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COMPARISON OF PHOTOCHEMICAL REACTIONS OF AROMATIC CARBONYL COMPOUNDS WITH A SILYL KETENE THIOACETAL AND A SILYL KETENE ACETAL

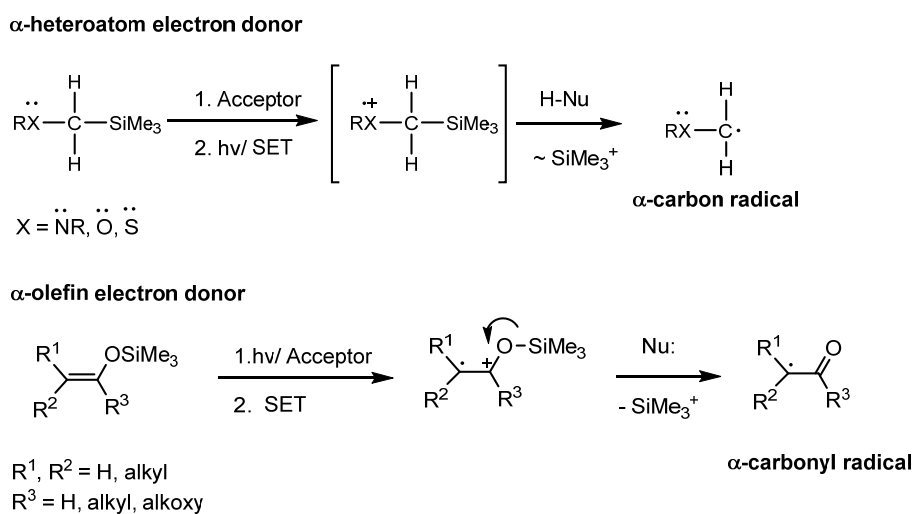
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Abstract – Photoaddition reactions of carbonyl compounds with silyl ketene thioacetals have been explored and the results are compared to those arising from investigations of analogous reactions with silyl ketene acetals. Observations made in this study show that photoirradiation of benzaldehyde (**8**) and benzophenone (**9**) and with the dimethyl substituted silyl ketene thioacetal (**13**) promotes reactions that take place predominantly via Paterno-Büchi type [2+2]-cycloaddition pathways to produce oxetanes. In addition, photoreactions between acetophenone (**10**) and *p*-cyanoacetophenone (**11**) and **13** occur via competitive sequential single electron transfer (SET)-desilylation or [2+2]-cycloaddition modes. Lastly, photochemical reaction of the highly electron deficient carbonyl compound, *p*-trifluoromethylacetophenone (**12**), and **13** gives rise to exclusive formation of β -hydroxythioester arising via the SET pathway. In contrast, photochemical reactions of all of these aromatic carbonyl compounds with the analogous dimethyl substituted silyl ketene acetal **14** take place predominantly via a sequential SET-desilylation pathway to form β -hydroxyesters. A comparison of these results reveals that replacement of an alkoxy by alkylthio group in the ketene derivatives brings about dramatic changes in chemoselectivities of the photoreactions with aryl-substituted ketones.

INTRODUCTION

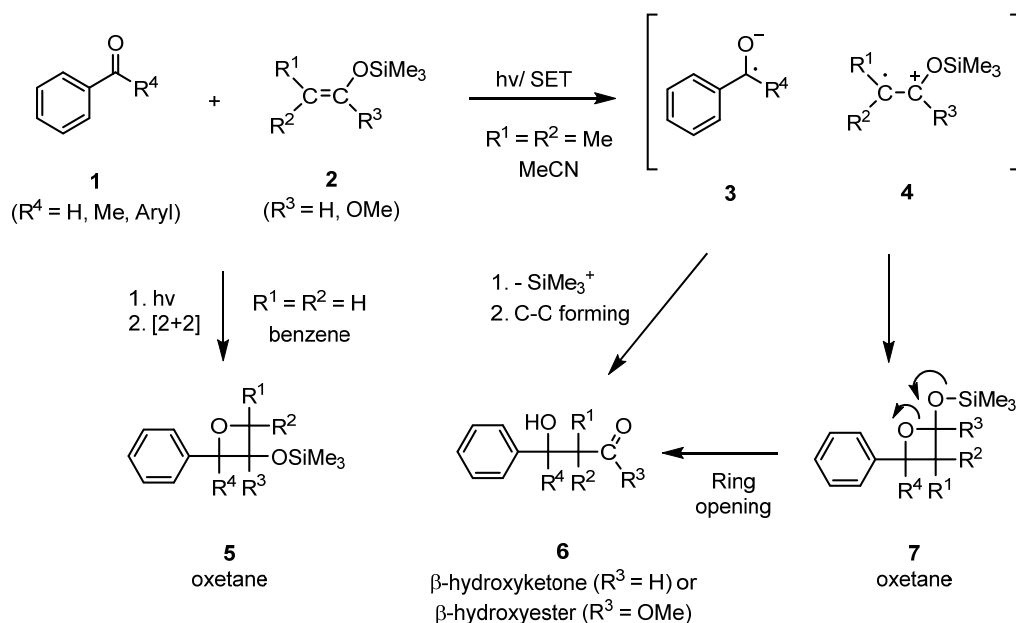
Previous studies have demonstrated that photochemical ground state reactions of α -trialkylsilyl electron donors taking place through sequential single electron transfer (SET) - desilylation mechanistic pathways (Scheme 1) serve as highly efficient and regioselective methods to generate α -carbon radicals.¹⁻³ Specifically, radical cations generated by SET from α -trialkylsilyl donors to excited states of acceptors or ground states of oxidants typically undergo rapid solvent-assisted desilylation to produce α -donor substituted carbon center free radicals.⁴⁻⁸



Scheme 1

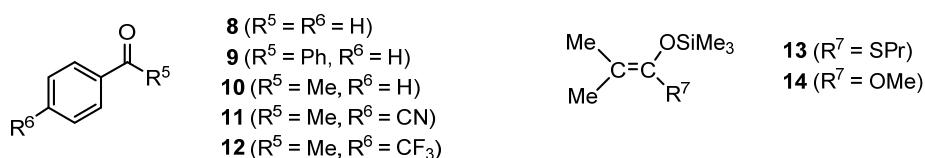
The results of a number of studies have demonstrated that Lewis acid catalyzed Claisen/Mukaiyama type reactions of carbonyl compounds with silyl ketene acetals and silyl enol ethers⁹⁻¹⁴ are highly useful synthetic protocols.

Recently, we explored photochemical versions of Mukaiyama type addition reactions of these types of substrates (Scheme 2).^{15,16} The observations made in this effort show that oxetane **5** and β -hydroxyketones/ β -hydroxyesters **6** are produced by respective sequential [2+2]-cycloaddition and SET-desilylation pathways,^{17,18} in a manner that is mainly dependent on electron donating ability (*i.e.*, oxidation potential) of the silyl ketene acetals and silyl enol ethers and solvent polarity.^{15,16,19} Specifically, when electron rich α -silyl donors and relatively polar solvents (*i.e.*, MeCN) are used, photoreactions with aromatic carbonyl compounds occur to form β -hydroxyketone/ β -hydroxyesters **6** predominantly. However, oxetanes **5** are dominant photoproducts of photoreactions occurring between carbonyl compounds and electron deficient α -silyl substituted donor in less polar solvents (*i.e.*, benzene). (Scheme 2)^{15,16}



Scheme 2

As a part of continuing investigations in this area, photoaddition reactions of aryl-substituted carbonyl compounds with the silyl ketene thioacetal **13** (Scheme 3) were explored. The mechanistic pathways followed in these processes, reflected in product distributions, were compared with those previously described¹⁵ for analogous photoreactions of aryl-substituted ketones with silyl ketene acetal **14** (Scheme 3). The results of this effort are described below.



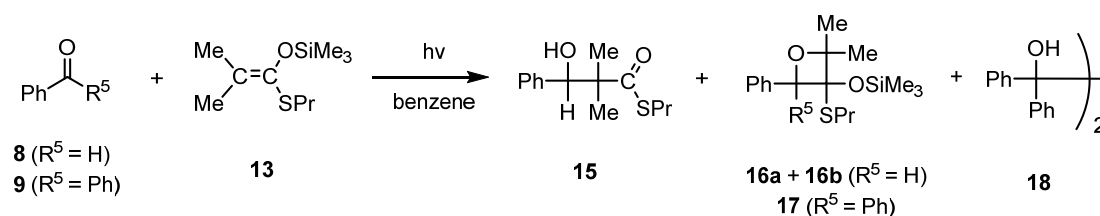
Scheme 3

RESULTS AND DISCUSSION

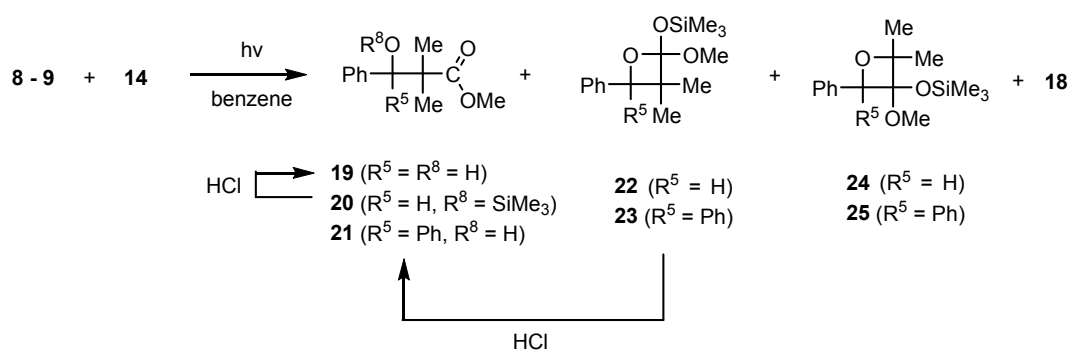
Photochemical reactions were carried out by using Pyrex glass filtered light (>290 nm) in independent benzene solutions (200 mL) containing the carbonyl compounds **8-12** (33 mM) and silyl ketene thioacetal **13** (66 mM) for time periods that bring about 61-77% conversions of the ketones. The concentrated photolysates were then subjected to silica gel chromatography to obtain the photoadducts, whose structures were assigned by comparing their NMR spectroscopic properties with those of structurally similar substances generated in previous studies.^{15,16}

The product distributions arising from photoreactions occurring between ketones **8** and **9** and ketene derivative in benzene solutions are displayed in Schemes 4 and Table 1. Firstly, irradiation of a benzene

solution containing benzaldehyde **8** and ketene thioacetal **13** for 3 h leads to formation of β -hydroxythioester **15a** (18%), generated through a SET-desilylation mechanistic pathway, along with a mixture of the diastereomeric oxetanes **16a** and **16b** (50%), arising through [2+2]-cycloaddition processes. In the photoreaction of benzophenone **9** and **13**, instead, both oxetane **17** (31%) and benzpinacol **18**¹⁵ (40%), formed by respective [2+2]-cycloaddition and photoreduction pathways, are produced as predominant products (Scheme 4 and Table 1). These observations indicate that the excited states of carbonyl compounds **8** and **9** react with silyl ketene thioacetal **13** by a classical [2+2]-cycloaddition pathway predominantly. In addition, photoreduction of **9** is common process occurring in ketone rather than aldehyde photochemistry.¹⁵



Scheme 4



Scheme 5

Table 1. Photoreactions of aryl-ketones **8** and **9** and with silyl ketene thioacetal **13** and acetal **14**^a

Reactants	Reaction Time (h)	Conversion (%)	Products (% yield) ^b
8 + 13	3	75	15 (18), 16a (39), 16b (11)
9 + 13	2.5	73	17 (31), 18 (40)
8 + 14 ^c	11	79	19 (72), 20 (14), 22 (4), 24 (8)
9 + 14 ^c	4	95	21 (11), 23 (27), 25 (3), 18 (40)

^a[silyl donor]: [carbonyl compound] is 2: 1. ^bYields are based on consumed carbonyl compounds.

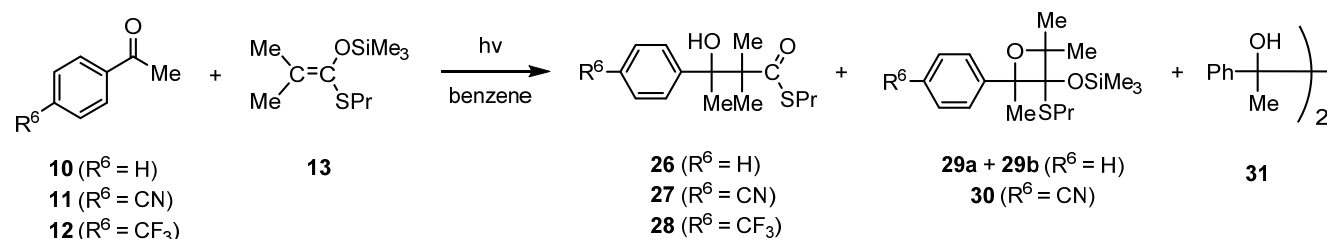
^cResults are those reported in a previous study.¹⁵

A comparison of the product distributions of reactions between aryl-ketones **8** and **9** and silyl ketene thioacetal **13** and the corresponding acetal **14** reveals the existence of an interesting trend. In previous studies,¹⁵ the results of which are displayed in Scheme 5 and Table 1, it was found that photochemical reactions of benzaldehyde with silyl ketene acetal **14** gives rise to predominant formation of β -hydroxyester **19** (72%) or its silyl ether derivative **20** (14%). In addition, photoreaction of benzophenone **9** with **14** leads to generation of **21** (11%), **23** (27%) and **25** (3%), and **18** (40%), which arise from the operation of respective SET-desilylation, [2+2]-cycloaddition and photoreduction pathways. A comparison of these product distributions with those coming from reactions of the same aryl-ketones with silyl ketene thioacetal **13** clearly shows that the nature of the reaction pathways followed is governed by the electronic properties of ketene derivative. Specifically, while photoreactions of carbonyl compounds **8** and **9** with silyl ketene thioacetal [2+2]-cycloaddition **13** take place predominantly through [2+2]-cycloaddition routes, those with the silyl ketene acetal **14** occur principally via sequential SET-desilylation pathway. Moreover, even though the absolute efficiencies of the photoreactions presented above were not determined, monitoring irradiation times vs percent conversions (Table 1) shows that the silyl ketene thioacetal **13** reacts more efficiently than silyl ketene acetal analog **14** in reactions with these ketones. This reactivity trend also exists for photoaddition reaction of acetophenone derivatives **10** and **11** with silyl substituted donors **13** and **14** (see below).

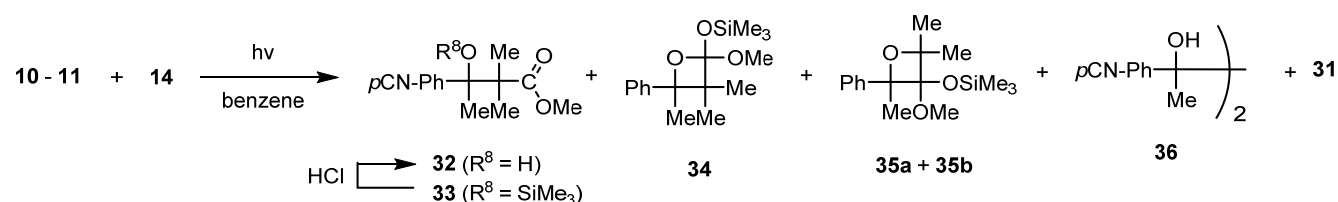
The products and yields of photoreactions occurring between acetophenone derivatives **10-12** and **13** and **14** in benzene were also determined (Schemes 6 and 7,¹⁵ and Table 2). Photoreaction of acetophenone **10** with silyl ketene thioacetal **13** yields pinacol **31** (38%) as the major product along with nearly equal amounts of β -hydroxythioester **26** (19%) and oxetanes **29a** and **29b** (20%) formed through SET-desilylation and [2+2]-cycloaddition routes, respectively. However, photoirradiation of a benzene solution containing **10** and silyl ketene acetal **14** leads to predominant production of oxetane **34** (64%), which is readily converted to β -hydroxyester **32** by treatment with acid, along with oxetanes **35a** and **35b** (11%) and pinacol **31**¹⁵ (3%).

When the strong electron withdrawing cyano group resides at the para-position of acetophenone, as in **11**, the photoreduction process forming **31** that is prevalent in the reaction of **10** is completely eliminated. Specifically, SET-desilylation and [2+2]-cycloaddition processes take place competitively in the photoreaction between **11** and **13** to form β -hydroxythioester **27** (24%) and oxetane **30** (36%). Compared to that between **11** and **13**, photochemical reaction of **11** and **14** in benzene gives rise to formation of chiefly β -hydroxyesters **32** and **33** (80%) along with a minor amount of diol **36** (5%). Importantly, no oxetane products are generated in this process. Interestingly, the acetophenone derivative **12**, which contains a strongly electron withdrawing trifluoromethyl group at the para-position of the aryl ring,

undergoes photoreaction with the silyl ketene thioacetal **13** by way of an SET-desilylation pathway exclusively to produce β -hydroxythioester **28** (52%).



Scheme 6



Scheme 7

Table 2. Photoreactions of aryl-ketones **10-12** and silyl ketene thioacetal **13** and silyl ketene acetal **14**^a

Reactant	Reaction Time (h)	Conversion (%)	Product (% yield) ^b
10 + 13	4	71	26 (19), 29a (11), 29b (9), 31 (38)
11 + 13	2	61	27 (24), 30 (36)
12 + 13	1.5	77	28 (52)
10 + 14 ^c	33	77	34 (64), 35a (5), 35b (6), 31 (3)
11 + 14 ^c	10	86	32 (86), 33 (trace), 36 (5)

^a[silyl donor]: [carbonyl compound] is 2: 1. ^bYields are based on consumed carbonyl compounds.

^cThe results were obtained in a previous study.¹⁵

Observations made in the studies described above provide qualitative information about the mechanisms and efficiencies of photoreactions occurring between aryl-ketones and substrates **13** and **14**. A comparison of photoproduct distributions generated in these processes show that replacement of alkylthio by an alkoxy group in the ketene derivative causes a dramatic change in the major excited state reaction pathway followed. While photochemical reactions of the aryl-substituted ketones with silyl ketene acetal **14** take place predominantly through a sequential SET-desilylation route, reactions with silyl ketene

thioacetal **13** occur by a classical [2+2]-cycloaddition pathway preferentially. Information about the source of this difference is found in observations made in our earlier studies¹⁶ of photoreactions of carbonyl compounds with variously methyl substituted silyl ketene acetals. In that effort, we observed that oxetane formation via a [2+2]-cycloaddition pathway becomes more dominant than the sequential SET-desilylation process in photoreactions of aryl-ketones with less methyl-substituted silyl ketene acetals, such as $\text{CH}_2=\text{C}(\text{OSiMe}_3)(\text{OMe})$, in nonpolar solvents like benzene. We attributed this trend to the less favorable thermodynamics ($\Delta G^\circ_{\text{SET}}$)¹⁶ and thus rates of SET to the triplet excited states of the aryl-ketones caused by removal of electron donor methyl groups from the silyl ketene acetal skeleton. The source of the different mechanistic behavior of reactions of **13** and **14** with the excited state of aryl-ketones might also be related to SET thermodynamics. For example, the change from reactions of **13** occurring predominantly via [2+2]-cycloaddition to SET-desilylation brought about by electron withdrawing group substitution on the acetophenone ring system is likely a consequence of an increase in the excited state reduction potential of the aryl-ketone substrate which makes SET from **13** more thermodynamically favorable. Although further studies are necessary in order to gain more convincing evidence for this conclusion, a possibility exists that the classical [2+2]-cycloaddition, oxetane forming pathway is more prominent in photochemical reactions of the silyl ketene thioacetal **13** than its acetal analog **14** is a result of the higher oxidation potential of **13** which would cause SET to the aryl-ketone triplets states to be less thermodynamically favored. Further studies are underway to gain more clear insight into the factors that govern the chemoselectivities of photochemical reactions of silyl ketene acetals and related thioacetal with carbonyl compounds.

EXPERIMENTAL

General Procedure ¹H and ¹³C NMR (200 MHz) spectra were recorded using CDCl_3 solutions and chemical shifts are reported in parts per million relative to CHCl_3 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 of carbonyl substrates used in the photoreactions derived from commercial sources and silyl ketene thioacetal **13** was prepared by using a well-known synthetic procedure.²⁰ All new compounds characterized in this study were isolated as oils in >90% purity (by NMR analysis) unless noted otherwise.

Irradiation of a benzene solution containing benzaldehyde 8 and thioacetal 13. A solution of benzaldehyde **8** (640 mg, 6 mmol) and dimethyl substituted silyl ketene thioacetal **13** (2.6 g, 12 mmol) in 180 mL of benzene was irradiated for 3 h (*ca.* 75% conversion of **8**). Concentration of photolysate gave a residue, which was subjected to silica gel column chromatography (EtOAc: *n*-hexane = 1: 40) giving 206 mg (18%) of **15a**, 581 mg (39%) of **16a** and 149 mg (11 %) of **16b**.

15a: ^1H NMR (CDCl_3) 0.97 (t, 3H, $J = 7.3$ Hz), 1.12 (s, 3H), 1.22 (s, 3H), 1.55-1.66 (m, 2H), 2.86 (t, 3H, $J = 7.3$ Hz), 4.94 (s, 1H), 7.20-7.34 (m, 5H); ^{13}C -NMR 13.3, 17.5, 18.9, 22.6, 30.6, 54.3, 78.6, 127.5, 127.6, 128.2, 139.8, 207.8; IR (neat, cm^{-1}) 3500 (br, OH), 1670 (C=O); HRMS (FAB) m/z 253.1262 ($\text{C}_{14}\text{H}_{21}\text{O}_2\text{S}$ requires 253.1262).

16a: ^1H -NMR (CDCl_3) -0.06 (s, 9H), 1.03 (t, 3H, $J = 7.3$ Hz), 1.42 (s, 3H), 1.67 (s, 3H), 1.49-1.75 (m, 2H), 2.67 (t, 3H, $J = 7.3$ Hz), 5.67 (s, 1H), 7.33-7.36 (m, 5H); ^{13}C -NMR 1.4, 13.8, 22.5, 25.0, 26.4, 30.5, 89.4, 89.5, 91.7, 127.3, 127.5, 137.8; HRMS (FAB) m/z 325.1657 ($\text{C}_{17}\text{H}_{29}\text{O}_2\text{SSi}$ requires 325.1658).

16b: ^1H -NMR (CDCl_3) 0.27 (s, 9H), 0.77 (t, 3H, $J = 7.3$ Hz), 1.65 (s, 3H), 1.69 (s, 3H), 1.50-1.76 (m, 2H), 2.65 (t, 3H, $J = 7.3$ Hz), 5.61 (s, 1H), 7.25-7.48 (m, 5H); ^{13}C -NMR 1.8, 13.8, 22.2, 24.6, 25.6, 29.5, 89.7, 90.7, 91.9, 128.2, 128.6, 137.4; HRMS (FAB) m/z 325.1655 ($\text{C}_{17}\text{H}_{29}\text{O}_2\text{SSi}$ requires 325.1658).

Irradiation of benzene solution containing benzophenone 9 and thioacetal 13. A solution of benzophenone **9** (1.1 g, 6 mmol) and dimethyl substituted silyl ketene thioacetal **13** (2.6 g, 12 mmol) in 180 mL of benzene was irradiated for 2.5 h (*ca.* 73% conversion of **9**). Concentration of photolysate gave a residue, which was subjected to silica gel column chromatography (EtOAc: *n*-hexane = 1: 40) giving trace of **15**, 550 mg (31%) of **17** and 333 mg (40%) of **18**.

15b: ^1H NMR (CDCl_3) 0.94 (t, 3H, $J = 7.3$ Hz), 1.12 (s, 3H), 1.22 (s, 3H), 1.55-1.66 (m, 2H), 2.86 (t, 3H, $J = 7.3$ Hz), 4.94 (s, 1H), 7.20-7.34 (m, 5H); ^{13}C -NMR 13.3, 17.5, 18.9, 22.6, 30.6, 54.3, 78.6, 127.5, 127.6, 128.2, 139.8, 207.8; IR (neat, cm^{-1}) 3500 (br, OH), 1670 (C=O); HRMS (FAB) m/z 253.1262 ($\text{C}_{14}\text{H}_{21}\text{O}_2\text{S}$ requires 253.1262).

17: ^1H -NMR (CDCl_3) 0.01 (s, 9H), 0.67 (t, 3H, $J = 7.3$ Hz), 1.17 (s, 3H), 1.62 (s, 3H), 1.41-1.70 (m, 2H), 2.26 (t, 2H, $J = 7.3$ Hz), 7.16-7.64 (m, 5H); ^{13}C -NMR 1.8, 13.7, 21.9, 25.4, 26.0, 29.6, 88.8, 94.1, 95.0, 126.4, 126.6, 127.1, 128.0, 142.5, 144.1; HRMS (FAB) m/z 401.1956 ($\text{C}_{23}\text{H}_{33}\text{O}_2\text{SSi}$ requires 401.1971).

Irradiation of a benzene solution containing acetophenone 10 and thioacetal 13. A solution of acetophenone **10** (700 mg, 6 mmol) and dimethyl substituted silyl ketene thioacetal **13** (2.6 g, 12 mmol) in 180 mL of benzene was irradiated for 4 h (*ca.* 71% conversion of **10**). Concentration of photolysate gave a residue, which was subjected to silica gel column chromatography (EtOAc: *n*-hexane = 1: 40) giving 320 mg (19%) of **26**, 243 mg (11%) of **29a**, 199 mg (9%) of **29b** and 150 mg (38%) of **31**.

26: ^1H -NMR (CDCl_3) 0.95 (t, 3H, $J = 7.3$ Hz), 1.19 (s, 3H), 1.17 (s, 3H), 1.40-1.60 (m, 2H), 1.60 (s, 3H), 2.81 (t, 3H, $J = 7.3$ Hz), 4.75 (s, 1H), 7.22-7.46 (m, 5H); ^{13}C -NMR 13.3, 21.7, 21.9, 22.4, 24.9, 30.9, 56.0,

77.6, 126.7, 127.1, 127.2, 143.3, 210.6; IR (neat, cm^{-1}) 3470 (br, OH), 1640 (C=O); HRMS (FAB) m/z 267.1419 ($\text{C}_{15}\text{H}_{23}\text{O}_2\text{S}$ requires 267.1419).

29a: $^1\text{H-NMR}$ (CDCl_3) -0.04 (s, 9H), 1.07 (t, 3H, $J = 7.3$ Hz), 1.24-1.30 (m, 2H), 1.57 (s, 3H), 1.67 (s, 3H), 1.79 (s, 3H), 2.67 (t, 2H, $J = 7.3$ Hz), 7.27-7.33 (m, 5H); $^{13}\text{C-NMR}$ 1.65, 13.8, 22.6, 26.1, 26.6, 27.2, 30.5, 88.4, 92.5, 93.0, 125.7, 126.1, 127.0, 144.5; HRMS (FAB) m/z 339.1814 ($\text{C}_{18}\text{H}_{31}\text{O}_2\text{SSi}$ requires 339.1814).

29b: $^1\text{H-NMR}$ (CDCl_3) 0.33 (s, 9H), 0.81 (t, 3H, $J = 7.3$ Hz), 1.24-1.30 (m, 2H), 1.51 (s, 3H), 1.57 (s, 3H), 1.70 (s, 3H), 2.81 (t, 3H, $J = 7.3$ Hz), 7.25-7.48 (m, 5H); $^{13}\text{C-NMR}$ 2.1, 13.9, 22.4, 26.1, 26.7, 27.3, 29.6, 89.6, 90.6, 92.9, 125.4, 126.9, 127.3, 144.2; HRMS (FAB) m/z 339.1816 ($\text{C}_{18}\text{H}_{31}\text{O}_2\text{SSi}$ requires 339.1814).

Irradiation of benzene solution containing *p*-cyanoacetophenone **11 and thioacetal **13**.** A solution of *p*-cyanoacetophenone **11** (870 mg, 6 mmol) and dimethyl substituted silyl ketene thioacetal **13** (2.6 g, 12 mmol) in 180 mL of benzene was irradiated for 2 h (*ca.* 61% conversion of **11**). Concentration of photolysate gave a residue, which was subjected to silica gel column chromatography (EtOAc: *n*-hexane = 1: 40) giving 256 mg (24%) of **27** and 474 mg (36%) of **30**.

27: $^1\text{H-NMR}$ (CDCl_3) 0.95 (t, 3H, $J = 7.3$ Hz), 1.16 (s, 3H), 1.22 (s, 3H), 1.42 (s, 3H), 1.54-1.64 (m, 2H), 2.81 (t, 2H, $J = 7.3$ Hz, 6.5 Hz), 4.75 (s, 1H), 7.52-7.62 (m, 5H); $^{13}\text{C-NMR}$ 13.4, 21.7, 21.9, 22.5, 24.8, 31.1, 55.8, 77.9, 110.9, 118.9, 128.2, 131.2, 148.9, 210.5; HRMS (FAB) m/z 292.1373 (M+1, $\text{C}_{16}\text{H}_{22}\text{NO}_2\text{S}$ requires 292.1371).

30: $^1\text{H-NMR}$ (CDCl_3) 0.32 (s, 9H), 0.81 (t, 3H, $J = 7.3$ Hz), 1.49 (s, 3H), 1.53 (s, 3H), 1.50-1.60 (m, 2H), 1.66 (s, 3H), 2.24 (t, 2H, $J = 7.3$ Hz), 7.56-7.63 (m, 5H); $^{13}\text{C-NMR}$ 2.2, 13.8, 22.5, 26.6, 27.0, 27.4, 30.8, 77.2, 90.6, 92.4, 110.9, 119.1, 126.2, 131.1, 149.7; HRMS (FAB) m/z 364.1769 (M+1, $\text{C}_{19}\text{H}_{30}\text{NO}_2\text{SSi}$ requires 364.1767).

Irradiation of a benzene solution containing *p*-trifluoromethylacetophenone **12 and thioacetal **13**.** A solution of *p*-trifluoromethylacetophenone **12** (790 mg, 6 mmol) and dimethyl substituted silyl ketene thioacetal **13** (2.6 g, 12 mmol) in 180 mL of benzene was irradiated for 1.5 h (*ca.* 77% conversion of **12**). Concentration of photolysate gave a residue, which was subjected to silica gel column chromatography (EtOAc: *n*-hexane = 1: 40) giving 560 mg (52%) of **28**. $^1\text{H-NMR}$ (CDCl_3) 0.94 (t, 3H, $J = 7.3$ Hz), 1.18 (s, 3H), 1.24 (s, 3H), 1.61 (s, 3H), 1.53-1.63 (m, 2H), 2.81 (t, 3H, $J = 7.3$ Hz), 4.71 (s, 1H), 7.56 (s, 5H); $^{13}\text{C-NMR}$ 13.3, 21.7, 21.9, 22.4, 24.9, 31.1, 55.9, 77.8, 124.1, 124.2, 127.8, 128.0, 147.5, 210.6; HRMS (FAB) m/z 335.1296 (M+1, $\text{C}_{16}\text{H}_{22}\text{F}_3\text{O}_2\text{S}$ requires 335.1293).

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