Medium Effects on the H-Atom Abstraction and Silyl-Transfer Photoreactions of Silylalkyl Ketones

Sun Wha Oh

Basic Science Research Institute, Pukyong National University, Busan, 608-737, Korea

Medium effects have been explored on the competitive H-atom abstraction and SET-promoted, silyl-transfer reactions of excited states of silylalkyl-substituted phenyl ketones. The chemical selectivities of photochemical reactions of silylalkyl phenyl ketones appear to depend on medium polarity, medium silophilicity, added metal cation and alkyl length. Irradiations of silylalkylketones in aqueous solvent system and in presence of metal cation such as Li^+ and Mg^{+2} lead to formation of acetophenone predominantly by the sequential SET-silyl transfer route.

key words: H-atom abstraction, SET, silyl-transfer, silylalkylketones medium effects.

INTRODUCTION

The most general and explored reactions in organic photochemistry are initiated by intramolecular hydrogen-atom abstraction by an excited state of a carbonyl compounds. [1] This process serves as the key chemical step in the Norrish Type¢½ fragmentation and Yang cyclization reactions, [2] both of which proceed *via* the intermediacy of 1,4-diradicals (Scheme 1).
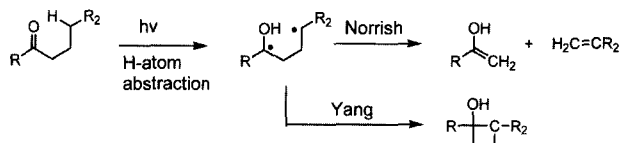
Scheme 1.

A number of studies in recent years have demonstrated that an indirect, excited-state electrons transfer (SET) pathway can be followed in bringing about formal H-atom migration. [1,3] This is the case for systems in which the carbonyl excited state has a sufficiently high reduction potential and/or in which a donor site of low oxidation potential is present in appended alkyl chain. As a result, SET can occur to generate zwitterionic diradicals (Scheme 2). Proton transfer in zwitterionic diradicals then generates the same types of 1,4-diradicals that would have arisen by H-atom abstraction. It is clear that efficiencies of hydrogen migration reactions proceeding by the sequential SET-proton transfer pathway are governed by the redox properties of the excited carbonyl group.
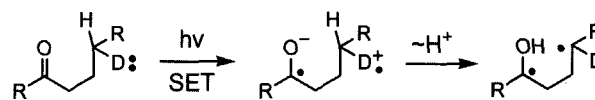
Scheme 2.

Photoreactions of silicon substituted carbonyl compound would be expected to mimic the familiar Norrish Type¢½ fragmentation and Yang cyclization processes. Mariano et al. reported that two mechanisms were responsible for generation of acylarene products in the photoreactions of silyl-substituted aryl ketone. [4,5] The major pathway involved initial g-hydrogen abstraction by the carbonyl n-p* triplet and generated the acylarene and vinylsilane products in equal amounts. Another route involving SET leaded to generation of acylarene and but not vinylsilane. Therefore, photoreactions of silicon substituted carbonyl compound were observed that H-atom abstraction and SET reaction were occurred competitively. The reaction mechanism would be determined by the ratio of photoproduct.

In this study, γ-(trimethylsilyl)butyrophenone (1) and δ-(trimethylsilyl)-valerophenone (2) were prepared and their photoreactions were studied in various solvent systems and including salts ($LiClO_4$, $Mg(ClO_4)_2$, nBu_4NF). The results of these investigations demonstrated the nature of solvent and salt effect in controlling the chemical selectivites of silylalkyl ketone photoreactions.

MATERIALS AND METHODS

General Procedures

^1H nuclear magnetic resonance (NMR) and ^{13}C-NMR spectra were recorded using 200MHz spectrometers and chemical shifts are reported in parts per million downfield from tetramethylsilane employed as an internal standard; abbreviations used are s (singlet), d (doublet), t (triplet) and m (multiplet). Infrared spectra were obtained using neat liquids

---

unless otherwise specified, and data are reported in units of cm^{-1}. Low (MS) and high (HRMS) mass spectra, reported as m/z (relative intensity), were recorded by using electron impact ionization (EI) or chemical ionization (CI).

Preparative photolyses were conducted with an apparatus consisting of a 450 W medium pressure mercury lamp surrounded by a pyrex filter in a quartz immersion well under an inert atmosphere. Photochemical reaction progress was monitored by TLC or ^{1}H-NMR. Sealed NMR tubes were devoided of air by using N$_2$ purging before irradiation.

Preparations of silylalkyl ketones (1-2)

γ-(Trimethylsilyl)butyrophenone (1) and δ-(trimethylsilyl) valerophenone (2) were synthesized according to the previous report [6] and conformed by NMR and MS.

Irradiations of γ-(trimethylsilyl)butyrophenone (1)

A solution of γ-(trimethylsilyl)butyrophenone (1, 10 mg, 0.045 mmol) in 1.0 mL of NMR solvent (CD$_3$CN, 5%, 35%, 50% D$_2$O-CD$_3$CN, CD$_3$OD, 5%, 35%, 50% D$_2$O-CD$_3$OD) was irradiated with Pyrex-filtered light under N$_2$ (100% conversion of 1). Photochemical reaction progress was monitored by ^{1}H-NMR. The ratio of photoproduct acetophenone 3 and vinyl trimethylsilane 4 was determined by ^{1}H-NMR integration. The reaction condition and product ratio are given in table 1.

Irradiations of γ-(trimethylsilyl)butyrophenone (1) and salts

A solution of γ-(trimethylsilyl)butyrophenone (1, 10 mg, 0.045 mmol) and salt (LiClO$_4$, 0.1 M: 5 mg, 0.2 M: 11 mg, 0.3 M: 16 mg, 0.4 M: 21 mg, 0.5 M: 27 mg; Mg(ClO$_4$)$_2$, 0.1 M: 11 mg, 0.2 M: 22 mg, 0.3 M: 33 mg, 0.4 M: 45 mg, 0.5 M: 55 mg; nBu$_4$NF$_x$H$_2$O, 0.1 M: 13 mg, 0.2 M: 26 mg, 0.3 M: 39 mg, 0.4 M: 52 mg, 0.5 M: 65 mg) in 0.5 mL of CD$_3$CN was irradiated with Pyrex-filtered light under N$_2$ (100% conversion of 1). Photochemical reaction progress was monitored by ^{1}H-

NMR. The ratio of photoproduct 3 and 4 was determined by ^{1}H-NMR integration. The reaction condition and product ratio are given in Table 2.

Irradiations of δ-(trimethylsilyl)valerophenone (2)

A solution of δ-(trimethylsilyl)valerophenone (2, 10 mg, 0.043 mmol) in 1.0 mL of NMR solvent (CD$_3$CN, 5%, 35%, 50% D$_2$O-CD$_3$CN, CD$_3$OD, 5%, 35%, 50% D$_2$O-CD$_3$OD) was irradiated with Pyrex-filtered light under N$_2$ (100% conversion of 2). Photochemical reaction progress was monitored by ^{1}H-NMR. The ratio of photoproduct acetophenone 3 and allyl trimethylsilane 7 was determined by ^{1}H-NMR integration. The reaction condition and product ratio are given in Table 2.

Irradiation of δ-(trimethylsilyl)valerophenone (2) in 35% H$_2$O-CH$_3$CN

A solution of δ-(trimethylsilyl)valerophenone (2, 110 mg, 0.47 mmol) in a solution of 21 mL of H$_2$O and 39 mL of CH$_3$CN was irradiated with Pyrex-filtered light under N$_2$ for 1h (100 conversion of 2). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate : hexane = 1:10), yielding 12 mg (11%) of 8 and 17 mg (15%) of 9. The yields of photoproducts (3, 7, 8, 9) were determined by ^{1}H-NMR integration using internal standard material (4,4'-bis(diethylamino)benzophenone).

8: ^{1}H-NMR (CDCl$_3$) -0.08 (s, 9H, SiMe$_3$), 1.28 (quin, 2H, J = 9.5 Hz, C(OH)CH$_2$CH$_2$), 2.04-2.25 (m, 2H, CH$_2$CH), 2.33 (s, 1H, OH), 2.62-2.71 (m, 2H, C(OH)CH$_2$), 7.26-7.50 (m, 5H, aromatic); ^{13}C-NMR (CDCl$_3$) -0.2 (SiMe$_3$), 19.2 (C(OH)CH$_2$CH$_2$), 22.0 (CHCH$_2$), 34.7 (C(OH)CH$_2$), 46.2 (CH), 80.4 (COH), 126.1, 126.9 and 128.0 (CH, aromatic), 142.8 (C, aromatic); IR(KBr) 3200-3600 (br. OH stretching); MS (EI), m/z (rel. intensity) 234 (M$^+$, 1), 203 (84), 105 (27), 103 (25), 74 (100); HRMS (EI), m/z 234.1442 (C$_{14}$H$_{22}$OSi requires 234.1440).

9: ^{1}H-NMR (CDCl$_3$) 0.01 (s, 9H, SiMe$_3$), 0.67-0.96 (m, 2H,

Table 1. Irradiations of γ-(trimethylsilyl)butyrophenone (1)

Solvent	Reaction Time (min)	4	3	Solvent	Reaction Time (min)	4	3
CD$_3$CN	20	1	0.8	CD$_3$OD	30	1	1.8
5%D$_2$O-CD$_3$-CN	20	1	2.4	5%D$_2$O-CD$_3$OD	30	1	3.6
35%D$_2$O-CD$_3$-CN	20	1	48	35%D$_2$O-CD$_3$OD	30	1	6.7
50%D$_2$O-CD$_3$-CN	20	none	only	50%D$_2$O-CD$_3$OD	30	none	only

Table 2. Irradiations of γ-(trimethylsilyl)butyrophenone (1) and salts in CD$_3$CN

[LiClO$_4$]	Reaction Time (min)	4	3	[Mg(ClO$_4$)$_2$]	Reaction Time (min)	4	3	[nBu$_4$NF]	Reaction Time (min)	4	3
0.1M	20	1	1.05	0.1M	40	1	0.84	0.1M	20	1	0.89
0.2M	20	1	1.10	0.2M	40	1	1.00	0.2M	20	1	0.86
0.3M	20	1	1.15	0.3M	40	1	1.08	0.3M	20	1	0.48
0.4M	20	1	1.46	0.4M	40	1	1.25	0.4M	20	1	0.46
0.5M	20	1	1.64	0.5M	40	1	1.40	0.5M	20	1	0.12

CH$_2$SiMe$_3$), 1.84-2.18 (m, 2H, CH$_2$CH), 2.38-2.45 (m, 2H, CH$_2$CH$_2$CH), 2.72-2.85 (m, 1H, CH), 7.25-7.46 (m, 5H, aromatic); ^{13}C-NMR (CDCl$_3$) -0.9 (SiMe$_3$), 16.0 (CH$_2$SiMe$_3$), 24.8 (CH$_2$CH), 34.0 (CH$_2$CH$_2$CH), 42.2 (CH), 79.5 (OH), 124.7, 126.9 and 128.3 (CH, aromatic), 147.0 (C, aromatic); IR(KBr) 3200-3550 (br. OH stretching); MS (EI), m/z (rel. intensity) 234 (M$^+$, 1), 120 (80), 115 (21), 104 (20), 74 (100); HRMS (EI), m/z 234.1449 (C$_{14}$H$_{22}$OSi requires 234.1440).

RESULTS AND DISCUSSION

The photoreaction of γ-(trimethylsilyl)butyrophenone (1) produced the photoproducts resulting from the operation of H-atom abstraction (acetophenone 3 and vinyltrimethylsilane 4) and SET-desilylation (acetophenone 3 and ethylene) pathways (Scheme 3).

The fraction of the products formed in the photoreaction of 1 would be expected to determine the reaction mechanism. Irradiations of 1 were investigated in polar-protic solvent (CD$_3$OD), less polar-aprotic solvent (CD$_3$CN), and mixing solvent (including silophilic D$_2$O). The results of these photoreactions are summarized in Table 1.
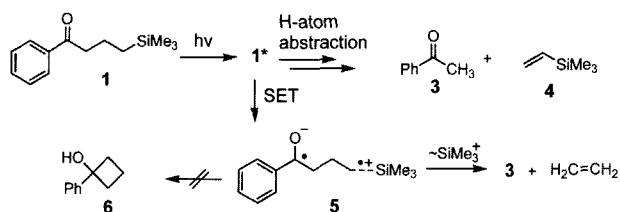
Scheme 3.

^{1}H-NMR analysis shows that photoreaction of 1 in CD$_3$OD gives acetophenone (3) and vinyltrimethylsilane (4) in a 1.8:1 ratio as compared to the 0.8:1 ratio of these products when 1 is irradiated in acetonitrile. Excited-state reactions of 1 in acetonitrile, like other N-alklyphthalimide family [7], follow well-known H-atom abstraction pathways. The photoreaction of 1 in methanol, this outcome invokes methanol-induced desilylation of a zwitterionic diradical 5 formed by SET interaction of the σ$_{c-si}$ and excited carbonyl moieties (Scheme 3). As the concentration of water increased in solvent system, the ratio of acetophenone 3 increased exclusively. This indicates that the solvent effect on photoreactions of 1 is associated with a change in reaction mechanism. Excited-state reactions of γ-(trimethylsilyl)butyrophenone (1) in

aqueous solvent system appear to occur predominantly by an SET-desilylation mechanism.

In previous investigation [8], the photoaddition reactions of cyclohexanones and silyl amines were observed to lead to formation of TMS and non-TMS adduct competitively. The non-TMS to TMS adduct ratio in this system could be controlled by the polarity of solvent and concentration of salts (LiClO$_4$, nBu$_4$NClO$_4$). The polarity and protic nature of solvents used for these photoreactions appear to control the TMS to non-TMS adduct ratios with the former being favored in low-polarity aprotic media (CH$_3$CN) and the latter in polar protic media (CH$_3$OH). Likewise, this ratio increases when the salts LiClO$_4$ and nBu$_4$NClO$_4$ are present in the photolysis solution.

It was reported that the decarboxylation rates of α-anilino carboxylate were moderately sensitive to solvent, nearly doubling in moving from less polar/aprotic CH$_3$CN to the more polar/protic CH$_3$OH [9]. Metal perchlorate salts appeared to influence the carboxylation rates. Addition of perchlorates of non-oxophilic metal cations such as Rb$^+$ and Cs$^+$ leads to an increase in the carboxylation rates, a likely result of a general salt effect. In contrast, the presence of highly oxophilic metal cations results in a modest (Li$^+$) to dramatic (Mg^{2+}, Ca^{2+}) decrease. Thus, tight-coordination of the carboxylate moiety to cations, brought about by the use of less polar/protic solvents or more oxophilic metal, slows decarboxylation.

Salts effect on the photoreaction of γ-(trimethylsilyl) butyrophenone (1) was evaluated. LiClO$_4$, Mg(ClO$_2$)$_2$ and nBu$_4$NF were used as a salt. The reaction condition and product ratio were summarized in Table 2. As the concentration of LiClO$_4$ and Mg(ClO$_2$)$_2$ increases, the portion of photoreaction of 1 appears to increase by SET-desilylation pathway. As the concentration of nBu$_4$NF increases, photoreaction of 1 appear to occur exclusively H-atom abstraction pathway. This results show that photoreactions by SET-desilylation pathways become more difficult to occur when cation size (Li$^+$ < Mg^{2+} < nBu$_4$N$^+$) increases and oxophilicity of the cation decreases.

By use of similar method, irradiations of δ-(trimethylsilyl) valerophenone (2) were investigated in various solvent system. Table 3 shows similar trend in irradiations of 2 to these of 1. The change to aqueous solvent system leads to only slight increase in the yields of acetophenone (3) by comparison with γ-(trimethylsilyl)butyrophenone (1) photolyses.

**Table 3.** Irradiations of δ-(trimethylsilyl)valerophenone (2)

Solvent	Reaction Time (min)	7	3	Solvent	Reaction Time (min)	7	3
CD$_3$CN	40	1	1.3	CD$_3$OD	30	1	1.2
5%D$_2$O-CD$_3$-CN	40	1	1.5	5%D$_2$O-CD$_3$OD	30	1	1.5
35%D$_2$O-CD$_3$-CN	40	1	1.7	35%D$_2$O-CD$_3$OD	30	1	1.7
50%D$_2$O-CD$_3$-CN	40	1	2.3	50%D$_2$O-CD$_3$OD	30	1	2.0
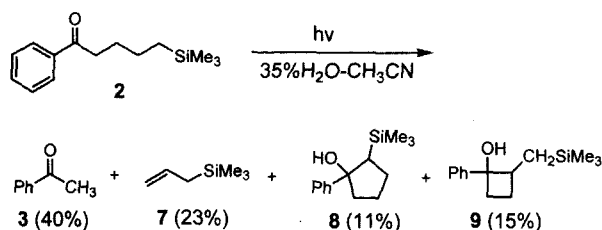
Scheme 4.

Preparative irradiation of **2** in 35%H₂O-CH₃CN leads to production of acetophenone **3**, allyltrimethylsilane **7**, cycolpentanol **8** and cyclobutanol **9** (Scheme 4). In photoreaction of **2** in 35%H₂O-CH₃CN, the major reaction pathway is γ-hydrogen atom abstraction leading to the formation of the 1,4-diradical **10**. Bond scission generates the enol **15** and allyltrimethylsilane **7**, then enol **15** tautomerizes to generate acetophenone **3**. Cyclobutanol **9** is formed by radical coupling reaction of 1,4-diradical **10**. 1,5-Diradical **11** formed by δ-hydrogen atom abstraction pathway leads to generate cycolpentanol **8**. Desilylation of a zwitterionic diradical **12** formed by SET of the excited **2** leads to diradical **13**, then acetophenone **3** is formed by bond cleavage. However, phenylcyclopentanol **14** is not formed by radical-radical coupling reaction of **13** (Scheme 5).
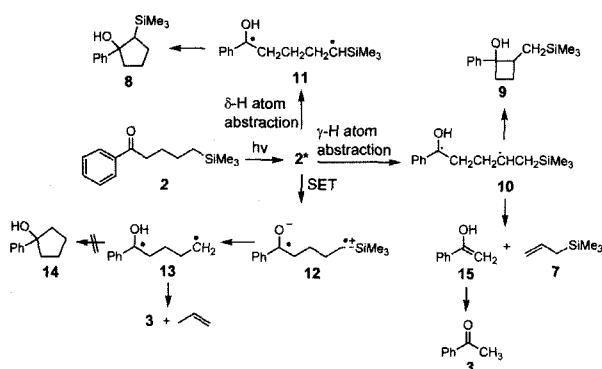
Scheme 5.

The photoreactions of **2** follow predominantly H-atom abstraction pathway rather than SET pathway due to increasing alkyl chain in contrast to those of **1**. Wagner reported that the rate of Norrish type in valerophenone was

Table 4. Effects of γ-substituents on Norrish typeII of PhCOCH₂ CH₂CHR₁R₂.

R_1	R_2	ϕ_{II}	$10^{-8}k_r, sec^{-1}$
H	H	0.36	0.08
CH₃	H	0.33	1.3

ca. 16 times faster than the case of butyrophenone (Table 4). [1] Therefore, the result that the photoreactions of **2** follow predominantly H-atom abstraction pathway is consistent with Wagner's report.

REFERENCES

1. Wagner, P. J. (1971) TypeII photoelimination and photocyclization of ketones. *Acc. Chem. Res.* **5**, 168-171.
2. Yang, N. C., Morduchowitz, A., Yang, D.-D. H. (1963) On the mechanism of photo-chemical formation of cyclobutanols. *J. Am. Chem. Soc.* **85(7)**, 1017-1018.
3. Kanaoka, Y., Yosida, K., Hatanaka, Y. (1979) Photoaddition of olefins to cyclic imides: Intermolecular oxetane formation and ring expansion. *J. Org. Chem.* **44(4)**, 664-666.
4. Lee, Y. J., Ling, R. Mariano, P. S., Yoon, U. C., Kim. D. U., Oh, S. W. (1996) Exploratory studies of H-atom abstraction and silyl-transfer photoreactions of silylalkyl ketones and (silylalkyl)-phthalimides. *J. Org. Chem.* **61(10)**, 3304-3314.
5. Cohen, S. G., Davis, G. A., Clark, W. D. K. (1972) Photoreduction of π,π* triplet by amines, 2-naphthaldehyde, and 2-acetophenone. *J. Am. Chem. Soc.* **94(3)**, 869-874.
6. Kuivila, H. G., Maxfield, P. L. (1967) Organometallic photochemistry of some acyclic ketosilanes. *J. Organomet. Chem.* **10(1)**, 41-51.
7. Yoon, U. C., Oh, S. W., Lee, S. M., Cho, S. J., Gamlin, J., Mariano. P. S. (1999) A solvent effect that influences the preparative utility of N-(silylalkyl)phthalimide and N-(silylalkyl)maleimide photochemistry. *J. Org. Chem.* **64(12)**, 4411-4418.
8. Hasegawa, E., Wu, W., Mariano, P. S., Yoon, U. C., Kim, J. U. (1988) Electron-transfer-induced photoadditions of the silyl amine Et₂NCH₂TMS to α,β-unsaturated cyclohexenones. Dual reaction pathways based on ion-pair-selective cation-radical chemistry. *J. Am. Chem. Soc.* **110**, 8099-8111.
9. Su, Z., Falvey, D. E., Yoon, U. C., Mariano, P. S. (1997) The dynamics of á-anilino carboxylate and related cation radical α-heterolytic fragmentations. *J. Am. Chem. Soc.* **119**, 5261-5262.