-diketones, such as 1-benzoylacetone and 2,4-pentanedione were also used in an attempt to isolate 1,5-diketones. The results was not as encouraging.
- (a) **9**: UV (MeOH)  $\lambda_{\max}$  340, 240, 220 nm; IR (KBr) 3020, 2929, 1703, 1277, 1022  $\text{cm}^{-1}$ ; 400 MHz  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ),  $\delta$  8.13-7.50 (16H, aromatic), 5.55 (2H, s); Mass (EI), m/e 406 (M), 105, 77. (b) **10**: UV (MeOH)  $\lambda_{\max}$  340, 245, 225 nm; IR (KBr) 3020, 2924, 1703, 1280, 1024  $\text{cm}^{-1}$ ; 400 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  8.20-7.51 (16H, aromatic), 4.71 (2H, s); Mass (EI), m/e 406 (M), 105, 77.

## Titanium Dioxide Mediated Photocatalytic Conversion of Arenealdehyde Phthalazinylhydrazones to *s*-Triazolo[3,4-*a*]phthalazines

Koon Ha Park\* and Kun Jun†

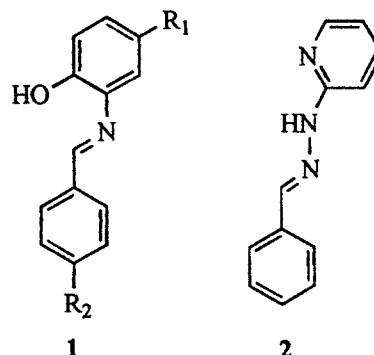
\*Department of Chemistry, Chungnam National University, 220 Kung Dong, Yusung Ku, Taejon 305-764, Korea

†Korea Research Institute of Chemical Technology, P.O. Box 107, Yusung Ku, Taejon 305-606, Korea

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We have recently investigated the reactions of Schiff's bases with cation radicals such as thianthrene cation radical perchlorate ( $\text{Th}^+$ ) and tris(2,4-dibromophenyl)aminium hexachloroantimonate ( $\text{Ar}_3\text{N}^+$ ) in nitrile solvents to give products of intramolecular cyclization and intermolecular cycloaddition.<sup>1,2</sup> In these reactions the major product seemed to largely dependent on the cation radical.  $\text{Th}^+$  gave intramolecular cyclization product in the reactions with phenolic Schiff's base **1** and arenealdehyde 2-pyridylhydrazone **2**.<sup>1,2</sup> On the other hand,  $\text{Ar}_3\text{N}^+$  with arenealdehyde 2-pyridylhydrazone **2** gave intermolecular cycloaddition product as a major product.<sup>2</sup>

The first step in these reactions has been well established



to be the formations of  $\mathbf{1}^+$  and  $\mathbf{2}^+$  through one electron