JOC Article

Photoaddition Reactions of 1,2-Diketones with Silyl Ketene Acetals. Formation of β-Hydroxy-γ-ketoesters

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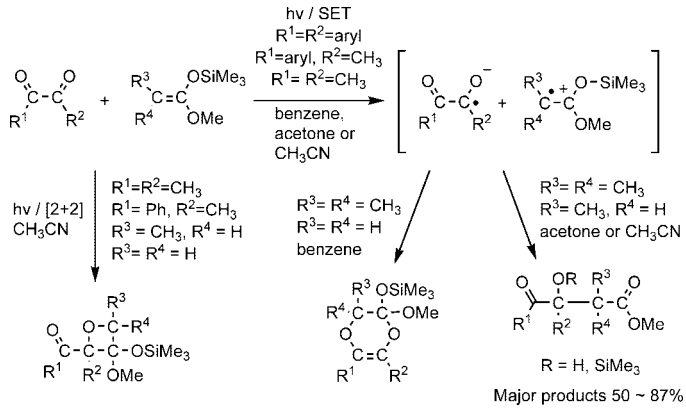

Photochemical reactions taking place between 1,2-diketones and silyl ketene acetals and their excited state reaction mechanisms have been explored. Irradiation of benzene, acetone, or acetonitrile solutions containing 1,2-diketones and silyl ketene acetals is observed to promote formation of 1,4-dioxenes, resulting from [4 + 2]-cycloaddition, oxetanes, arising by Paterno−Buchi processes, and β-hydroxy-γ-ketoesters, generated by SET-promoted Claisen-type condensation. These competitive pathways leading from the excited states of the 1,2-diketones to these products are influenced by solvent polarity and the nature of the silyl ketene acetal and 1,2-diketone. The Claisen-type condensation process, following an SET desilylation pathway and predominating when the photoreactions are carried out in the polar solvent acetonitrile, represents an efficient method to prepare a variety of diversely substituted β-hydoxy-γ-ketoesters.

Introduction

Mechanistic pathways involving sequential single electron transfer (SET) desilylation are now well documented in photoreactions of electron acceptors and α-trialkylsilyl-substituted electron donors.[1] Owing to its high rate, silophile-assisted desilylation of α-trialkylsilyl cation radicals normally takes place much more rapidly than other possible cation radical α-heterolytic fragmentation processes such as deprotonation.[2] Consequently, cation radical desilylation serves as an efficient and regioselective method to generate carbon-centered radical intermediates in carbon−carbon bond forming processes

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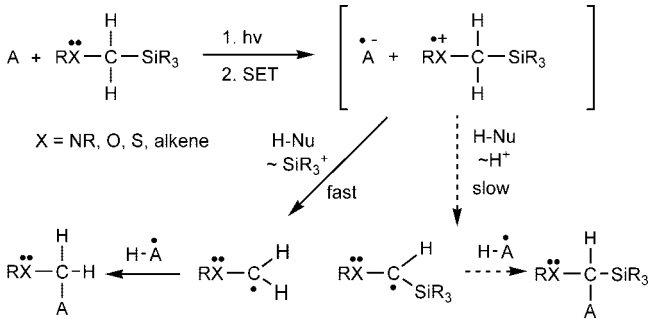
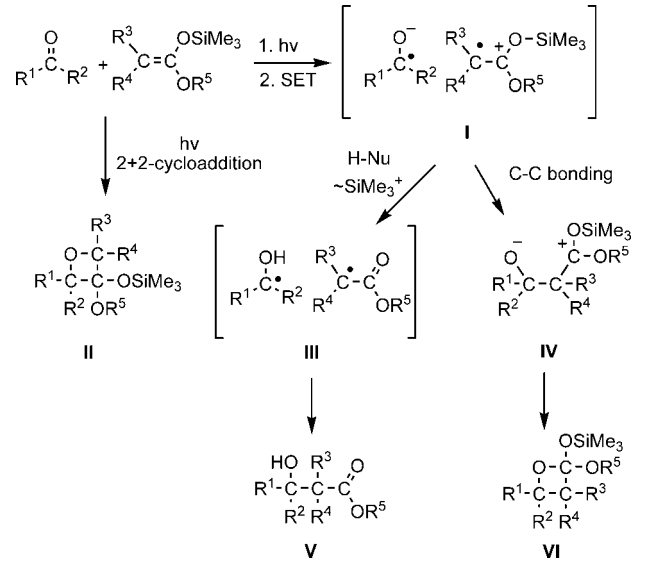
SCHEME 1



(Scheme 1).[1–7] Numerous examples of SET photochemical reactions promoted in this manner are found in the excited state chemistry of iminium salts,[3] cyanoarenes,[4] conjugated enones,[5] *ortho*-quinones,[6] and phthalimides.[7]

In recent studies, we explored photochemical reactions of aromatic carbonyl compounds and silyl ketene acetals[8] and showed that versatile C−C bond forming processes take place.[9–11] The results of this effort demonstrated that several types of reaction pathways can be followed (Scheme 2). In these processes, SET from silyl ketene acetal electron donors to excited states of aromatic carbonyl acceptors, which generates ion radical intermediates **I**, effectively competes with other

SCHEME 2



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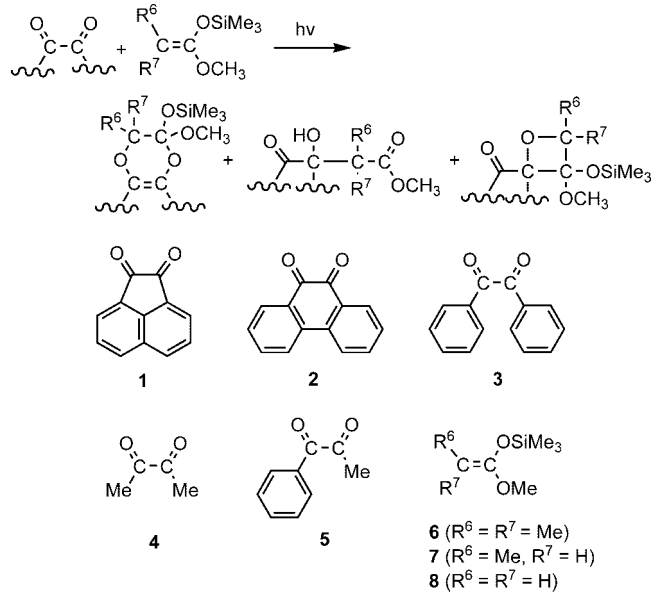

decay processes. The ion radical pairs react further to form radical pairs **III** or zwitterions **IV** which are then converted to the respective β-hydroxyester **V** and oxetane **VI** products. In competition, the excited aromatic carbonyl compound can couple with the silyl ketene acetal in a classical Paterno−Buchi manner to produce oxetane **II**.

When ground state and excited state redox properties and solvent polarities are taken into account, photoreactions of 1,2-diketones[12,13] with silyl ketene acetals are expected to follow three major routes involving (1) SET induced or direct [4 + 2]-cycloaddition to generate dioxenes,[12b,14] (2) classical Paterno−Buchi [2 + 2]-cycloaddition to form oxetanes,[15] and (3) sequential SET desilylation to produce β-hydroxy-γ-ke-

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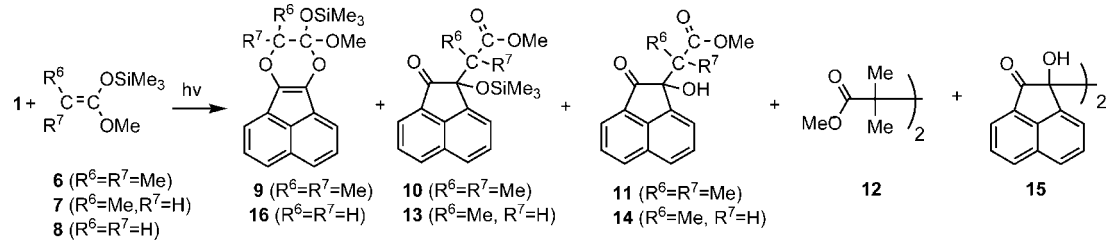
TABLE 1. Photoreactions of 1,2-Diketones 1−3 and Silyl Ketene Acetals 6−8[a]

entry	reactant	solvent	reaction time (h)	conversion (%)	product (% yield)[b]
1	**1** + **6**	benzene	4	89	**9** (19), **10** (7), **11** (49)
2	**1** + **6**	acetone	3.5	93	**9** (2), **10** (12), **11** (58), **12** (4)
3	**1** + **6**	CH_3CN	2	93	**9** (trace), **10** (7), **11** (77), **12** (7)
4	**1** + **7**	CH_3CN	6	66	**13a** (6), **13b** (5), **14a** (28), **14b** (28), **15** (3)
5	**1** + **8**	CH_3CN	18	77	**15** (42)
6	**1** + **8**	benzene	11	81	**16** (18), **15** (42)
7	**2** + **6**	benzene	8.5	48	**17** (30), **18** (trace), **19** (trace), **12** (trace)
8	**2** + **6**	acetone	5	47	**17** (trace), **18** (6), **19** (81), **12** (3)
9	**2** + **6**	CH_3CN	5.5	85	**17** (trace), **18** (6), **19** (55), **12** (7)
10	**2** + **7**	acetone	16	80	**20a** (4), **20b** (4), **21a** (12), **21b** (12), **22** (12), **23** (23)
11	**2** + **7**	CH_3CN	4	81	**20a** (8), **20b** (6), **21a** (28), **21b** (19), **22** (5)
12	**2** + **8**	acetone	16	80	**22** (23), **23** (25)
13	**2** + **8**	CH_3CN	10	53	**22** (27)
14	**3** + **6**	benzene	3	80	**24** (41), **25** (25), **12** (trace)
15	**3** + **6**	acetone	5	71	**24** (trace), **25** (71), **12** (trace)
16	**3** + **6**	CH_3CN	4	80	**24** (trace), **25** (76), **12** (21)
17	**3** + **7**	CH_3CN	9	54	**26** (61), **27** (5)
18	**3** + **8**	CH_3CN	14.5	87	**28** (23), **27** (40), **29** (19)

[a] Concentrations of reactants, [1,2-diketone compound]/[silyl ketene acetal], are 8.9/17.9 mM. [b] Yields are based on consumed 1,2-diketones.

SCHEME 4



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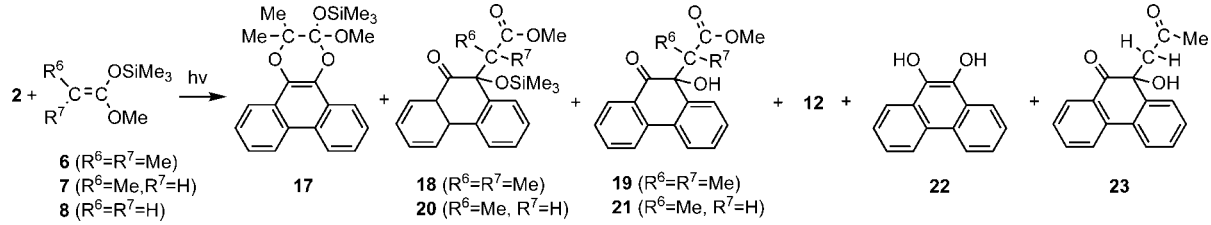
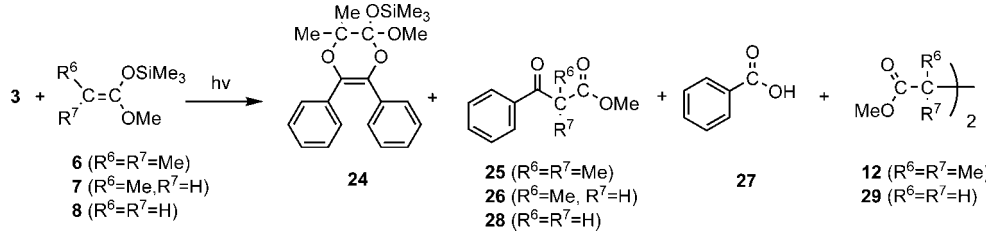


SCHEME 6



toesters or oxetanes[8] (Scheme 3). In the effort described below, we investigated photoinduced reactions of 1,2-diketones **1**−**5** with silyl ketene acetals **6**−**8** and observed that competing excited state reaction pathways are followed that lead to the generation of product distributions which are dependent on the nature of 1,2-diketone electron acceptors, silyl ketene acetal electron donors, and the polarity of the solvent.

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Results and Discussion

Photochemical reactions were performed by irradiation with uranium glass filtered light ($\lambda > 330$ nm) of benzene, acetone, or acetonitrile solutions of the 1,2-diketones **1**−**5** (9 mM) and the silyl ketene acetals **6** and **7** (18 mM) for time periods that bring about 47−93% conversion of the 1,2-diketones. In each case, the crude photoreaction mixtures were subjected to silica gel chromatography to obtain pure products.

Photochemistry of 1,2-Diketones 1−3. The products/yields arising from photoreactions of aromatic 1,2-diketones **1**−**3** with silyl ketene acetals **6** and **7** are displayed in Table 1 and

Schemes 4–6. Irradiation of a benzene solution of acenaphthenequinone (**1**) and dimethyl-substituted silyl ketene acetal **6** results in the formation of a mixture of products composed of the β-silyloxy- and β-hydroxy-γ-ketoester, **10** and **11**, and dioxene **9** in a ca. 3:1 ratio of **10** + **11**:**9** (Scheme 4 and Table 1, entry 1). When photoreaction of **1** with **6** is conducted in the more polar solvents acetone or acetonitrile, ketoesters **10** and **11** are produced nearly exclusively along with minor amounts of the dimer **12** (entries 2 and 3).

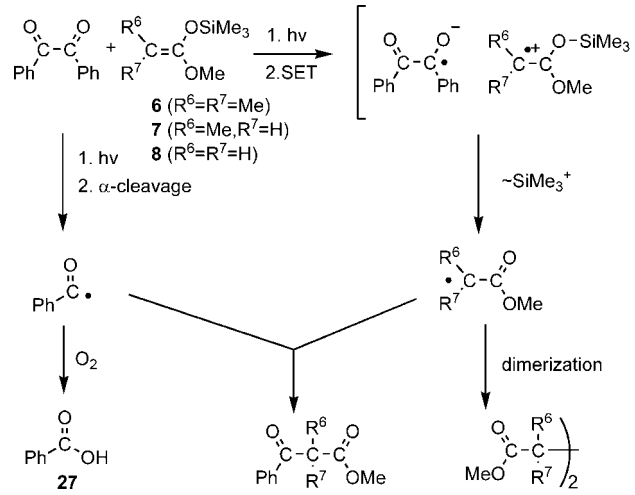
Photolysis of 1,2-diketone **1** and monomethyl silyl ketene acetal **7** in acetonitrile leads to formation of the ketoesters **13** and **14** as mixtures of diastereomers, along with pinacol-type dimer **15**[6] (Table 1, entry 4). Interestingly, **15** is the sole product generated when an acetonitrile solution of **1** and the unsubstituted silyl ketene acetal **8** is irradiated (Table 1, entry 5). In contrast, photoreaction of a benzene solution of **1** and **8** forms dioxene **16** and dimer **15** (Table 1, entry 6).

Irradiation of a benzene solution of phenanthrenequinone **2** with dimethyl silyl ketene acetal **6** brings about nearly exclusive formation of the [4 + 2]-cycloadditon product[16,17] **17**, albeit in low yield (Scheme 5 and Table 1, entry 7). When the higher polarity solvents acetone and acetonitrile are used for this photoreaction, products arising via sequential SET desilylation (i.e., ketoesters **18** and **19**) are generated predominantly in high yield (entries 8 and 9). Reactions of phenanthrenequinone **2** with the monomethyl silyl ketene acetal **7** in acetone and acetonitrile also yield the corresponding ketoesters **20** and **21** as mixtures of diastereomers along with 9,10-dihydroxyphenanthrene **22**[16] and the acetone adduct **23** (only in acetone) as minor products (entries 10 and 11). Solvent-assisted 1,2-addition takes place in several photochemical reaction of 1,2-diketones.[13] Finally, **22** and **23** are the only substances formed when solutions of **2** and the unsubstituted ketene acetal **8** in either acetone or acetonitrile are irradiated (entries 12 and 13).

An analysis of the results presented thus far shows that the classical Paterno−Buchi-type [2 + 2]-cycloaddition reaction to form oxetanes does not take place in the photoreactions of diketones **1** and **2**. In addition, the relative efficiencies of processes promoted by desilylation versus [4 + 2]-cycloaddition of the ion radical pairs generated by SET are highly dependent on the polarity of the solvent. Last, the yields of the β-hydroxy and β-silyloxy ketoesters formed by SET desilylation pathways vary depending on the degree of methyl substitution in the silyl ketene acetals.[9a,18] The observations summarized above can be rationalized on the basis of solvent and substituent effects on the nature and reactivity of ion radical pairs that serve as intermediates in these reactions. For example, radical ion pairs generated by photoinduced SET in less polar benzene do not readily undergo desilylation. In addition, close association required for stabilization of the ion radical components in this nonpolar solvent (i.e., formation of contact ion pairs) likely enhances [4 + 2]-cyloaddition. Enhanced solvent polarity leads to stabilization/separation of the ion radical species, thus facilitating silophile-assisted desilylation to form radical pairs that couple to produce ketoester products.

The photochemical behavior of benzil **3** in the presence of silyl ketene acetals differs markedly from that of other 1,2-diketones. Previous studies have shown that irradiation of **3** promotes homolytic cleavage of the central carbon−carbon bond to generate benzoyl radicals, which ultimately react to form benzoic acid, benzaldehyde, and benzoin.[13,19] Indeed, irradiation of a benzene solution of benzil in the presence of the dimethyl-substituted silyl ketene acetal **6** gives rise to production of a ca. 1.6:1 mixture of 1,4-dioxene **24** and the β-ketoester **25**[20] (Scheme 6 and Table 1, entry 14), the latter of which likely arises by a pathway involving coupling between radicals that are generated by α-cleavage of the 1,2-diketone and sequential SET desilylation.

SCHEME 7



In the photoreactions of **3** with ketene acetal **6** in acetone and acetonitrile (Table 1, entries 15 and 16), formation of **25** prevails over other processes. Likewise, irradiation of an acetonitrile solution of **3** and monomethyl-substituted ketene acetal **7** (entry 17) gives rise to **26**[21] and benzoic acid **27**, exclusively. Finally, photoreaction of **3** with the unsubstituted acetal **8** in acetonitrile leads to production of **27**, **28**,[22] and **29**[23] (entry 18). The high yield (40%) of benzoic acid formed in this process is caused by a reduction in the rate of SET from the less electron-rich alkene **8** in contrast to homolytic cleavage of the excited state of benzil (Scheme 7).

Photochemistry of 1,2-Diketones 4 and 5. The products/yields arising from photoreactions of aromatic 1,2-diketones **4** and **5** with silyl ketene acetals **6**−**8** are displayed in Table 2 and Schemes 8 and 9. Photoreactions of 2,3-butanedione **4** with silyl ketene acetals **6**−**8** give rise to different types of products as compared with those produced from diketones **1**−**3**. For example, regardless of the solvent used, photoreaction of **4** with dimethyl ketene acetal **6** leads to predominant formation of ketoesters **30** and **31**, arising by way of sequential SET desilylation pathways, along with the dimer **12** as a minor product (Scheme 8 and Table 2, entries 1−3). However, irradiation of an acetonitrile solution of **4** containing acetal **7** leads to generation of not only the ketoesters **32** and **33** but also the Paterno−Buchi-type [2 + 2]-adduct **34** (entry 4).

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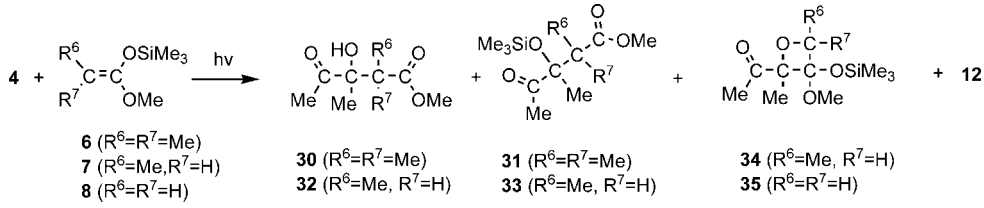
TABLE 2. Photoreactions of 1,2-Diketone Compounds 4 and 5 and Silyl Ketene Acetals 6-8[a]

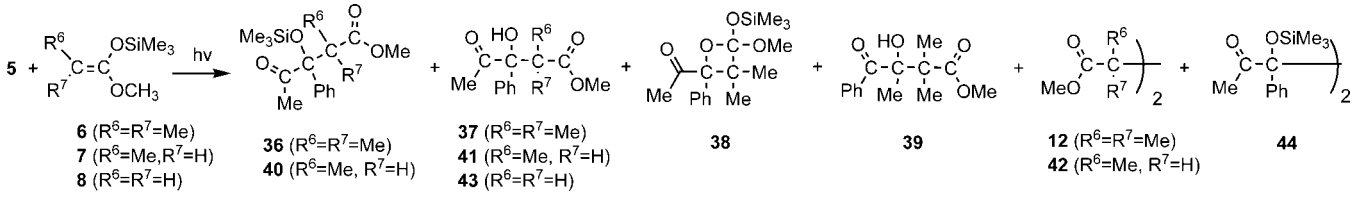
entry	reactant	solvent	reaction time (h)	conversion (%)	product (% yield)[b]
1	**4** + **6**	benzene	2.5	72	**30** (52), **31** (15), **12** (trace)
2	**4** + **6**	acetone	2	70	**30** (53), **31** (15), **12** (7)
3	**4** + **6**	CH_3CN	2	73	**30** (54), **31** (17), **12** (7)
4	**4** + **7**	CH_3CN	2.5	73	**32** (46), **33** (4), **34** (12)
5	**4** + **8**	CH_3CN	2.5	73	**35a** (37), **35b** (19)
6	**5** + **6**	benzene	2	88	**36** (12), **37** (44), **38a** (19), **38b** (6), **39** (8)
7	**5** + **6**	acetone	2	86	**36** (23), **37** (53), **12** (9)
8	**5** + **6**	CH_3CN	1.5	79	**36** (22), **37** (51), **12** (9)
9	**5** + **7**	CH_3CN	2	80	**40a** (14), **40b** (9), **41a** (30), **41b** (18), **42** (10)
10	**5** + **8**	CH_3CN	5	53	**43** (33), **44** (12)

[a] Concentrations of reactants, [1,2-diketone compound]/[silyl ketene acetal], are 8.9/17.9 mM. [b] Yields are based on consumed 1,2-diketones.

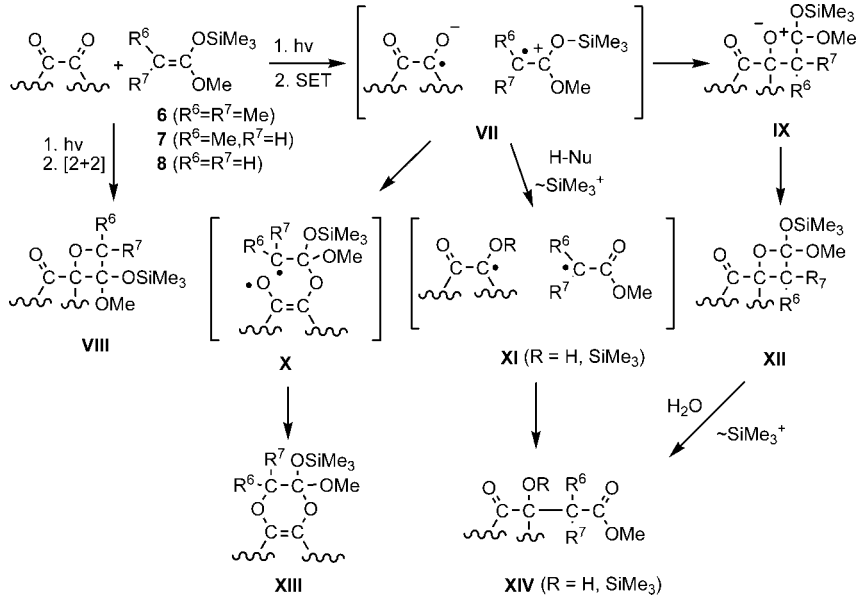
SCHEME 8



SCHEME 9



SCHEME 10



Photoreaction of **4** with the unsubstituted acetal **8** in acetonitrile produces the Paterno−Buchi-type oxetane **35** exclusively (entry 5).

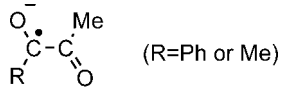
Observations made in studies of the photoreactions of the aryl-alkyl-substituted diketone, 1-phenyl-1,2-propanedione **5**, with silyl ketene acetals **6**−**8** show that sequential SET desilylation pathways take place highly efficiently and regioselectively. Accordingly, irradiation of **5** in a benzene solution containing **6** leads to the formation of aryl carbonyl functionalized adducts, **36** and **37**, and alkyl carbonyl functionalized adducts, **38** and **39** (Scheme 9 and Table 2, entry 6). Photoreactions of **5** with **6** in acetone and acetonitrile as well as that of **5** with **7** in acetonitrile proceed in a similar manner, giving only the aryl carbonyl functionalized products along with dimers **12**[24] or **42** (entries 7−9). Also, the aryl carbonyl functionalized

(24) (a) Suzuki, Y.; Katoh, H.; Ishii, Y.; Hidai, M. *J. Mol. Catal. A* **1995**, *95*, 129. (b) Kondo, H.; Kageyama, A.; Yamaguchi, Y.; Haga, M. A.; Kirchner, K.; Nagashima, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1927.

adduct **43** is the major product formed in reaction of **5** with ketene acetal **8** in acetonitrile (entry 10).

Several conclusions can be drawn from the results shown in Table 2. First, the ratios of products arising by SET desilylation versus Paterno−Buchi pathways are largely dependent on the nature of the silyl ketene acetal donor. Similar trends have been noted in previous reports describing photoreaction of silyl enol ethers with aromatic carbonyl compounds.[18] Second, 1,4-dioxene products resulting by [4 + 2]-cycloadditions are not produced in photoreactions of the dimethyl- or methylphenyl-substituted diketones **4** and **5** with silyl ketene acetals **6**−**8**. Third, the exclusive production of β-hydroxy and β-silyloxy ketoesters and oxetanes, produced by sequential SET desilylation routes in reactions of **5** with **6** and **7**, clearly demonstrates that alkyl-aryl substituents are the major factors responsible for governing the excited state reaction pathways. Finally, products formed in photoreactions of **4** and **5** with the dimethyl-substituted ketene acetal **6** do not reflect significant effects of solvent polarity.

On the basis of an analysis of the photoproduct distributions presented above and results arising from our recent studies of related reactions of monoketones,[8,18] it is possible to propose a plausible general mechanistic pathway for photochemical reactions of 1,2-diketones **1**−**5** with the silyl ketene acetals **6** and **7** (Scheme 10). SET and classical photochemical [2 + 2]-cycloaddtion compete for deactivation of the diketone excited states by the silyl ketene acetal. These respective processes generate ion radical pairs **VII** and oxetanes **VIII**. Desilylation of **VII** produces radical pairs **XI**, which undergo coupling to form ketoester products **XIV**. Alternatively, radical and/or ionic coupling of ion radical pairs **VII** produces biradicals **X** or zwitterionic intermediates **IX**, which are the precursors of the respective 1,4-dioxenes **XIII** and oxetanes **XII**, the latter of which should easily convert to ketoesters **XIV**. The observations made in photoreactions of acyclic 1,2-diketones **4** and **5** that 1,4-dioxene products by [4 + 2]-cycloadditions are not produced and the product formations are not significantly affected by solvent polarity are understandable considering predominant existence of acyclic 1,2-diketone radical anions in the solutions with more favorable *anti*-conformations **XV** which do not lead to formation of [4 + 2]-cycloaddition products.



XV

Importantly, the relative importance of these excited state reaction pathways is controlled by nature of the diketone, ketene acetal, and solvent. The results of this study demonstrate that photoinduced SET desilylation pathways predominate in photochemical reactions of the diketones when electron-rich silyl ketene acetals and highly polar solvents are employed. Moreover, the process can be used as an efficient methodology for the generation of highly substituted Claisen condensation type products.

Experimental Section

Irradiation of Acenaphthenequinone (1) and 1-(Methoxy)-2-methyl-1-(trimethylsilyloxy)propene (6). Benzene: A solution of acenaphthenequinone **1** (260 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of benzene was irradiated for 4 h (ca. 89% conversion of **1**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) giving 86 mg (19%) of **9**, 32 mg (7%) of **10**, and 177 mg (49%) of **11**.

Acetone: A solution of acenaphthenequinone **1** (260 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetone was irradiated for 3.5 h (ca. 93% conversion of **1**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) gave 9 mg (2%) of **9**, 57 mg (12%) of **10**, 219 mg (58%) of **11**, and 5 mg (4%) of **12**.[24]

Acetonitrile: A solution of acenaphthenequinone **1** (260 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 2 h (ca. 93% conversion of **1**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) gave trace of **9**, 33 mg (7%) of **10**, 291 mg (77%) of **11**, and 9 mg (7%) of **12**.

9: ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 9H), 1.41 and 1.54 (s, 3H), 3.39 (s, 3H), 7.38−7.46 (m, 4H), 7.58−7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.9, 21.6, 22.3, 48.7, 79.9, 111.7, 117.8, 119.5, 125.9, 126.4, 127.2, 127.3, 121.6, 127.1, 130.9, 131.2, 132.7, 136.2; HRMS is not measured due to the decomposition.

10: ^{1}H NMR ($CDCl_3$) δ −0.22 (s, 9H), 1.42 and 1.47 (s, 3H), 3.13 (s, 3H), 7.61−7.76 (m, 3H), 7.86−7.90 (m, 2H), 8.05−8.09 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 1.0, 20.4, 20.9, 51.1, 51.7, 83.3, 120.6, 122.2, 125.4, 128.1, 128.2, 130.9, 130.3, 132.6, 139.1, 140.7, 175.0, 203.8; IR (KBr) 1730 (C═O); HRMS (EI) *m/z* 356.1441 (M^+, $C_{20}H_{24}O_4Si$ requires 356.1444).

11: mp 93−95 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 and 1.51 (s, 3H), 3.81 (s, 3H), 5.49 (s, 1H), 7.62−7.71 (m, 3H), 7.84−7.91 (m, 2H), 8.05−8.09 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.2, 21.0, 47.3, 52.4, 82.6, 121.4, 121.5, 125.6, 128.1, 128.4, 130.5, 130.5, 131.4, 137.4, 142.2, 177.3, 204.4; IR (KBr) 3600−3200 (br, OH), 1730 and 1710 (C═O); HRMS (EI) *m/z* 284.1037 (M^+, $C_{17}H_{16}O_4$ requires 284.1049).

12: known compound, ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 12H), 3.65 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 21.9, 47.5, 51.7, 176.5.

Irradiation of Acenaphthenequinone (1) and 1-(Methoxy)-1-(trimethylsilyloxy)propene (7). A solution of acenaphthenequinone **1** (260 mg, 1.43 mmol) and silyl ketene acetal **7** (460 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 6 h (ca. 66% conversion of **1**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5), giving diastereomeric adducts **13** (**13a**, 19 mg, 6% and **13b**, 16 mg, 5%), diastereomeric photoadducts **14** (**14a**, 71 mg, 28% and **14b**, 71 mg, 28%), and 5 mg (3%) of **15**.[16]

13a: ^{1}H NMR ($CDCl_3$) δ −0.23 (s, 9H), 1.58 (d, 3H, J = 7.1 Hz), 3.07 (s, 3H), 3.45 (q, 1H, J = 7.1 Hz), 7.62−7.77 (m, 3H), 7.87−7.99 (m, 2H), 8.07−8.11 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 1.2, 11.0, 47.9, 51.1, 81.1, 121.3, 121.9, 125.7, 128.1, 128.3, 131.4, 130.5, 131.9, 138.4, 141.3, 172.4, 203.9; IR (KBr) 1740 (C═O); HRMS (EI) *m/z* 342.1291 (M^+, $C_{19}H_{22}O_4Si$ requires 342.1287).

13b: ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9H), 0.90 (d, 3H, J = 7.2 Hz), 3.44 (q, 1H, J = 7.2 Hz), 3.59 (s, 3H), 7.65−7.77 (m, 3H), 7.89−7.99 (m, 2H), 8.11−8.15 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 1.2, 12.2, 48.0, 51.4, 81.7, 121.4, 123.2, 125.5, 128.0, 128.6, 121.8, 130.5, 131.5, 137.9, 141.9, 174.2, 203.8; IR (KBr) 1730 (C═O); HRMS (EI) *m/z* 342.1296 (M^+, $C_{19}H_{22}O_4Si$ requires 342.1287).

14: (1:1 mixture of two diastereomers based on ^{1}H NMR integration) ^{1}H NMR ($CDCl_3$) of **14a** δ 1.03 (d, 3H, J = 7.1 Hz), 3.20 (q, 1H, J = 7.2 Hz), 3.80 (s, 3H), 7.64−7.78 (m, 3H), 7.90−8.00 (m, 2H), 8.12−8.16 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 12.3, 44.9, 52.2, 80.3, 122.0, 122.2, 125.7, 128.2, 128.7, 132.2, 130.7, 131.2, 137.2, 142.2, 174.4, 203.7; IR (KBr) 3600−3200 (br, OH), 1730 (C═O); HRMS (EI) *m/z* 270.0889 (M^+, $C_{16}H_{14}O_4$ requires 270.0892). ^{1}H NMR ($CDCl_3$) of **14b** δ 1.10 (d, 3H, J = 7.3 Hz), 3.28 (q, 1H, J = 7.2 Hz), 3.64 (s, 3H), 7.64−7.78 (m, 3H), 7.90−8.00 (m, 2H), 8.11−8.15 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 11.2, 45.3, 52.1, 80.2, 122.6, 122.0, 125.7, 128.3, 128.7, 131.8, 130.6, 131.2, 138.1, 142.0, 175.5, 204.1; IR (KBr) 3600−3200 (br, OH), 1730 (C═O); HRMS (EI) *m/z* 270.0889 (M^+, $C_{16}H_{14}O_4$ requires 270.0892).

15: known compound, ^{1}H NMR (DMSO-d_6) δ 7.05−7.20 (m, 2H), 7.40−7.55 (m, 2H), 7.65−7.80 (m, 4H), 7.90−8.00 (m, 1H), 8.15−8.25 (m, 2H, aromatic); ^{13}C NMR (DMSO-d_6) δ 82.8, 121.6, 123.6, 126.2, 128.8, 130.8, 132.1, 132.2, 137.9, 142.3, 203.3; IR (KBr) 3400 (OH).

Irradiation of Acenaphthenequinone (1) and 1-(Methoxy)-1-(trimethylsilyloxy)ethene (8). Benzene: A solution of acenaphthenequinone **1** (260 mg, 1.43 mmol) and silyl ketene acetal **8** (420 mg, 2.87 mmol) in 160 mL of benzene was irradiated for 11 h (ca. 81% conversion of **1**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) giving 66 mg (18%) of **16** and 176 mg (42%) of **15**.

Acetonitrile: A solution of acenaphthenequinone **1** (260 mg, 1.43 mmol) and silyl ketene acetal **8** (420 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 18 h (ca. 77% conversion of **1**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) gave 99 mg (49%) of **15**.

16: ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 9H), 3.45 (s, 3H), 3.94 and 4.30 (two d, 1H, J = 10.7 Hz), 7.42−7.59 (m, 4H), 7.63−7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.2, 29.7, 48.6, 70.2, 118.5, 119.6, 126.4, 126.5, 127.2, 108.2, 127.1, 127.4, 128.7; HRMS (EI) *m*/*z* 328.1139 (M^+, $C_{18}H_{20}O_4Si$ requires 328.1131).

Irradiation of Phenanthrenequinone (2) and Silyl Ketene Acetal (6). Benzene: A solution of phenanthrenequinone **2** (298 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of benzene was irradiated for 8.5 h (ca. 48% conversion of **2**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) giving 79 mg (30%) of **17**, trace of **18**, **12**, and **19**.

Acetone: A solution of phenanthrenequinone **2** (298 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetone was irradiated for 5 h (ca. 47% conversion of **2**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) gave trace of **17**, 15 mg (6%) of **18**, 169 mg (81%) of **19**, and 2 mg (3%) of **12**.

Acetonitrile: A solution of phenanthrenequinone **2** (298 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 5.5 h (ca. 85% conversion of **2**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) gave trace of **17**, 28 mg (6%) of **18**, 207 mg (55%) of **19**, and 9 mg (7%) of **12**.

17: mp 115−117 °C; ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 9H), 1.41 and 1.65 (s, 3H), 3.37 (s, 3H), 7.57−7.66 (m, 4H), 8.15−8.29 (m, 2H), 8.61−8.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 2.0, 21.9, 22.3, 48.8, 78.0, 110.5, 119.9, 121.4, 122.3, 122.7, 124.6, 125.2, 126.6, 126.8, 125.8, 126.5, 126.7, 127.1, 129.9, 132.2; HRMS (EI) *m*/*z* 382.1605 (M^+, $C_{22}H_{26}O_4Si$ requires 382.1600).

18: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 1.03 and 1.13 (s, 3H), 3.24 (s, 3H), 7.36−7.40 (m, 3H), 7.60−7.68 (m, 2H), 7.84−7.89 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 1.8, 20.8, 21.9, 51.3, 53.3, 86.2, 122.6, 123.5, 127.3, 127.8, 128.4, 128.6, 129.0, 134.3, 131.6, 131.7, 137.6, 138.8, 174.4, 201.9; IR (KBr) 1730 and 1700 (C═O); HRMS (EI) *m*/*z* 382.1593 (M^+, $C_{22}H_{26}O_4Si$ requires 382.1600).

19: mp 90−92 °C; ^{1}H NMR ($CDCl_3$) δ 0.96 and 1.20 (s, 3H), 3.39 (s, 3H), 4.47 (s, 1H), 7.37−7.44 (m, 3H), 7.67−7.91 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 20.5, 21.5, 51.6, 52.8, 81.4, 122.7, 123.5, 127.0, 128.0, 128.4, 128.7, 128.9, 135.0, 130.3, 131.2, 136.1, 138.2, 174.5, 202.8; IR (KBr) 3600−3200 (br, OH), 1730 and 1680 (C═O); HRMS (EI) *m*/*z* 310.1207 (M^+, $C_{19}H_{18}O_4$ requires 310.1205).

Irradiation of Phenanthrenequinone (2) and Silyl Ketene Acetal (7). Acetonitrile: A solution of phenanthrenequinone **2** (298 mg, 1.43 mmol) and silyl ketene acetal **7** (460 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 4 h (ca. 81% conversion of **2**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) giving diastereomeric adducts **20** (**20a**, 34 mg, 8% and **20b**, 26 mg, 6%), diastereomeric photoadducts **21** (**21a**, 96 mg, 28% and **21b**, 65 mg, 19%), and 12 mg (5%) of **22**.[17]

Acetone: A solution of phenanthrenequinone **2** (298 mg, 1.43 mmol) and silyl ketene acetal **7** (460 mg, 2.87 mmol) in 160 mL of acetone was irradiated for 16 h (ca. 80% conversion of **2**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) gave diastereomeric adducts **20** (**20a**, 17 mg, 4% and **20b**, 17 mg, 4%) and **21** (**21a**, 41 mg, 28% and **21b**, 41 mg, 19%), 29 mg (12%) of **22**, and 70 mg (23%) of **23**.

20: ^{1}H NMR ($CDCl_3$) of **20a** δ 0.14 (s, 9H), 1.02 (d, 3H, J = 7.0 *Hz*), 2.87 (q, 1H, J = 7.0 *Hz*), 3.28 (s, 3H), 7.35−7.45 (m, 3H), 7.56−7.70 (m, 2H), 7.82−7.94 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 1.9, 11.9, 51.0, 51.1, 84.0, 123.0, 124.0, 127.0, 127.3, 128.4, 128.5, 134.5, 135.0, 130.0, 130.2, 137.2, 140.1, 172.0, 201.2; IR (KBr) 1740 and 1710 (C═O); HRMS (EI) *m*/*z* 368.1435 (M^+, $C_{21}H_{24}O_4Si$ requires 368.1444). ^{1}H NMR ($CDCl_3$) of **20b** δ 0.14 (s, 9H), 1.00 (d, 3H, J = 7.0 *Hz*), 2.90 (q, 1H, J = 7.0 *Hz*), 3.49 (s, 3H), 7.36−7.47 (m, 3H), 7.60−7.68 (m, 2H), 7.78−7.90 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 2.0, 11.1, 50.9, 51.2, 84.7, 122.7, 124.3, 127.5, 127.7, 128.3, 128.5, 134.1, 134.5, 130.3, 131.1, 136.3, 139.7, 172.0, 202.4; IR (KBr) 1740 and 1710 (C═O); HRMS (EI) *m*/*z* 368.1443 (M^+, $C_{21}H_{24}O_4Si$ requires 368.1444).

21: ^{1}H NMR ($CDCl_3$) of **21a** (mp 95−97 °C) δ 1.10 (d, 3H, J = 7.0 Hz), 2.86 (q, 1H, J = 7.0 Hz), 3.56 (s, 3H), 4.21 (s, 1H), 7.37−7.47 (m, 3H), 7.64−7.92 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 11.2, 49.7, 51.5, 80.4, 123.0, 124.5, 127.5, 127.8, 128.4, 128.6, 128.7, 134.8, 129.3, 129.8, 136.9, 137.4, 172.6, 203.1; IR (KBr) 3600−3200 (br, OH), 1730 and 1700 (C═O); HRMS (EI) *m*/*z* 296.1053 (M^+, $C_{18}H_{16}O_4$ requires 296.1049). ^{1}H NMR ($CDCl_3$) of **21b** (mp 83−85 °C) δ 1.00 (d, 3H, J = 7.1 Hz), 2.89 (q, 1H, J = 7.1 Hz), 3.40 (s, 3H), 4.39 (s, 1H), 7.34−7.48 (m, 3H), 7.63−7.97 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 11.9, 50.7, 51.5, 79.7, 123.3, 124.1, 126.8, 127.3, 128.6, 128.8, 129.5, 135.2, 129.4, 129.9, 137.7, 138.0, 172.4, 202.0; IR (KBr) 3600−3200 (br, OH), 1730 and 1700 (C═O); HRMS (EI) *m*/*z* 296.1046 (M^+, $C_{18}H_{16}O_4$ requires 296.1049).

22: known compound, mp 245−250 °C; ^{1}H NMR ($CDCl_3$) δ 7.78−7.84 (m, 8H), 8.26−8.36 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 127.2, 134.1, 183.1; IR (KBr) 3600−3200 (br, OH), 1710 (C═O); HRMS (EI) *m*/*z* 210.0673 (M^+, $C_{14}H_{10}O_2$ requires 210.0681).

23: ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 3H), 2.80 and 3.00 (two d, 2H, J = 14.5 Hz), 7.38−7.48 (m, 3H), 7.69−7.96 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 32.1, 55.6, 78.3, 123.1, 124.4, 125.9, 127.6, 128.6, 128.7, 129.3, 134.8, 128.9, 139.4, 136.7, 139.4, 202.9, 206.0; IR (KBr) 3600−3200 (br, OH), 1710 (C═O); HRMS (EI) *m*/*z* 266.0933 (M^+, $C_{17}H_{14}O_3$ requires 266.0943).

Irradiation of Phenanthrenequinone (2) and Silyl Ketene Acetal (8). Acetonitrile: A solution of phenanthrenequinone **2** (298 mg, 1.43 mmol) and silyl ketene acetal **8** (420 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 10 h (ca. 53% conversion of **2**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) giving 43 mg (27%) of **22**.

Acetone: A solution of phenanthrenequinone **2** (298 mg, 1.43 mmol) and silyl ketene acetal **8** (420 mg, 2.87 mmol) in 160 mL of acetone was irradiated for 16 h (ca. 80% conversion of **2**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) gave 37 mg (4%) of **22** 50 mg (25%) of **23**.

Irradiation of Benzil (3) and Silyl Ketene Acetal (6). Benzene: A solution of benzil **3** (300 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of benzene was irradiated for 3 h (ca. 80% conversion of **3**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:10) giving 180 mg (41%) of **24**, 59 mg (25%) of **25**,[20] and trace of **12**.

Acetone: A solution of benzil **3** (300 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetone was irradiated for 5 h (ca. 71% conversion of **3**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:10) gave trace of **24**, 148 mg (71%) of **25**, and trace of **12**.

Acetonitrile: A solution of benzil **3** (300 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetonitrile

was irradiated for 4 h (ca. 80% conversion of **3**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:10) gave trace of **24**, 179 mg (76%) of **25**, and 92 mg (21%) of **12**.

24: ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9H), 1.41 and 1.49 (s, 3H), 3.53 (s, 3H), 7.16−7.27 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 1.9, 21.2, 22.0, 48.7, 77.0, 110.4, 127.7, 128.1, 128.3, 128.4, 129.0, 129.8, 130.9, 133.5, 135.0, 135.3; HRMS (EI) *m/z* 384.1749 (M^+, $C_{22}H_{28}O_4Si$ requires 384.1757).

Irradiation of Benzil (3) and Silyl Ketene Acetal (7). A solution of benzil **3** (300 mg, 1.43 mmol) and silyl ketene acetal **7** (460 mg, 2.87 mmol) in 160 mL of benzene was irradiated for 9 h (ca. 54% conversion of **3**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:10) giving 90 mg (61%) of **26**[21] and 5 mg (5%) of **27**.

Irradiation of Benzil (3) and Silyl Ketene Acetal (8). A solution of benzil **3** (300 mg, 1.43 mmol) and silyl ketene acetal **8** (420 mg, 2.87 mmol) in 160 mL of benzene was irradiated for 14.5 h (ca. 87% conversion of **3**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:10) giving 51 mg (23%) of **28**,[22] 61 mg (40%) of **27**, and 34 mg (19%) of **29**.[23]

29: known compound, ^{1}H NMR ($CDCl_3$) δ 2.63 (s, 4H), 3.69 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 28.8, 51.8, 172.7; IR (KBr) 1740 (C=O); HRMS (EI) *m/z* 146.0572 (M^+, $C_6H_{10}O_4$ requires 146.0579).

Irradiation of 2,3-Butanedione (4) and Silyl Ketene Acetal (6). Benzene: A solution of 2,3-butanedione **4** (123 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of benzene was irradiated for 2.5 h (ca. 72% conversion of **4**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) giving 101 mg (52%) of **30**, 40 mg (15%) of **31**, and trace of **12**.

Acetone: A solution of 2,3-butanedione **4** (123 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetone was irradiated for 2 h (ca. 70% conversion of **4**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) gave 100 mg (53%) of **30**, 39 mg (15%) of **31**, and 14 mg (7%) of **12**.

Acetonitrile: A solution of 2,3-butanedione **4** (123 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 2 h (ca. 73% conversion of **4**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) gave 106 mg (54%) of **30**, 46 mg (17%) of **31**, and 15 mg (7%) of **12**.

30: ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H), 1.31 (s, 6H), 2.25 (s, 3H), 3.69 (s, 3H), 4.40 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.0, 21.7, 21.8, 25.8, 48.6, 52.2, 81.7, 178.7, 212.0; IR (KBr) 3600−3200 (br, OH), 1710 (C=O); HRMS (EI) *m/z* 188.1040 (M^+, $C_9H_{16}O_4$ requires 188.1049).

31: ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.18 (s, 6H), 1.40 (s, 3H), 2.18 (s, 3H), 3.64 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 2.3, 20.8, 21.3, 21.8, 27.5, 51.0, 51.7, 85.5, 175.7, 213.8; IR (KBr) 1720 (C=O); HRMS (EI) *m/z* 260.1433 (M^+, $C_{12}H_{24}O_4Si$ requires 260.1444).

Irradiation of 2,3-Butanedione (4) and Silyl Ketene Acetal (7). A solution of 2,3-butanedione **4** (123 mg, 1.43 mmol) and silyl ketene acetal **7** (460 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 2.5 h (ca. 73% conversion of **4**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) giving 118 mg (46%) of **32**, 10 mg (4%) of **33**, and 31 mg (12%) of **34**.

32: ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 3H), 1.27 (d, 3H, J = 7.4 Hz), 2.30 (s, 3H), 3.04 (q, 1H, J = 7.4 Hz), 3.64 (s, 3H), 4.07 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 10.8, 22.2, 24.2, 44.9, 52.0, 79.6, 176.4, 213.3; IR (KBr) 3600−3200 (br, OH), 1710 (C=O); HRMS (EI) *m/z* 174.0886 (M^+, $C_8H_{14}O_4$ requires 174.0892).

33: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9H), 1.14 (d, 3H, J = 7.1 Hz), 1.33 (s, 3H), 2.23 (s, 3H), 2.99 (q, 1H, J = 7.2 Hz), 3.60 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 2.3, 10.8, 22.4, 27.0, 47.7, 51.5, 83.6, 173.3, 212.6; IR (KBr) 1720 (C=O); HRMS (EI) *m/z* 246.1283 (M^+, $C_{11}H_{22}O_4Si$ requires 246.1287).

34: ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9H), 1.33 (d, 3H, J = 7.3 Hz), 1.47 (d, 3H), 2.26 (s, 3H), 3.31 (s, 3H), 4.81 (q, 1H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 1.4, 16.8, 19.1, 27.0, 51.3, 84.1, 96.5, 102.1, 211.2; IR (KBr) 1750 (C=O); HRMS (EI) *m/z* 246.1293 (M^+, $C_{11}H_{22}O_4Si$ requires 246.1287).

Irradiation of 2,3-Butanedione (4) and Silyl Ketene Acetal (8). A solution of 2,3-butanedione **4** (123 mg, 1.43 mmol) and silyl ketene acetal **8** (420 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 2.5 h (ca. 73% conversion of **4**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) giving diastereomeric photoadducts **35** (**35a**, 83 mg, 37% and **35b**, 43 mg, 19%).

35: (2:1 mixture of two diastereomers based on ^{1}H NMR integration) ^{1}H NMR of major diastereomer **35a** ($CDCl_3$) δ 0.16 (s, 9H), 1.50 (s, 3H), 2.28 (s, 3H), 3.29 (s, 3H), 4.51 (d, 1H, J = 6.8 Hz), 4.60 (q, 1H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 0.7, 18.5, 26.2, 50.8, 79.7, 99.9, 100.5, 209.5; HRMS (EI) *m/z* 232.1143 (M^+, $C_{10}H_{20}O_4Si$ requires 232.1131). ^{1}H NMR of minor diastereomer **35b** ($CDCl_3$) δ 0.21 (s, 9H), 1.44 (s, 3H), 2.31 (s, 3H), 3.21 (s, 3H), 4.52 (d, 1H, J = 7.0 Hz), 4.65 (q, 1H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 1.0, 19.2, 26.6, 50.4, 79.0, 99.0, 99.8, 210.2; HRMS (EI) *m/z* 232.1143 (M^+, $C_{10}H_{20}O_4Si$ requires 232.1131).

Irradiation of 1-Phenyl-1,2-propanedione (5) and Silyl Ketene Acetal (6). Benzene: A solution of 1-phenyl-1,2-propanedione **5** (232 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of benzene was irradiated for 2 h (ca. 88% conversion of **5**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) giving 49 mg (12%) of **36**, 138 mg (44%) of **37**, diastereomeric photoadducts **38** (**38a**, 77 mg, 19% and **38b**, 24 mg, 6%), and 24 mg (8%) of **39**.

Acetone: A solution of 1-phenyl-1,2-propanedione **5** (232 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetone was irradiated for 2 h (ca. 86% conversion of **5**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) gave 91 mg (23%) of **36**, 163 mg (53%) of **37**, and 22 mg (9%) of **12**.

Acetonitrile: A solution of 1-phenyl-1,2-propanedione **5** (123 mg, 1.43 mmol) and silyl ketene acetal **6** (500 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 1.5 h (ca. 79% conversion of **5**). Workup and silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) gave 80 mg (22%) of **36**, 144 mg (51%) of **37**, and 2 mg (9%) of **12**.

36: ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 9H), 1.15 (s, 3H), 1.19 (s, 3H), 2.19 (s, 3H), 3.64 (s, 3H), 7.33−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 2.7, 22.6, 23.5, 28.4, 51.2, 51.6, 89.8, 127.4, 127.6, 127.8, 138.9, 176.6, 208.1; IR (KBr) 1730 and 1720 (C=O); HRMS (EI) *m/z* 322.1590 (M^+, $C_{17}H_{26}O_4Si$ requires 322.1600).

37: ^{1}H NMR ($CDCl_3$) δ 1.13 and 1.21 (s, 3H), 2.09 (s, 3H), 3.76 (s, 3H), 5.58 (s, 1H), 7.36−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.1, 22.6, 25.9, 47.6, 52.5, 86.2, 127.4, 127.6, 128.0, 135.7, 181.5, 209.6; IR (KBr) 3600−3200 (br, OH), 1720 and 1700 (C=O); HRMS (EI) *m/z* 250.1201 (M^+, $C_{14}H_{18}O_4$ requires 250.1205).

38: (3.2:1 mixture of two diastereomers based on ^{1}H NMR integration) ^{1}H NMR of major diastereomer **38a** ($CDCl_3$) δ 0.25 (s, 9H), 0.83 (s, 3H), 1.23 (s, 3H), 2.22 (s, 3H), 3.42 (s, 3H), 7.27−7.34 (m, 3H), 7.49−7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.5, 19.7, 22.3, 26.7, 48.9, 54.5, 88.5, 115.5, 125.9, 127.4, 127.8, 137.1, 210.5; IR (KBr) 1720 (C=O); HRMS is not measured due to the decomposition. ^{1}H NMR of minor diastereomer **38b** ($CDCl_3$) δ 0.28 (s, 9H), 0.84 (s, 3H), 1.26 (s, 3H), 2.19 (s, 3H), 3.40 (s, 3H), 7.27−7.34 (m, 3H), 7.49−7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.4, 20.5, 22.2, 26.7, 49.4, 54.5, 88.5, 115.2, 126.0, 127.5, 127.7, 137.0, 209.7; IR (KBr) 1720 (C=O); HRMS is not measured due to the decomposition.

39: ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3H), 1.38 (s, 3H), 1.51 (s, 3H), 3.70 (s, 3H), 4.98 (s, 1H), 7.40−7.47 (m, 3H), 8.12−8.17 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.1, 21.8, 22.2, 48.7, 52.3, 83.2, 128.0, 130.0,

132.2, 136.3, 180.5, 203.1; IR (KBr) 1730 and 1680 (C═O); HRMS (EI) *m*/*z* 250.1198 (M^+, $C_{14}H_{18}O_4$ requires 250.1205).

Irradiation of 1-Phenyl-1,2-propanedione (5) and Silyl Ketene Acetal (7). A solution of 1-phenyl-1,2-propanedione **5** (232 mg, 1.43 mmol) and silyl ketene acetal **7** (460 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 2 h (ca. 80% conversion of **5**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) giving diastereomeric photoadduct **40** (**40a**, 49 mg, 14% and **40b**, 32 mg, 9%), **41** (**41a**, 81 mg, 30% and **41b**, 49 mg, 18%), and 20 mg (10%) of **42**.[25]

40: (1.6:1 mixture of two diastereomers based on ^{1}H NMR integration) ^{1}H NMR of major diastereomer **40a** ($CDCl_3$) δ 0.13 (s, 9H), 1.18 (d, 3H, J = 7.1 Hz), 2.22 (s, 3H), 3.52 (q, 1H, J = 7.1 Hz), 3.56 (s, 3H), 7.33−7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 2.2, 13.5, 27.0, 47.5, 51.5, 87.1, 126.8, 128.0, 128.9, 139.7, 173.9, 209.4; IR (KBr) 1740 and 1720 (C═O); HRMS (EI) *m*/*z* 308.1444 (M^+, $C_{16}H_{24}O_4Si$ requires 308.1444). ^{1}H NMR of minor diastereomer **40b** ($CDCl_3$) δ 0.13 (s, 9H), 1.06 (d, 3H), 2.22 (s, 3H), 3.51 (q, 1H, J = 7.1 Hz), 3.56 (s, 3H), 7.29−7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 2.2, 13.5, 27.0, 47.3, 51.7, 87.1, 126.9, 128.2, 128.9, 139.9, 173.7, 209.8; IR (KBr) 1740 and 1720 (C═O); HRMS (EI) *m*/*z* 308.1449 (M^+, $C_{16}H_{24}O_4Si$ requires 308.1444).

41: ^{1}H NMR of **41a** δ 1.27 (d, 3H, J = 7.1 Hz), 2.16 (s, 3H), 3.44 (s, 3H), 3.71 (q, 1H, J = 7.0 Hz), 4.47 (s, 1H), 7.28−7.38 (m, 3H), 7.50−7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.1, 25.2, 45.6, 51.8, 83.9, 125.4, 128.0, 128.4, 140.2, 176.8, 208.3; HRMS (EI) *m*/*z* 236.1065 (M^+, $C_{13}H_{16}O_4$ requires 236.1049). ^{1}H NMR of **41b** δ 0.96 (d, 3H, J = 7.5 Hz), 2.12 (s, 3H), 3.47 (q, 1H, J = 7.0 Hz), 3.74 (s, 3H), 4.96 (s, 1H), 7.31−7.44 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 11.6, 24.4, 44.9, 52.3, 84.1, 125.2, 127.9, 128.6, 137.3, 178.7, 210.9; HRMS (EI) *m*/*z* 236.1048 (M^+, $C_{13}H_{16}O_4$ requires 236.1049).

42: known compound, ^{1}H NMR δ 1.16 (d, 3H, J = 6.7 Hz), 2.81 (q, 2H, J = 6.0 Hz), 3.67 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.6, 41.6, 51.8, 175.6; IR (KBr) 1730.

Irradiation of 1-Phenyl-1,2-propanedione (5) and Silyl Ketene Acetal (8). A solution of 1-phenyl-1,2-propanedione **5** (232 mg, 1.43 mmol) and silyl ketene acetal **8** (420 mg, 2.87 mmol) in 160 mL of acetonitrile was irradiated for 5 h (ca. 53% conversion of **5**). Concentration of photolysate gave a residue which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:15) giving 56 mg (33%) of **43** and 40 mg (12%) of **44**.

43: ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 3H), 2.82 (d, 1H, J = 16.7 Hz), 3.41 (d, 1H, J = 16.7 Hz), 5.15 (s, 1H), 7.33−7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.0, 42.4, 52.1, 81.2, 124.9, 128.1, 128.7, 139.1, 173.5, 209.0; IR (KBr) 3600−3200 (br, OH), 1740 and 1710 (C═O); HRMS (EI) *m*/*z* 222.0887 (M^+, $C_{12}H_{14}O_4$ requires 222.0892).

44: mp 91−94 °C; ^{1}H NMR ($CDCl_3$) −0.07 (s, 9H), 2.27 (s, 3H), 7.31−7.33 (m, 6H), 7.46−7.49 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 2.4, 29.6, 91.1, 127.4, 128.1, 141.4, 207.4; HRMS (EI) *m*/*z* 442.2015 (M^+, $C_{24}H_{34}O_4Si_2$ requires 442.1996).

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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