

Photoadditions of Silyl Butadienyl Ether to 1,2-Diketones

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In a recent study,¹ we explored photochemical reactions of 1,2-diketones in the presence of silyl ketene acetals electron donors^{2–6} and showed that C–C or C–O bond forming reaction takes place via three major excited state processes, 1) single electron transfer or direct [4+2]-cycloaddition to generate dioxenes,^{1,7} 2) Paterno-Buchi type [2+2]-cycloaddition to form oxetanes,^{1,8} and 3) sequential SET-desilylation pathway that produce β -hydroxy- γ -ketoesters or oxetanes.^{1–3} In addition, the exploration uncovered that the competition between these excited state reaction pathways is largely dependent on solvent polarity and the nature of silyl ketene acetals (i.e., oxidation potentials).

Silyl enol ethers, which have properties that are closely related to those of silyl ketene acetals, are known to produce α -carbonyl radicals in the photochemical, electrochemical, or metal oxidation conditions (Scheme 1).^{9–12}

As an continuing effort, we explored photoreactions of 1,2-diketones, naphthenequinone (**3**), 9,10-phenanthrenequinone (**4**) with silyl butadienyl ether **5**. (Scheme 2) The result of this study, described below, revealed that photoproduct formations in these reactions take place via SET-

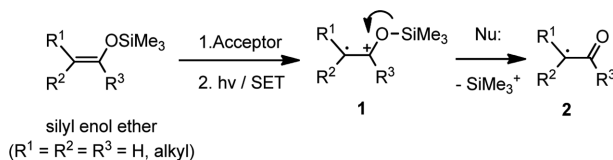
desilylation and SET-promoted [4+2]-cycloaddition processes.

Photochemical reactions were performed by using uranium filtered light ($\lambda > 330$ nm) in acetonitrile and benzene solution containing 1,2-diketones **3–4** (11 mM) and silyl butadienyl ether **5** (22 mM) for time periods that bring about 96–97% conversion of 1,2-diketones.

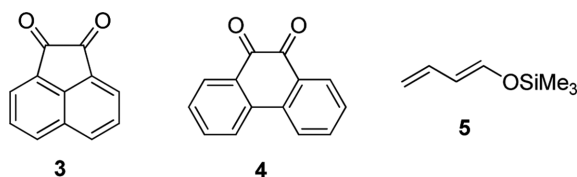
The products/yields arising from photoreactions of acetonitrile and benzene solution of acenaphthenequinone **3** with ether **5** are displayed in Scheme 3 and Table 1. Irradiation of acetonitrile solution of **3+5** resulted in the predominant formation of ϵ -keto- δ -hydroxyaldehyde **6**¹³ (93%) and diastereomeric 2-oxene **7**¹⁴ (4%) as a minor product. In benzene solution of **3+5**, **7** was produced nearly exclusively along with trace of **6**.

Photoreaction of 9,10-phenanthrenequinone **4** with silyl butadienyl ether **5** in acetonitrile gave rise to the generation of 1,4-dioxene **9** and **10**¹⁵ (46%) as major products and ϵ -keto-d-hydroxyaldehyde **8** (24%) as a minor adduct (Scheme 4 and Table 1). In the irradiation of benzene solution of **4+5**, SET promoted [4+2]-cycloaddition pathway leading to the formation of 1,4-dioxene **9** and became more predominant (ca. 9:1 ratio).

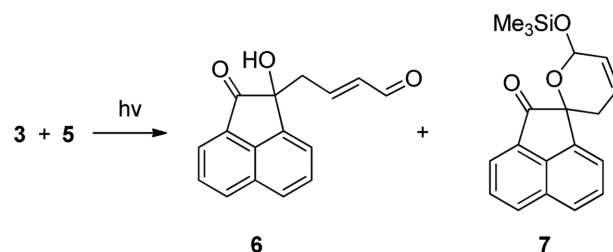
An analysis of the product distributions observed in the exploration provides feasible mechanistic pathways that lead to the generation of each photoproduct (Scheme 5).



Scheme 1.



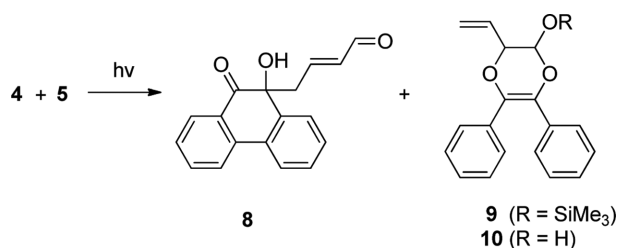
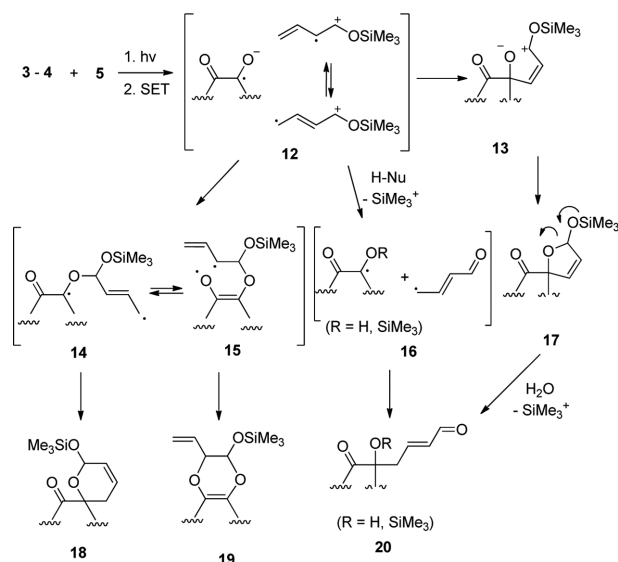
Scheme 2.



Scheme 3.

Table 1. Photoreactions of 1,2-diketones 3–4 and silyl butadienyl ether 5

Reactants	Solvent	Rxn Time (h)	% conv.	Product(% yield) ^a
3+5	MeCN	1.5	97	6(93), 7a(2), 7b(2)
3+5	Benzene	2	96	6(58), 7a(trace), 7b(trace)
4+5	MeCN	1.5	90	8(24), 9(36), 10(10)
4+5	Benzene	2	97	8(6), 9(34), 10(22)

^aYields are based on consumed 1,2-diketone 3–4**Scheme 4.****Scheme 5.**

For example, radical ion pairs **12** arising by SET would have several excited state deactivation pathways i.e., 1) C–C bond forming reaction giving **13** and **20** through **16**, and 2) C–O bond formation process to yield **14** and **15**. Firstly, generated intermediate **17** (from **13**) and radical pair **16** generated by solvent assisted desilylation produce photoproduct **20**. Especially, this process becomes predominant or exclusive in the photo-irradiation of acetonitrile or benzene solution of acenaphthenequinone **3** with silyl butadienyl ether **5**. Secondly, C–O bond formation between radical ion pairs **12** produce biradical intermediates **14** and **15**, which are precursors of cyclic products, 2-oxene **18** and 1,4-dioxene **19**. In the photoreaction of

acetonitrile solution containing 9,10-phenanthrenequinone **4** and ether **5**, it appears that two reaction pathways are competing. However, decreased solvent polarity (from acetonitrile to benzene) made C–O bond forming process resulting in intermediate **15** be dominated. In addition, silyl tethered 1,4-dioxene **9** is easily converted to **10** by acidic hydrolysis.

Results arising from this preliminary study show that photoaddition reactions of 1,2-diketones with silyl butadienyl ether are proceeded through SET-desilylation or SET-promoted [4+2]-cycloaddition processes depending on the nature of substrates and reaction solvent and the processes have a potential for the synthesis of highly functionalized e-keto-d-hydroxyaldehyde and oxetanes.

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13. Structural assignment of **6** was made on the basis of NMR and HRMS spectroscopic data. $^1\text{H-NMR}$ (CDCl_3) 2.87 (q, 1H, $J = 8.4 \text{ Hz}$), 3.04 (q, 1H, $J = 8.0 \text{ Hz}$), 6.05 (q, 1H), 6.88 (q, 1H), 7.59–7.79 (m, 3H), 7.89–7.98 (m, 2H), 8.15 (d, 1H), 9.36 (d, 1H); $^{13}\text{C-NMR}$ 41.1, 79.0, 120.7, 122.5, 125.7, 128.4, 128.7, 129.8, 130.5, 132.4, 136.1, 138.4, 140.9, 150.7, 193.5, 204.0; HRMS (EI) m/z 252.0788 (calc. $\text{C}_{16}\text{H}_{12}\text{O}_3$, 252.0786).
14. NMR spectroscopic data of **7a** and **7b** are followed. **7a**: $^1\text{H-NMR}$ –0.21 (s, 9H), 2.22 (m, 1H), 2.77 (d, 1H), 5.79 (d, 1H), 6.08 (m, 1H), 6.19 (m, 1H), 7.56–8.16 (m, 6H); $^{13}\text{C-NMR}$ –0.1, 30.1, 77.2, 89.7, 122.2, 123.6, 124.6, 125.0, 127.8, 128.3, 128.7, 130.5, 130.6, 132.1, 140.2, 141.5, 202.1. **7b**: $^1\text{H-NMR}$ –0.21 (s, 9H), 2.13 (d, 1H), 2.83 (m, 1H), 6.09 (d, 1H), 6.17–6.30 (m, 2H), 7.56–8.16 (m, 6H); $^{13}\text{C-NMR}$ –0.1, 30.3, 77.4, 89.9, 122.1, 123.4, 124.7, 125.1, 127.7, 128.3, 128.8, 130.6, 130.7, 132.0, 140.3, 141.7, 202.2.
15. Photoproduct **9** and **10** were obtained as one of possible diastereomers.
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