

Photoaddition Reactions of 1,2-Diketone

Hea Jung Park¹, Jung Soo Seo¹, Ung Chan Yoon^{1*}, Dae Won Cho^{2*}

¹Department of Chemistry and Chemical Institute for Functional Materials,
Pusan National University, Busan 609-735, Korea

²Department of Chemistry, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea

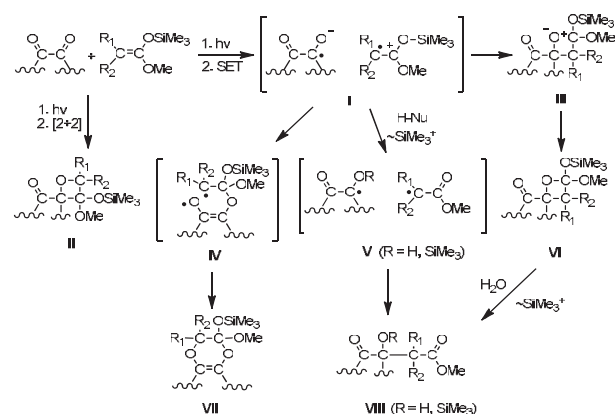
ABSTRACT: Photoaddition reactions between 1,2-dicarbonyl compounds and silyl enol ethers in acetonitrile and benzene were explored. Irradiation of acetonitrile or benzene solutions containing 1,2-diketone, acenaphthalquinone, phenanthrene-quinone and silyl enol ethers is observed to promote the production of 1,4-dioxenes, oxetanes, and β -hydroxyketone by the [4+2]-cycloaddition, Paterno-Buchi processes, and SET promoted Claisen-type condensation. Among these competitive pathways leading to the generation of each types of products, SET promoted 1,4-dioxene and β -hydroxyketone formation are more favored regardless of solvent polarity.

In recent studies, we explored photochemical reactions of 1,2-diketone and silyl ketene acetals and showed that versatile C-C or C-O bond forming processes take place. On the basis of an analysis of the protoproducts presented previous study¹, ground state/ excited state redox properties of 1,2-diketone electron acceptor²⁻³ and silyl ketene acetal electron donor^{4,5}, and results of photoreactions of monoketone analogs^{4,6-8} give plausible mechanistic pathways for 1,2-diketone with silyl ketene acetals (Scheme 1). Single electron transfer (SET)-promoted or direct [4+2] cycloaddition^{1,9}, classical Paterno-Buchi [2+2] cycloaddition^{1,4,10}, and sequential SET-desilylation processes compete for deactivation of the 1,2-dicarbonyl excited state by the silyl ketene acetals. These respective processes generate ion radical pairs **I** and oxetanes **II**. Desilylation of **I** produces ion radical pairs **V**, which undergo coupling to form ketoester products **VIII**. Alternatively, radical and/or ionic coupling of ion radical pairs **I** produces biradicals **IV** or zwitterionic intermediates **III**, which are the precursors of the respective 1,4-dioxenes **VII** and oxetanes **VI**, the latter of which should easily convert to ketoesters **VIII**.

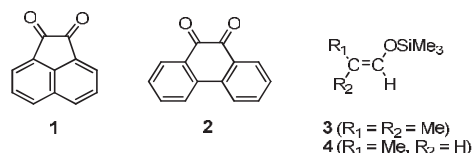
In this study, as a continuing effort, we explored the photoaddition reactions of acenaphthenequinone/phenanthrenequinone as 1,2-diketones **1-2** and dimethyl-/monomethyl-substituted silyl enol ethers **3-4**¹¹⁻¹³ as silyl electron donors¹⁴ (Scheme 2).

*To whom correspondence should be addressed.
E-mail: ucyoon@pusan.ac.kr
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Scheme 1.

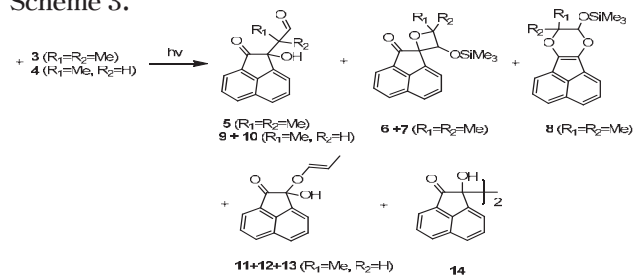


Scheme 2.



Photochemical reactions were performed by irradiation with Uranium glass filtered light ($\lambda > 330$ nm) of acetonitrile or benzene solutions of **1-2** (11 mM) and the **3-4** (22 mM).

Scheme 3.



The products/yields arising from photoreactions of aromatic 1,2-diketone **1-2** with silyl enol ether **3-4** are displayed in Scheme 3-4 and Table 1. Irradiation of acetonitrile solution of acenaphthenequinone (**1**) and dimethyl-substituted silyl enol ether **3** results in the formation of β -hydroxyketone **5** (32 %) as major and oxetanes **6+7**¹⁵ as minor products (4%, 2%). In benzene, both hydroxyketone **5** (22 %) and 1,4-dioxene **8** (14 %) are major products, which are arisen by SET-promoted

addition pathway. Though the yields of oxetanes are quite small, Paterno–Buchi type [2+2] cycloaddition reaction seem to take place. When replaced to monomethyl substituted silyl enol ether **4** for photoreaction with **1**, SET–desilylation process took place predominantly to form β –hydroxyketone **9–10**¹⁴ and α –vinyloxy– α –silyloxyketone **11–13**¹⁴ along with minor amounts of the dimer **14**¹ in both acetonitrile and benzene solvents. Interestingly, no Paterno–Buchi [2+2] cycloadducts were found in the photoreaction of **1** and relatively electron–deficient silyl enol ether **4**.

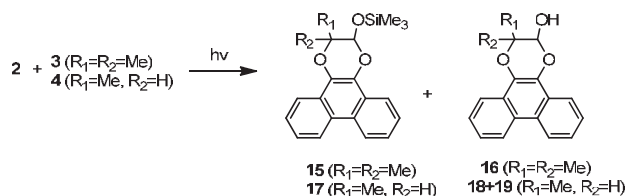
Table 1. Photoreactions of 1,2–diketones **1–2** and silyl enol ethers **3–4**.

| Reactant | Solvent | Reaction Time (min) | Conversion (%) | Product (% yield) ^a |
|----------|--------------------|---------------------|----------------|--|
| 1+3 | CH ₃ CN | 30 | 72 | 5(32), 6(4), 7(2), 8(2) |
| 1+3 | Benzene | 40 | 68 | 5(22), 6(4), 7(3), 8(14) |
| 1+4 | CH ₃ CN | 90 | 96 | 9(21), 10(21), 11(2), 12(33), 13(2), 14(6) |
| 1+4 | Benzene | 90 | 95 | 9(15), 10(15), 11(3), 12(28), 13(3), 14(9) |
| 2+3 | CH ₃ CN | 40 | 77 | 15(27), 16(59) |
| 2+3 | Benzene | 50 | 73 | 15(50), 16(38) |
| 2+4 | CH ₃ CN | 50 | 87 | 17(8), 18(36), 19(36) |
| 2+4 | Benzene | 60 | 90 | 17(34), 18(24), 19(24) |

^aYields are determined based on consumed 1,2–diketones

Photolysis of phenantrenequinone (**2**) with silyl enol ethers **3–4** give rise to different product distribution pattern as compared with those produced from photoreaction of **1** and **3–4**. For example, regardless of the solvent used, photoreactions of **2** with silyl enol ethers **3–4** lead to the formation of 1,4–dioxenes as sole products. (Table 1 and Scheme 4).

Scheme 4.



Two major conclusions can be drawn from the results shown in Table 1. First, SET promoted deactivation pathway is major or predominant in the photoreactions of 1,2–diketone and silyl enol ethers. Second, solvent polarity is not significant factor that governs the reaction pathways, which are found in previous studies.^{1,4,13}

Even though more studies are necessary to investigate the substituent's effect of silyl enol ether and reaction pathways in detail about the photoreaction of 1,2–diketones and silyl enol ethers, observations made in this study show that SET promoted pathways take place highly efficiently and regioselectively.

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15. Diastereomeric mixtures were formed due to the generation of stereocenter. Yields were determined based on integration ratios of ¹H–NMR