Photochemical reactions of 1,2-diketones with silyl enol ethers

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Abstract Results arising from the current study demonstrate that UV irradiationinduced photoaddition reactions of the 1,2-diketones, acenaphthenequinone, 9, 10-phenanthrenequinone, and benzil, with silyl enol ethers derived from propionaldehyde and isobutyraldehyde take place to form a variety of adducts. Product formation in these cases takes place mainly via two mechanistic pathways, one initiated by single electron transfer (SET) and the other by [2 + 2]-cycloaddition. In addition, observations show that the competition between these pathways depends on the nature of the substrates. An exploration of the photoreactions of acenaphthenequinone revealed that photoinduced SET is the predominant process occurring when the dimethyl-substituted silyl enol ether serves as a reactant, while cycloaddition and other excited state reactions become competitive with SET when the mono-methyl substituted silyl enol ether is used as a substrate. In the case of 9,10-phenanthrenequinone, photoreactions take place by [4 + 2]-cycloaddition routes regardless of the nature of the silvl enol ether employed. Finally, irradiation of benzil in the presence of both silyl enol ethers leads to exclusive or predominant formation of products arising by [2 + 2]-cycloaddition and photoinduced benzoyl radical forming α-cleavage.

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P. S. Mariano Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131, USA **Keywords** Photoaddition \cdot 1,2-diketone \cdot Silyl enol ether \cdot Single electron transfer (SET) \cdot [4 + 2]-cycloaddition

Introduction

Much attention has been given to electrochemical and photochemical reactions of 1,2-diketones [1–23]. The results of these investigations show that the electronic excited states of aryl 1,2-diketones participate in single (SET)- and double-electron transfer processes under appropriate reaction conditions to produce the respective radical anions and dianions, both of which are readily converted to products whose distribution/ratio depends on the conditions and electrophile employed (Scheme 1) [1–15].

In a recent study [23], we explored photochemical reactions between 1, 2-diketones and silvl ketene acetals [24–29]. The results of this effort demonstrated that C–C or C–O bond-forming processes occur via three major routes involving (1) SET or direct [4 + 2]-cycloaddition promoted generation of 1,4-dioxenes [22, 23], (2) classical Paterno-Buchi type [2 + 2]-cycloaddition to form oxetanes [30, 31], and (3) sequential SET-desilvlation pathways that produce β -hydroxy- γ -ketoesters or oxetanes [24, 25]. Moreover, we observed that the competition between these excited state reactions pathways is highly dependent on solvent polarity and the oxidation potential (electron donor nature) of the silvl ketene acetals [22, 23]. Similar, competitive SET and [2 + 2]-cycloaddition processes are involved in photochemical reactions of simple ketones with silvl ketene acetals [24, 25]. For instance, irradiation of a solution of acetophenone (1) in the polar solvent acetonitrile containing silvl ketene acetal $2(R^1 = R^2 = Me)$ promotes predominant formation of the β -hydroxyketone **6**, generated through a consecutive SETdesilylation pathway involving the intermediacy of radical ion pair 4 and radical pair 7. The chemical selectivity of this process is a consequence of the relatively low oxidation potential (+0.90 V vs. SCE) of silyl ketene acetal 2, which results in thermodynamically favorable SET (ΔG_{SET} ca. -0.21 V) from this donor to the triplet excited state of acetophenone [23-29]. In contrast, photoreaction of 1 with







Scheme 2 Photochemical reactions of acetophenone 1 containing silyl ketene acetal 2-3

the non-methyl substituted silyl ketene acetal **3** (E_{ox} +1.28 V vs. SCE, ΔG_{SET} ca. 0.17 V) [23–29] in acetonitrile leads to formation of oxetane **5** as the major product, which is generated through a [2 + 2]-cycloaddition reaction pathway (Scheme 2).

Silyl enol ethers, which have properties that are closely related to those of silyl ketene acetals, are known to produce α -carbonyl alkyl radicals when subjected to photochemical, electrochemical, or metal oxidation conditions [32–45]. For example, photoirradiation of electron acceptors in solutions containing silyl enol ethers **8** promotes SET processes that form radical cations **9**, which undergo subsequent desilylation to form α -carbonyl alkyl radicals **10** (Scheme 3). In addition, this process takes place in linked silyl enol ether–electron-acceptor systems, where intramolecular SET followed desilylation and protonation give rise to the formation of biradical intermediates that serve as precursor of cyclic products (Scheme 4) [44–48].



silyl enol ether ($R^3 = R^4 = R^5 = H$, alkyl) silyl ketene acetal ($R^3 = R^4 = H$, alkyl, $R^5 =$ alkoxy)





Scheme 4 SET-desilylation promoted photocyclization of acceptor-silyl enol ether linked system

In our continuing investigation in this area [49-54], we explored photoreactions occurring between the 1,2-diketones, acenaphthenequinone (11), 9,10-phenan-threnequinone (12) and benzyl (13) with the silyl enol ethers, 14–15 derived from propionaldehyde and isobutyraldehyde, respectively. The results of this effort, described below, show that product formation in these processes occurs mainly via two mechanistic pathways involving SET and cycloadditions, and that the competition between these pathways depends on the nature of the substrates and the solvent.



Results and discussion

Photochemical reactions were performed by using Uranium glass filtered light $(\lambda > 330 \text{ nm})$ and acetonitrile or benzene solutions containing 1,2-diketones **11–13** (11 mM) and silyl enol ethers **14** and **15** (22 mM) for time periods that bring about 34–100 % conversion of the 1,2-diketones (Tables 1, 2, 3). In each case, the photolysate was concentrated and the residue was subjected to silica gel chromatography to obtain pure photoproducts.

The products/yields arising from photoreactions of acetonitrile and benzene solutions of 11 + 14 and 11 + 15 are displayed in Scheme 5 and Table 1. Irradiation of acetonitrile and benzene solutions containing 11 and 14 results in the formation of a ca. 1:1 ratio of the diastereomeric γ -keto- β -hydroxyaldehydes 16a and 16b (SET-desilylation adducts), a single diastereomer of oxetane 18 ([2 + 2] adduct), and a minor amount of the pinacol 19 [23] (Scheme 5; Table 1, entries 1, 2). ¹H-NMR spectra of γ -keto- β -hydroxyaldehydes 16a and 16b gave decisive

Reactants	Solvent	Reaction time (h)	% Conversion ^a	Product (% yield) ^b
11 + 14	CH ₃ CN	2	96	16a (21), 16b (21), 18 (37), 19 (6)
11 + 14	Benzene	3	95	16a (15), 16b (15), 18 (34), 19 (9)
11 + 15	CH ₃ CN	1.5	51	17 (42), 20 (4)
11 + 15	Benzene	1.5	40	17 (30), 20 (16)

Table 1 Photoreactions of acenaphthenequinone 11 and silyl enol ethers 14 and 15

Concentrations of 11 is 11 mM and the concentrations of 14 and 15 are 22 mM

^a % Conversions are based on consumed acenaphthenequinone **11**

^b Yields are based on consumed acenaphthenequinone 11

 Table 2 Photoreactions of 9,10-phenanthrenequinone 12 and silyl enol ethers 14 and 15

Reactants	Solvent	Reaction time (h)	% Conversion ^a	Product (% yield) ^b
12 + 14	CH ₃ CN	1	87	21 (8), 23a (36), 23b (36)
12 + 14	Benzene	1	90	21 (34), 23a (24), 23b (24)
12 + 15	CH ₃ CN	1	77	22 (27), 24 (59)
12 + 15	Benzene	1	73	22 (50), 24 (38)

Concentrations of 12 is 11 mM and the concentrations of 14 and 15 are 22 mM

^a % Conversions are based on consumed 9,10-phenanthrenequinone **12**

^b Yields are based on consumed 9,10-phenanthrenequinone 12

Reactants	Solvent	Reaction time (h)	% Conversion ^a	Product (% yield) ^b
13 + 14	CH ₃ CN	1.5	38	34 (40), 36 (10), 38 (5)
13 + 14	Benzene	1.5	34	34 (44), 36 (8), 38 (5)
13 + 15	CH ₃ CN	3	48	33 (29), 35a (40), 35b (17),
				37 (3), 38 (trace)
13 + 15	Benzene	3	69	33 (21), 35a (28), 35b (17),
				37 (2), 38 (trace)

Table 3 Photoreactions of benzil 13 and silyl enol ethers 14 and 15

Concentrations of 13 is 11 mM and the concentrations of 14 and 15 are 22 mM

^a % Conversions are based on consumed benzil 13

^b Yields are based on consumed benzil 13

evidence for their identification. For example, the respective methyl protons of **16a** and **16b** appear as doublets at 0.68 (J = 7.0 Hz) and 1.00 ppm (J = 7.2 Hz), the methine protons of these substances appear at 3.26 (J = 7.0 Hz) and 3.11 ppm (J = 7.2 Hz) as quartets, and the aldehyde protons resonate at 10.26 and 9.98 ppm as singlets.

In contrast, irradiation of an acetonitrile solution of **11** and the dimethylsubstituted silyl enol ether **15** leads to exclusive formation of the γ -keto- β hydroxyaldehyde **17** (42 %), while photoreaction in a benzene solution of **11** and **15** gives rise to **17** (30 %) as well as 1,4-dioxene **20** (16 %). In addition, oxetane



Scheme 5 Photoreactions of acenaphthenequinone 11 and silyl enol ethers 14-15

compound arising by the [2 + 2]-cycloaddition pathway was not observed. Assignments of the structures of these photoproducts are made by comparing their NMR spectroscopic properties with those of structurally similar substances [22, 25].

An investigation of the photochemical reactions of 12 with 14 and 15 in acetonitrile and benzene solutions gave the product/yield profiles displayed in Scheme 6 and Table 2. Inspection of the results shows that photoreactions of 12 with 14 and 15 in both benzene and acetonitrile results in exclusive generation of the respective pairs of 1,4-dioxenes 21 and 23a, b (ca. 82–90 %), and 22 and 24 (ca. 86–88 %) respectively [55, 56]. Rigorous chromatographic and ¹H-NMR spectroscopic analysis of the crude product mixtures showed that no other photoadducts are produced in these reactions. Finally, silylacetals 21 and 22 are converted to the corresponding hemiacetals 23a, b and 24 by acidic hydrolysis.

The product profiles observed for the photochemical reactions described above show that the mechanistic pathways followed are highly dependent on the electron-accepting and -donating natures of the respective 1,2-diketone and silyl enol ethers. For instance, in the photoreaction of **11** with **14**, processes initiated by sequential SET-desilylation and Paterno–Buchi [2 + 2]-cycloaddition take place competitively to give **32** and **27**. However, in photoreactions involving the dimethyl substituted silyl enol ether **15** and 1,2-diketone **11**, the SET promoted [4 + 2]-cycloaddition and desilylation routes predominate (Scheme 7). Thus, it appears that the nature of the photochemical reaction pathways followed parallel to the oxidation potentials of the silyl enol ether [22–29]. Specifically, in the case of reactions of the electron-rich (low oxidation potential) [**33**] silyl enol ether **15** in acetonitrile solvent,



Scheme 6 Photoreactions of 9,10-phenanthrenequinone 12 and silyl enol ethers 14-15

SET to the excited state of **11** (E_{red} -0.76 V vs. SCE) is thermodynamically favorable and, thus, takes place rapidly to form an ion radical pair **25** (Scheme 7). Desilylation of the silyl enol ether radical cation then occurs to form the radical pair **29** that serves as the precursor of β -hydroxyester product **32**. In addition, radical ion pair **25** undergoes C-C bond formation to produce zwitterion **26**, which then produces the acetal containing oxetane **30**, a possible precursor of β -hydroxyester product **32**. Finally, O-C bond formation in the radical ion pair **25** produces the biradical precursor **28** of 1,4-dioxene **31**.

However, when SET to the excited 1,2-dione 11 is slow owing to the higher oxidation potential of the less methyl substituted silyl enol ether 14, classical Paterno–Buchi [2 + 2]-cycloaddition reaction of acenaphthenequinone (11) becomes a major process. It is important to note that the patterns observed for photoreactions of 11 with 14 and 15 match well the trends seen in previous studies with a number of substrates [22–25].

Another important observation worthy of discussion is related to the product distributions arising from photoreactions of **12** with **14** and **15** (Scheme 6, 7). Contrary to those of **11**, reactions of **12** (E_{red} –0.67 V vs. SCE) cleanly generate 1,4-dioxenes independent of the degree of alkyl substitution on the silyl enol ether and solvent polarity. Although it is difficult to provide an exact explanation for these observations, the nature of the pathways followed in photoreactions of **12** seems to be a consequence of gaining aromatic stabilization through phenanthrene ring formation that guides reactions of cation radical intermediates and direct cycloaddition reactions [12].



Scheme 7 Mechanistic pathways of photoreactions of 1,2-diketones and silyl enol ethers



Scheme 8 Photoreactions of benzil 13 and silyl enol ethers 14-15



Scheme 9 &-Cleavage process of benzil 13 in photoreactions with silyl enol ethers 14-15

Observations made in studies of photoreactions of 13 with 14 and 15 differ markedly from those made in investigations with the other 1,2-diketones 11 and 12. Specifically, the results (Scheme 8; Table 3) show that SET-promoted reactions that form the γ -keto- β -hydroxyaldehyde do not take place when acetonitrile or benzene solutions containing 13 ($E_{red} - 0.71$ V vs. SCE) and 14 are irradiated. Instead, [2 + 2]-cycloaddition, producing of oxetane 34, and α -cleavage [19, 23, 57, 58], generating β -ketoaldehyde 36 [59] and benzoic acid 38 (Scheme 9), are the major pathways. Moreover, even when the more methyl-substituted silyl enol ether 15 is employed as a substrate, cycloaddition and α -cleavage reactions dominate the SETpromoted process that produces γ -keto- β -hydroxyaldehyde 33.

Conclusion

Results arising from the studies described above demonstrate that photoaddition reactions of 1,2-diketones with silyl enol ethers lead to formation of a variety of photoadducts that arise via competitive SET and [2 + 2]-cycloaddition mechanistic pathways, whose relative efficiencies depend on the nature of substrates. For example, SET-promoted processes are predominant in photoreactions of acenaph-thenequinone with the dimethyl-substituted silyl enol ether, while excited state cyloaddition becomes competitive when the less methyl-substituted enol ether is used. In the cases of photoreactions of 9,10-phenanthrenequinone with silyl enol ethers, SET [4 + 2]-cycloaddition pathways are followed exclusively regardless of the degree of silyl enol ether methyl substitution. Finally, photoreactions of benzil with silyl enol ethers are unique, in that excited state cycloaddition and α -cleavage

occur exclusively or nearly exclusively depending on the electron-donating ability of the silyl enol ether.

Experimental

General procedure

¹H- and ¹³C-NMR (200 MHz) spectra were recorded using CDCl₃ solutions and chemical shifts are reported in parts per million relative to CHCl₃ peak (7.24 ppm for ¹H-NMR and 77.0 ppm for ¹³C-NMR) as an internal standard. Preparative photochemical reactions were conducted using an apparatus consisting of a 450-W Hanovia medium vapor pressure mercury lamp surrounded by a Uranium glass filter in a water-cooled quartz immersion well surrounded by the solution being irradiated. The photolysis solutions were purged with nitrogen before and during irradiation. The photolysates were concentrated under reduced pressure giving residues, which were subjected to silica gel column chromatography. All the 1,2-diketone materials used in the photoreactions were derived from commercial sources. All new compounds described were isolated as oils in >90 % purity (by NMR analysis) unless noted otherwise.

Irradiation of acenaphthenequinone 11 and trimethylsilyl enol ether 14

In Acetonitrile A solution of acenaphthenequinone **11** (365 mg, 2.00 mmol) and trimethylsilyl enol ether **14** (520 mg, 4.00 mmol) in 180 mL of acetonitrile was irradiated for 2 h (ca. 96 % conversion of **11**). Concentration of photolysate gave a residue, which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:10) giving 97 mg (21 %) of **16a**, 97 mg (21 %) of **16b**, 222 mg (37 %) of **18**, and 42 mg (6 %) of **19** [23].

In Benzene A solution of acenaphthenequinone **11** (365 mg, 2.00 mmol) and trimethylsilyl enol ether **14** (520 mg, 4.00 mmol) in 180 mL of benzene was irradiated for 3 h (ca. 95 % conversion of **11**). Concentration of photolysate followed by column chromatography (ethyl acetate: *n*-hexane = 1: 10) gave 68 mg (15 %) of **16a**, 68 mg (15 %) of **16b**, 202 mg (34 %) of **18**, and 63 mg (9 %) of **19**.

16a. ¹H-NMR (CDCl₃) δ 0.68 (d, 3H, J = 7.0 Hz), 3.26 (q, 1H, J = 7.0 Hz), 7.52-8.35 (m, 6H), 10.26 (s, 1H); ¹³C-NMR δ 9.0, 52.0, 81.5, 121.7, 122.5, 126.0, 127.5, 128.5, 128.8, 132.5 132.6 133.4 135.3, 203.7, 204.2.

16b. ¹H-NMR (CDCl₃) δ 1.00 (d, 3H, J = 7.2 Hz), 3.11 (q, 1H, J = 7.2 Hz), 7.52–8.35 (m, 6H), 9.98 (s, 1H); ¹³C-NMR δ 9.1, 52.3, 81.5, 121.8, 122.4, 126.1, 127.3, 128.3, 129.0, 132.3 132.4 133.2 135.5, 203.9, 204.5.

18. ¹H-NMR (CDCl₃) δ -0.38 (s, 9H), 1.57 (d, 3H, J = 6.5 Hz), 4.90 (d, 1H, J = 6.5 Hz), 5.49 (quintet, 1H, J = 6.3 Hz), 7.67–7.76 (m, 2H), 7.89–7.97 (m, 3H), 8.10 (d, 1H, J = 8.3 Hz); ¹³C-NMR δ -1.0 (3C), 16.1, 71.9, 81.7, 92.2, 121.5, 124.5, 125.7, 127.8, 128.2, 130.2, 130.4, 131.8, 134.2, 141.9, 203.2; LRMS (EI)

m/z (rel. intensity) 312 (M⁺, 5), 255 (41), 240 (4), 153 (10), 130 (100), 114 (72), 74 (77); HRMS (EI) m/z 312.1177 (C₁₈H₂₀O₃Si requires 312.1182).

Irradiation of acenaphthenequinone 11 and trimethylsilyl enol ether 15

In Acetonitrile A solution of acenaphthenequinone **11** (364 mg, 2.00 mmol) and trimethylsilyl enol ether **15** (577 mg, 4.00 mmol) in 180 mL of acetonitrile was irradiated for 1.5 h (ca. 51 % conversion of **11**). Concentration of photolysate followed by column chromatography (ethyl acetate:*n*-hexane = 1:4) yielded 109 mg (42 %) of **17** and 13 mg (4 %) of **20**.

In Benzene A solution of acenaphthenequinone **11** (364 mg, 2.00 mmol) and trimethylsilyl enol ether **14** (577 mg, 4.00 mmol) in 180 mL of benzene was irradiated for 1.5 h (ca. 40 % conversion of **11**). Concentration of photolysate followed by column chromatography (ethyl acetate:*n*-hexane = 1:4) yielded 61 mg (30 %) of **17** and 42 mg (16 %) of **20**.

17. ¹H-NMR (CDCl₃) δ 0.89 (s, 3H), 1.12 (s, 3H), 3.97 (s, 1H), 7.54–7.66 (m, 3H), 7.70–7.85 (m, 2H), 8.00–8.08 (m, 1H), 10.05 (s, 1H); ¹³C-NMR δ 17.5, 17.6, 51.3, 83.3, 121.7, 121.8, 125.7, 128.2, 128.5, 130.4, 130.9, 132.1, 132.6, 137.3, 204.6, 205.6.

20. ¹H-NMR (CDCl₃) δ 0.22 (s, 9H), 1.40 (s, 6H), 5.13 (s, 1H), 7.35–7.43 (m, 4H), 7.56–7.62 (m, 2H); ¹³C-NMR δ 0.0 (3C), 20.4, 23.0, 76.1, 96.5, 118.2, 119.0, 125.8 (2C), 126.2, 127.3 (3C), 130.9, 131.2, 132.7, 136.2.

Irradiation of 9,10-phenanthrenequinone 12 and trimethylsilyl enol ether 14

In Acetonitrile A solution of 9,10-phenanthrenequinone **12** (416 mg, 2.00 mmol) and trimethylsilyl enol ether **14** (520 mg, 4.00 mmol) in 180 mL of acetonitrile was irradiated for 1 h (ca. 87 % conversion of **12**). Concentration of photolysate followed by column chromatography (ethyl acetate:*n*-hexane = 1:30) yielded 47 mg (8 %) of **21**, 167 mg (36 %) of **23a**, and 167 mg (36 %) of **23b**.

In Benzene A solution of 9,10-phenanthrenequinone **12** (416 mg, 2.00 mmol) and trimethylsilyl enol ether **14** (520 mg, 4.00 mmol) in 180 mL of benzene was irradiated for 1 h (ca. 90 % conversion of **12**). Concentration of photolysate followed by column chromatography (ethyl acetate:*n*-hexane = 1:30) gave 207 mg (34 %) of **21**, 115 mg (24 %) of **23a**, and 115 mg (24 %) of **23b**.

21. ¹H-NMR (CDCl₃) δ 0.2 (s, 9H), 1.54 (d, 3H, J = 6.6 Hz), 4.34 (q, 1H, J = 6.6 Hz), 5.64 (s, 1H), 7.53–7.67 (m, 4H), 8.15–8.30 (m, 2H), 8.58–8.65 (m, 2H); ¹³C-NMR δ 0.0 (3C), 15.3, 71.9, 91.7, 120.6, 121.0, 122.3, 122.5, 124.7, 124.8, 126.2, 126.4, 126.5, 126.6, 130.2, 133.0.

23a. ¹H-NMR (CDCl₃) δ 1.51 (d, 3H, J = 6.5 Hz), 4.35 (dd, 1H, J = 3.8 Hz, 6.5 Hz), 5.42 (d, 1H, J = 3.8 Hz), 7.52–7.65 (m, 4H), 8.16–8.25 (m, 2H), 8.57-8.63 (m, 2H); ¹³C-NMR δ 15.7, 72.0, 93.0, 120.5, 120.7, 122.3 (2C), 124.9, 125.0, 125.9, 126.0, 126.5, 126.7, 126.9, 130.4, 132.7.

23b. ¹H-NMR (CDCl₃) δ 1.61 (d, 3H, J = 6.5 Hz), 4.34 (d, 1H, J = 6.5 Hz), 5.64 (s, 1H), 7.52–7.65 (m, 4H), 8.16–8.25 (m, 2H), 8.57–8.63 (m, 2H); ¹³C-NMR δ 15.9, 71.4, 91.3, 120.6, 120.8, 122.3 (2C), 125.0, 125.2, 125.8, 126.0, 126.6, 126.7, 127.0, 130.4, 130.2, 131.4.

Irradiation of 9,10-phenanthrenequinone 12 and trimethylsilyl enol ether 15

In Acetonitrile A solution of 9,10-phenanthrenequinone **12** (416 mg, 2.00 mmol) and trimethylsilyl enol ether **15** (580 mg, 4.00 mmol) in 180 mL of acetonitrile was irradiated for 1 h (ca. 77 % conversion of **12**). Concentration of photolysate followed by column chromatography (ethyl acetate:*n*-hexane = 1:40) yielded 147 mg (27 %) of **22** and 255 mg (59 %) of **24**.

In Benzene A solution of 9,10-phenanthrenequinone **12** (416 mg, 2.00 mmol) and trimethylsilyl enol ether **15** (580 mg, 4.00 mmol) in 180 mL of benzene was irradiated for 1 h (ca. 73 % conversion of **12**). Concentration of photolysate followed column chromatography (ethyl acetate:*n*-hexane = 1:40) gave 257 mg (50 %) of **22** and 156 mg (38 %) of **24**.

22. ¹H-NMR (CDCl₃) δ 0.29 (s, 9H), 1.45 (s, 3H), 1.49 (s, 3H), 5.33 (s, 1H), 7.54–7.69 (m, 4H), 8.19–8.31 (m, 2H), 8.63–8.67 (m, 2H); ¹³C-NMR δ 0.1 (3C), 20.2, 23.2, 75.3, 95.3, 120.6, 121.0, 122.4, 122.5, 124.5, 124.9, 126.3, 126.5, 126.9, 129.9 (2C), 131.7.

24. ¹H-NMR (CDCl₃) δ 1.44 (s, 3H), 1.55 (s, 3H), 3.35 (s, 1H), 5.37 (s, 1H), 7.57–7.65 (m, 4H), 8.17–8.26 (m, 2H), 8.59–8.64 (m, 2H); ¹³C-NMR δ 22.1, 22.7, 74.8, 94.3, 120.7, 120.9, 122.5 (2C), 124.9, 125.1, 126.6, 126.7, 126.9 (2C), 127.1, 129.3, 130.5, 136.0.

Irradiation of benzil 13 and trimethylsilyl enol ether 14

In Acetonitrile A solution of benzil **13** (420 mg, 2.00 mmol) and trimethylsilyl enol ether **14** (520 mg, 4.00 mmol) in 180 mL of acetonitrile was irradiated for 1.5 h (ca. 40 % conversion of **13**). Concentration of photolysate followed by column chromatography (ethyl acetate:*n*-hexane = 1:30) yielded 109 mg (40 %) of **34**, 13 mg (10 %) of **36** [59], and 5 mg (5 %) of **38**.

In Benzene A solution of benzil 13 (420 mg, 2.00 mmol) and trimethylsilyl enol ether 14 (520 mg, 4.00 mmol) in 180 mL of benzene was irradiated for 1.5 h (ca. 32 % conversion of 13). Concentration of photolysate followed by column chromatography (ethyl acetate:*n*-hexane = 1:30) gave 96 mg (44 %) of 34, 8 mg (8 %) of 36, and 4 mg (5 %) of 38.

34. ¹H-NMR (CDCl₃) δ 0.02 (s, 9H), 1.36 (d, 3H, J = 6.4 Hz), 5.02 (quintet, 1H, J = 6.4 Hz), 5.32 (d, 1H, J = 6.2 Hz), 7.23-7.50 (m, 6H), 7.91–7.95 (m, 2H), 7.52–7.56 (m, 2H); ¹³C-NMR δ –0.3 (3C), 16.2, 72.3, 81.2, 96.8, 125.9, 127.6 (2C), 128.1, 128.2, 128.6 (3C), 130.3, 133.6, 136.9, 142.5, 199.4.

Irradiation of benzil 13 and trimethylsilyl enol ether 15

In Acetonitrile A solution of benzil 13 (420 mg, 2.00 mmol) and trimethylsilyl enol ether 15 (580 mg, 4.00 mmol) in 180 mL of acetonitrile was irradiated for 3 h (ca. 48 % conversion of 13). Concentration of photolysate followed by column chromatography (ethyl acetate:*n*-hexane = 1:30) yielded 79 mg (29 %) of 33, 136 mg (40 %) of 35a, and 58 mg (17 %) of 35b, 5 mg (3 %) of 37 [60], and trace of 38.

In Benzene A solution of benzil 13 (420 mg, 2.00 mmol) and trimethylsilyl enol ether 15 (580 mg, 4.00 mmol) in 180 mL of benzene was irradiated for 3 h (ca. 69 % conversion of 13). Concentration of photolysate followed by column chromatography (ethyl acetate:*n*-hexane = 1:30) gave 82 mg (21 %) of 33, 137 mg (28 %) of 35a, and 83 mg (17 %) of 35b, 5 mg (2 %) of 37, and trace of 38.

33. ¹H-NMR (CDCl₃) ¹H-NMR (CDCl₃) δ 1.07 (s, 3H), 1.30 (s, 3H), 5.15 (s, 1H), 7.18–7.36 (m, 8H), 7.74–7.79 (m, 2H), 9.97 (s, 1H); ¹³C-NMR δ 15.0 (2C), 51.4, 83.2, 125.5, 126.2, 126.9, 127.6, 127.7, 128.6, 128.7, 128.8 (2C), 133.1, 135.7, 142.4, 203.4, 203.6.

35a. ¹H-NMR (CDCl₃) δ 0.19 (s, 9H) 0.73, (s, 3H), 1.35 (s, 3H), 5.36 (s, 1H), 7.29–7.46 (m, 6H), 7.72–7.77 (m, 2H), 7.89–7.93 (m, 2H); ¹³C-NMR δ 0.1 (3C), 16.3 (2C), 74.1, 81.7, 97.2, 125.8, 127.8 (2C), 128.0 (2C), 128.6 (2C), 130.4 (2C), 133.7, 136.8, 144.1, 199.4.

35b. ¹H-NMR (CDCl₃) δ 0.22 (s, 9H), 0.72 (s, 3H), 1.34 (s, 3H), 5.35 (s, 1H), 7.24–7.48 (m, 6H), 7.72–7.78 (m, 2H), 7.91–7.96 (m, 2H); ¹³C-NMR δ –0.2 (3C), 16.5 (2C), 74.3, 82.0, 97.4, 125.9, 127.8 (2C), 128.2 (2C), 128.6 (2C), 130.2 (2C), 133.7, 136.9, 144.3, 199.6.

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