Addition of Organosilanes with Aromatic Carbonyl Compounds via Photoinduced Electron Transfer in the Presence of Magnesium Perchlorate

Shunichi Fukuzumi* and Toshihiko Okamoto

Department of Applied Chemistry, Faculty of Engineering
Osaka University, Suita, Osaka 565, Japan

Junzo Otera*

Department of Applied Chemistry
Okayama University of Science
Ridai-cho, Okayama 700, Japan

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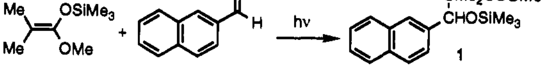
The addition of organosilane and organostannane reagents with various carbonyl compounds has been one of the most useful procedures for carbon–carbon bond formation.[1,2] The process requires the presence of strong Lewis acids such as $TiCl_4$ which activate the electrophilic function of carbonyl compounds toward nucleophilic attack by the organometallic reagent controlling the acyclic stereoselection.[1-4] On the other hand, photochemical carbon–carbon bond formation via photoinduced electron transfer from organometallic reagents to various electrophiles has recently attracted considerable interest from both synthetic and mechanistic viewpoints.[5-8] However, electrophiles employed for photoaddition by organometallic reagents have so far been limited to luminescent electron acceptors such as iminium cations and cyanoaromatics, the excited states of which should have more positive one-electron reduction potentials (E°_{red}) than the one-electron oxidation potentials (E°_{ox}) of organometallic reagents.[5-8] Thus, no photoaddition of weak electron donors such as organosilanes possessing higher E°_{ox} values than the corresponding stannanes with carbonyl compounds has so far been reported.[9] We report herein that efficient photoaddition of benzyl- and allyltrimethylsilane with aromatic carbonyl compounds is made possible by the presence of $Mg(ClO_4)_2$, which forms complexes with carbonyl compounds. Of special significance is a remarkable increase in the reactivity of the photoexcited states of the Mg^{2+}–carbonyl complexes, which become strongly fluorescent in contrast with the nonfluorescent excited states of uncomplexed carbonyl compounds in photoinduced electron transfer from organosilanes.

Aromatic carbonyl compounds with the lowest $n-\pi^*$ singlet states are generally nonfluorescent, possessing large $\pi-\pi^*$ triplet formation quantum yields (ca. 0.7) via fast intersystem crossing.[10] The E°_{red} values (vs SCE) of the triplet excited sates of 1-naphthaldehyde (1-NA) and 2-naphthaldehyde (2-NA) are determined as 0.83 and 0.90 V by adding the triplet excitation energies to the E°_{red} values of the ground states.[11] Thus, photoinduced electron transfer from β,β-dimethyl-substituted ketene silyl acetal ($Me_2C{=}C(OMe)OSiMe_3$) to the triplet excited states of aldehydes is energetically feasible, since it has a low E°_{ox} value (0.90 V)[12] compared with benzyltrimethylsilane ($PhCH_2SiMe_3$: 1.38 V)[12] and allyltrimethylsilane ($CH_2{=}CHCH_2SiMe_3$: 1.39 V).[12] In fact, irradiation of an acetonitrile solution containing 2-NA (5.0×10^{-2} M) and $Me_2C{=}C(OMe)OSiMe_3$ (1.0×10^{-1} M) with a mercury lamp through a Pyrex filter gives in 1.5 h the adduct (**1**) quantitatively, eq 1.[13]



(1)

The photochemical reaction may be initiated by photoinduced electron transfer from the ketene silyl acetal to the triplet excited state of 2-NA, followed by efficient radical coupling to give the adduct as reported in the photoaddition of ketene silyl acetal to 10-methylacridone.[14] In fact, the limiting quantum yield (Φ_∞ = 0.77), determined from the disappearance of the absorption band of 2-NA using a ferrioxalate actinometer according to the standard procedure,[15] agrees well with the quantum yield for the triplet formation of 2-NA.[10] When $Me_2C{=}C(OMe)OSiMe_3$ is replaced by $PhCH_2SiMe_3$ or $CH_2{=}CHCH_2SiMe_3$, no photochemical reaction with 1-NA or 2-NA has occurred under otherwise identical conditions, as expected from the higher E°_{ox} values of organosilanes than the E°_{red} values of the triplet excited states of the carbonyl compounds.

Addition of $Mg(ClO_4)_2$ to an MeCN solution of 1-NA or 2-NA results in a red shift of ca. 20 nm in the long-wavelength absorption band. The appearance of a new absorption band at ca. 360 nm is ascribed to the 1:1 complex formation between Mg^{2+} and the carbonyl compound. From linear Benesi–Hildebrand plots are obtained the small formation constants at 298 K (0.17 and 0.27 M^{-1} for 1-NA and 2-NA, respectively). Irradiation of the absorption band due to the Mg^{2+}–carbonyl complex in deaerated MeCN (0.70 cm^3) containing 2-NA (5.1×10^{-2} M), $PhCH_2SiMe_3$ (1.0×10^{-1} M), and $Mg(ClO_4)_2$ (2.0×10^{-1} M) with

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(13) The yield of **1** was 100%. ^1H NMR of **1** (CD_3CN): δ 0.06 (9H, s), 1.06 (3H, s), 1.15 (3H, s), 3.65 (3H, s), 5.06 (1H, s), 7.46–7.52 (3H, m), 7.78–7.88 (4H, m). Similar adducts were obtained in the photochemical reactions with 1-NA and 1- and 2-acetonaphthone.

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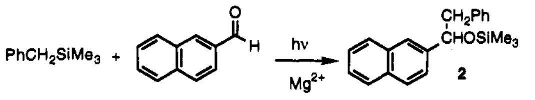
Table 1. Fluorescence Maxima (λ_{max}) and the Liftimes (τ) of Mg^{2+}–Carbonyl COmplexes, the One-Electron Reduction Potentials ($E°_{red}$) of the Singlet Excited States, Fluorescence Quenching Rate Constants (k_q), Rate Constants (k_{et}) of Electron Transfer from $RSiMe_3$ to the Singlet Excited States, Observed Rate Constants (k_{obs}), and Limiting Quantum Yields (Φ_∞) for Photoaddition of $RSiMe_3$ to the Carbonyl Compounds in the Presence of $Mg(ClO_4)_2$ (1.0 M) in MeCN at 298 K

aromatic CO compd	λ_{max}, nm	τ, ns	$E°_{res}$ vs SCE,[a] V	k_q,[b] $M^{-1}\,s^{-1}$	k_{et},[b,c] $M^{-1}\,s^{-1}$	k_{obs},[b,d] $M^{-1}\,s^{-1}$	Φ_∞[b,d]
2-naphthaldehyde	440	10.3	1.87	4.3×10^9 (2.3×10^9)	4.5×10^9 (2.2×10^9)	4.6×10^9 (2.3×10^9)	7.1×10^{-2} (1.2×10^{-1})
2-acetonaphthone	430	11.8	1.77	3.0×10^9	3.7×10^9	3.5×10^9	1.1×10^{-1}
1-naphthaldehyde	437	6.7	1.98	4.9×10^9	5.2×10^9	5.4×10^9	9.6×10^{-2}
1-acetonaphthone	432	3.3	1.90	3.7×10^9	4.7×10^9	3.9×10^9	1.0×10^{-1}

[a] Determined by adaptation of the Rehm–Weller free energy relationship for photoinduced electron transfer (see text). [b] Rate constants for $PhCH_2SiMe_3$. The values in parentheses denote those for $CH_2{=}CHCH_2SiMe_3$. [c] Calculated by using the Rehm–Weller free energy relationship for photoinduced electron transfer (see text). [d] Determined from the quantum yield data.

monochromatized light of 360 nm from a xenon lamp gives in 6.5 h the benzyl adduct (**2**: 70% yield) as shown in eq 2.[16] The

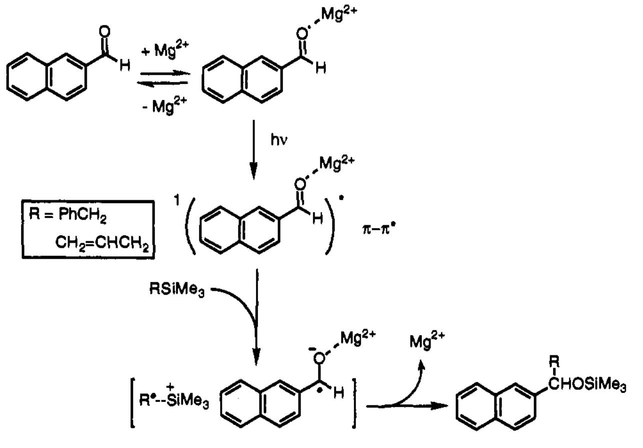


(2)

benzyl adducts are also obtained in the photochemical reactions with other carbonyl compounds [1-NA, 1-acetonaphthone (1-AN), 2-acetonaphthone (2-AN)] in the presence of Mg^{2+} in MeCN. When benzyltrimethylsilane is replaced by allyltrimethylsilane ($CH_2{=}CHCH_2SiMe_3$), the corresponding allyl adducts are also obtained.

Although the carbonyl compounds are nonfluorescent, irradiation of the new absorption band in the presence of $Mg(ClO_4)_2$ causes strong fluorescence at 430–440 nm (Table 1). The fluorescence lifetimes (τ) of the Mg^{2+}–carbonyl complexes in MeCN at 298 K were determined by single-photon counting as listed in Table 1. The change in excited-state properties upon complex formation with Mg^{2+} may be attributed to increased energy of the n–π^* singlet state relative to the fluorescent π–π^* singlet excited state as reported for similar change in the photophysical and photochemical properties of carbonyl compounds upon complex formation with Lewis acids.[17] The $E°_{red}$ values (vs SCE) of the singlet excited states of the Mg^{2+}–carbonyl complexes are determined as shown in Table 1 by adaptation of the Rehm–Weller free energy relationship[18] for photoinduced electron transfer from various aromatic electron donors to the singlet excited states of the Mg^{2+}–carbonyl complexes in the presence of Mg^{2+} (1.0 M) in MeCN at 298 K according to a method described elsewhere.[5d,12,19] The remarkable positive shifts (ca. 1.2 V) of the $E°_{red}$ values of the singlet excited states of the Mg^{2+}–carbonyl complexes compared with those of the triplet excited states of uncomplexed carbonyl compounds (Table 1) result in a significant increase in the reactivity of the Mg^{2+} complexes vs noncomplexed carbonyl compounds in photoinduced electron transfer reactions.[20] Since the $E°_{red}$ values of the singlet excited states of Mg^{2+}–carbonyl complexes become higher than the $E°_{ox}$ values of $RSiMe_3$ (R = $PhCH_2$, $CH_2{=}CHCH_2$), the photoinduced electron transfer from $RSiMe_3$ to the singlet excited states of Mg^{2+}–carbonyl complexes would occur efficiently. In fact, the fluorescence of Mg^{2+}–carbonyl complexes is quenched efficiently by $RSiMe_3$ in MeCN at 298 K. The quenching rate constants k_q determined from the slopes of the Stern–Volmer plots and the fluorescence lifetimes are listed in Table 1, where the k_q values agree well with the calculated rate constants (k_{et}) of photoinduced electron transfer from $RSiMe_3$ to the singlet excited states of Mg^{2+}–carbonyl complexes by using the Rehm–Weller free energy relationship.

Scheme 1



The quantum yields (Φ) of the photoaddition reactions in the presence of $Mg(ClO_4)_2$ (1.0 M) increase with an increase in $[RSiMe_3]$ to reach a constant value (Φ_∞). From the standard linear plots of Φ^{-1} vs $[RSiMe_3]^{-1}$ are obtained the values of Φ_∞ and the rate constants (k_{obs}), which are also listed in Table 1. The k_{obs} values agree well with both k_q and k_{et} values. Such agreements strongly indicate that the photoaddition reactions proceed via photoinduced electron transfer from $RSiMe_3$ to the singlet excited states of Mg^{2+}–carbonyl complexes, followed by the cleavage of the R–Si bond in the radical cation and the radical coupling with the carbonyl radical anion to yield the adduct as shown in Scheme 1.

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(16) ^1H NMR of **2** (CD_3CN): δ 0.14 (9H, s), 3.08–3.26 (2H, m), 5.70 (1H, m), 7.28–7.32 (5H, m), 7.51–8.26 (7H, m). No coupling product of the benzyl group (1,2-diphenylethane) has been detected. The yields of the adducts with 1-NA, 2-AN, and 1-AN after 7-, 7-, and 13-h irradiation with monochromatized light of λ = 350, 358, and 340 nm are 65, 72, and 32%, respectively.

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