

Addition of Ketene Silyl Acetals to 10-Methylacridone via Photoinduced Electron Transfer

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Photoaddition of β,β -dimethyl-substituted ketene silyl acetals to 10-methylacridone occurs efficiently under irradiation of the visible light in benzene as well as acetonitrile to yield the siloxy adduct. The carbon-oxygen bond of the adduct is readily cleaved by an acid to yield the corresponding 9-alkylated 10-methylacridinium ion. The comparison of the observed rate constants determined from the dependence of the quantum yields on the concentrations of ketene silyl acetals as well as the fluorescence quenching by ketene silyl acetals with those predicted for the electron transfer processes indicates that the photoaddition proceeds via the photoinduced electron transfer from β,β -dimethyl-substituted ketene silyl acetals to the singlet and triplet excited states. No photoaddition of nonsubstituted ketene silyl acetal to 10-methylacridone occurs, since the electron donor ability is too weak to transfer an electron to the excited states of 10-methylacridone as expected from the higher oxidation potential compared with the β,β -dimethyl-substituted analogues.

Introduction

The Mukaiyama version of Michael reaction of ketene silyl acetals is recognized as one of the most useful reactions in modern synthetic chemistry because of its capability of complementing an alternative alkali metal enolate method.¹ The substrates are activated by Lewis acids and thereby the Mukaiyama reaction is carried out under acidic conditions in contrast with the basic conditions when alkali metal enolates are employed. Although neutral conditions are preferred to acidic or basic conditions, no appropriate neutral activator has so far been available. On the other hand, we have recently disclosed that an electron transfer mechanism was likely to operate, especially when β,β -dimethyl-substituted ketene silyl acetals were employed.² We have also reported the one-electron oxidation properties of ketene silyl acetals, demonstrating the unique one-electron oxidation properties of β,β -dimethyl-substituted ketene silyl acetals as compared to nonsubstituted ketene silyl acetals.³ Such electron transfer oxidation of ketene silyl acetals and enol silyl ethers has been receiving increased attention recently because of its synthetic utility for the C-C bond formation.⁴ However, no C-C bond formation via photoinduced electron transfer reactions of ketene silyl acetals has so far been reported.

This study reports that the use of the excited state of 10-methylacridone is effective for the reactions with β,β -dimethyl-substituted ketene silyl acetals under neutral

conditions without acid or base catalysts under irradiation of the visible light. Recently Kawata et al. reported that the photodimerization of 10-methylacridone occurs in the presence of an organic electron donor, *N,N*-dimethylaniline.⁵ In our case selective C-C bond formation between the ketene silyl acetals and 10-methylacridone occurs to yield the 1,2-adduct exclusively. The photoinduced electron transfer mechanism of such novel photoaddition reaction of ketene silyl acetals under neutral conditions is revealed on the basis of the quantum yield determinations, the fluorescence quenching by ketene silyl acetals, and the comparison of the observed rate constants with those predicted for the photoinduced electron transfer processes from ketene silyl acetals to the excited states of 10-methylacridone.

Experimental Section

Materials. Ketene silyl acetal ($\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$) was obtained from Aldrich. The other ketene silyl acetals ($\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ and $\text{H}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$) used in this study were prepared according to the literature method.⁶ 10-Methylacridone (AcrCO) was obtained from Tokyo Kasei Organic Chemicals. Tetrabutylammonium perchlorate used as a supporting electrolyte for the cyclic voltammetry was also obtained commercially. Acetonitrile and benzene used as solvents were purified and dried by the standard procedure.⁷

Reaction Procedure. Typically, after an [$^2\text{H}_6$]benzene (C_6D_6) solution (0.8 cm³) containing AcrCO (1.0×10^{-2} M) in a square quartz cuvette (1 mm i.d.) was deaerated by bubbling with argon gas for 10 min, $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ (5.0×10^{-2} M) was added by means of a microsyringe and mixed. The solution was irradiated with a high pressure mercury lamp through acetophenone-methanol filter transmitting $\lambda > 300$ nm. After the reaction was complete in 3 h, the products were analyzed by ^1H NMR spectroscopy. Then, 10 μL of HClO_4 solution (70%) was added to the product solution and the benzene layer was decanted.

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The residue dried in vacuum was dissolved in $[\text{D}_3]\text{acetonitrile}$ (CD_3CN) and analyzed by ^1H NMR spectroscopy. The ^1H NMR measurements were performed using a Japan Electron Optics JNM-GSX-400 (400 MHz) NMR spectrometer at 300 K. ^1H NMR (C_6D_6): 1 δ 0.31 (s, 9H), 0.83 (s, 3H), 0.84 (s, 3H), 2.81 (s, 3H), 3.43 (s, 3H), 6.65 (t, 2H, $J = 6.8$ Hz), 7.1–7.2 (m, 4H), 8.16 (d, 1H, $J = 6.8$ Hz), 8.25 (d, 1H, $J = 6.8$ Hz); 2 δ 0.50 (q, 6H, $J = 7.8$ Hz), 0.83 (s, 3H), 0.84 (s, 3H), 0.95 (t, 9H, $J = 7.8$ Hz), 1.21 (t, 3H, $J = 7.1$ Hz), 2.82 (s, 3H), 4.05–4.15 (m, 3H), 6.64–6.67 (m, 2H), 7.1–7.2 (m, 4H), 8.19 (d, 1H, $J = 7.3$ Hz), 8.27 (d, 1H, $J = 7.3$ Hz). ^1H NMR (CD_3CN): $\text{AcrR}^+\text{ClO}_4^-$ (R = Me) δ 2.19 (s, 6H), 3.48 (s, 3H), 4.73 (s, 3H) 7.87 (t, 2H, $J = 7.8$ Hz), 8.27 (t, 2H, $J = 7.8$ Hz), 8.51 (d, 2H, $J = 7.8$ Hz), 8.57 (d, 2H, $J = 7.8$ Hz); $\text{AcrR}^+\text{ClO}_4^-$ (R = Et) δ 0.87 (t, 3H, $J = 7.3$ Hz), 2.19 (s, 6H), 3.97 (q, 2H, $J = 7.3$ Hz), 4.74 (s, 3H), 7.87 (t, 2H, $J = 7.8$ Hz), 8.28 (t, 2H, $J = 7.8$ Hz), 8.52 (d, 2H, $J = 7.8$ Hz), 8.60 (d, 2H, $J = 7.8$ Hz).

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)⁸ was used for the quantum yield determination of the photoreduction of AcrCO by ketene silyl acetals. A square quartz cuvette (10 mm i.d.) which contained a deaerated MeCN or benzene solution (3.0 cm^3) of AcrCO (5.7×10^{-4} M) and ketene silyl acetals (1×10^{-3} – 1.5×10^{-1} M) was irradiated with monochromatized light of $\lambda = 400$ nm from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, both the actinometer and AcrCO absorbed essentially all the incident light of $\lambda = 400$ nm. The light intensity of monochromatized light of $\lambda = 400$ nm was determined as 1.52×10^{-5} einstein $\text{dm}^{-3} \text{s}^{-1}$ with the slit width of 20 nm. The photochemical reaction was monitored using a Hewlett-Packard 8452A Diode-Array spectrophotometer. The quantum yields were determined from the decrease in absorbance due to AcrCO ($\lambda = 362$ nm, $\epsilon = 3.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

Fluorescence Quenching. Fluorescence quenching measurements were carried out on a Shimadzu RF-5000 spectrofluorophotometer. The excitation wavelength of AcrCO was 400 nm in MeCN. The monitoring wavelength was the corresponding to the maximum of the emission band at 414 nm. The solution was deoxygenated by argon purging for 10 min prior to the measurements. Relative emission intensities were measured for MeCN solution containing AcrCO (5.0×10^{-5} M) with a ketene silyl acetal at various concentrations (1.5×10^{-2} – 6.2×10^{-2} M). There was no change in the shape but there was a change in the intensity of the fluorescence spectrum by the addition of a ketene silyl acetal. The Stern–Volmer relationship (eq 1) was obtained for the ratio of the emission intensities in the absence and presence

$$I_0/I = 1 + K_{\text{SV}}[D] \quad (1)$$

of ketene silyl acetals (I_0/I) and the concentrations of ketene silyl acetals [D]. The fluorescence lifetime τ of AcrCO was determined as 8.7 ns in MeCN by single photon counting using a Horiba NAES-1100 time-resolved spectrofluorophotometer. The observed quenching rate constants k_q ($= K_{\text{SV}}\tau^{-1}$) were obtained from the Stern–Volmer constants K_{SV} and the emission lifetime τ .

Cyclic Voltammetry. The cyclic voltammetry measurements were performed on a Hokuto Denko Model HA-301 potentiostat-galvanostat in deaerated MeCN containing 5×10^{-2} M Bu_4NClO_4 as a supporting electrolyte at 298 K. The measured potentials were recorded with respect to the saturated calomel electrode (SCE). The platinum microelectrode was routinely cleaned by soaking it in concentrated nitric acid, followed by repeating rinsing with water and acetone and drying at 353 K prior to use in order to avoid possible fouling of the electrode surface. The cyclic voltammograms of AcrCO exhibit the reversible cathodic and anodic waves.

Theoretical Calculations. The theoretical studies were performed using the PM3 molecular orbital method.⁹ The calculations were performed by using the MOLGRAPH program Ver. 2.8 by Daikin Industries, Ltd. Final geometry and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The geometry of the radical

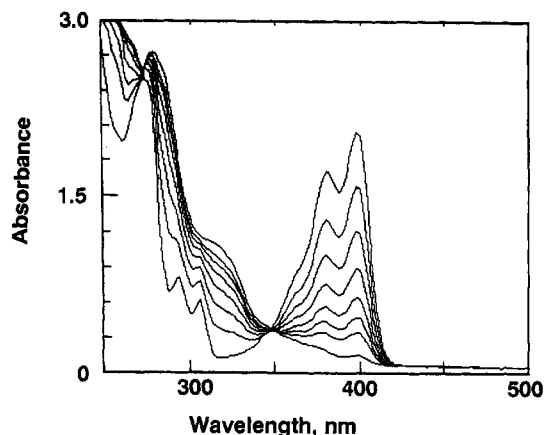


Figure 1. Electronic absorption spectra observed in photoreduction of AcrCO (1.9×10^{-4} M) by $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ in deaerated MeCN at 298 K (30-s interval).

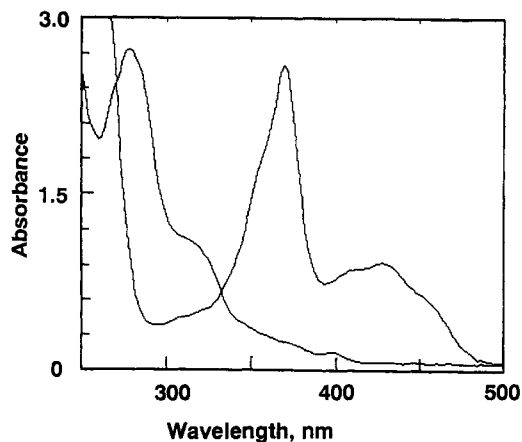


Figure 2. The spectrum change observed in the addition of HClO_4 to the resulting solution of Figure 1.

anion (AcrCO^-) was optimized using the unrestricted Hartree–Fock (UHF) formalism. The value of heat of formation (ΔH_f°) of AcrCO^- was calculated with the UHF-optimized structures using the half-electron (HE) method with the restricted Hartree–Fock (RHF) formalism.¹⁰

Results and Discussion

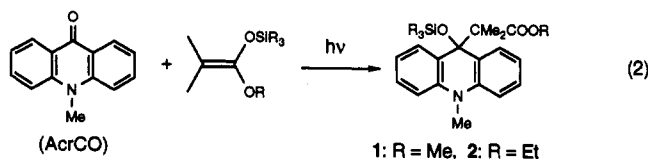
Photoaddition of Ketene Silyl Acetals. Irradiation of the absorption band of ($\lambda_{\text{max}} = 398, 380$ nm) of 10-methylacridone (AcrCO) in deaerated acetonitrile (MeCN) solution containing a β,β -dimethyl-substituted ketene silyl acetal, ($\text{Me}_2\text{C}=\text{C}(\text{OR})\text{OSiR}_3$; R = Me, Et) results in the increase in the absorbance at $\lambda_{\text{max}} = 278$ nm which is characteristic of a dihydroacridine derivative¹¹ with a clean isosbestic point at 348 nm as shown in Figure 1. When HClO_4 is added to the resulting solution, the spectrum is changed to that with $\lambda_{\text{max}} = 428$ and 370 nm, which is characteristic of a 10-methylacridinium ion derivative as shown in Figure 2. Essentially the same results were obtained when the photochemical reaction was performed in benzene instead of MeCN. The initial photoproduct is identified as 9-alkyl-9-(trimethylsiloxy)-10-methyl-9,10-dihydroacridine (1: R = Me, 2: R = Et) by the ^1H NMR spectrum (see Experimental Section), eq 2. The C(9)-O bond of 1 as well as 2 is desiloxynated by an acid to yield

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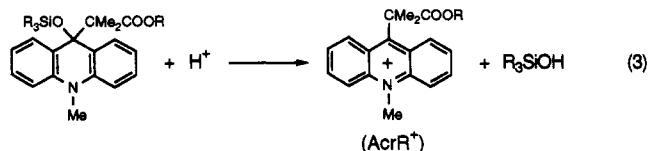
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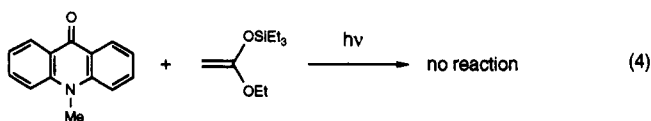
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9-alkyl-10-methylacridinium ion (AcrR⁺) as identified by the ¹H NMR spectrum (eq 3).



When the β,β -dimethyl-substituted ketene silyl acetal is replaced by a nonsubstituted ketene silyl acetal, $\text{H}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ which is generally more reactive nucleophile than the β,β -dimethyl-substituted ketene silyl acetal,² no photochemical reaction with AcrCO has occurred under irradiation of the visible light (eq 4). Such



a drastically diminished reactivity of the nonsubstituted ketene silyl acetal as compared to the β,β -dimethyl-substituted ketene silyl acetals is reminiscent of the significant difference in their reactivities for the electron transfer reactions.³ The one-electron oxidation potentials (E^0_{ox}) of $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ (0.90 V) and $\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ (0.87 V) are by ca. 0.4 V less positive than that of $\text{H}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ (1.30 V).³

Photoinduced Electron Transfer from Ketene Silyl Acetals to ¹AcrCO*. Irradiation of the absorption band of AcrCO results in fluorescence at 488 nm in MeCN. The fluorescence of ¹AcrCO* is quenched efficiently by $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ and $\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$. However, no quenching of ¹AcrCO* has occurred by $\text{H}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$. The quenching rate constants k_q are determined from the slopes of the Stern-Volmer plots and lifetime of the singlet excited state ¹AcrCO* ($\tau_s = 8.7$ ns). The k_q values thus determined are listed in Table I. The Gibbs energy change of photoinduced electron transfer from ketene silyl acetals to ¹AcrCO* (ΔG^0_{et}) is given by eq 5, where E^0_{ox} and E^0_{red} are the one-electron oxidation

$$\Delta G^0_{\text{et}} = F(E^0_{\text{ox}} - E^0_{\text{red}}) \quad (5)$$

potentials of ketene silyl acetals and the one-electron reduction potential of ¹AcrCO*, respectively. The E^0_{red} value is obtained as 1.13 V (vs SCE) by adding the excitation energy to the one-electron reduction potential of the ground state (-1.92 V), which has been determined by the cyclic voltammogram (see Experimental Section). The singlet excitation energy is determined as 3.05 eV from the absorption maximum (398 nm) and fluorescence maximum (414 nm). The ΔG^0_{et} values of $\text{Me}_2\text{C}=\text{C}(\text{OR})\text{OSiR}_3$ (R = Me, Et) thus evaluated by eq 5 are negative (-5.3 and -6.0 kcal mol⁻¹, respectively), while that of $\text{H}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ is positive (= 3.9 kcal mol⁻¹). The dependence of the activation Gibbs energy of photoinduced electron transfer ΔG^* on the Gibbs energy change of electron transfer (ΔG^0_{et}) has well been established as given

Table I. Fluorescence Quenching Rate Constants k_q of ¹AcrCO* by Ketene Silyl Acetals, Electron Transfer Rate Constant k_{et} from Ketene Silyl Acetals to ¹AcrCO*, Observed Singlet Quenching Rate Constants k_{obs} in the Photoreduction of AcrCO by Ketene Silyl Acetals, and the Limiting Quantum Yields Φ_{e} via the Singlet Quenching in MeCN at 298 K

ketene silyl acetal	$k_q, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{et}}, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{obs}}, \text{M}^{-1} \text{s}^{-1}$	Φ_{e}
$\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$	2.4×10^9	1.1×10^9	2.3×10^9	~0
$\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$	1.5×10^9	1.4×10^9	1.7×10^9	0.034
$\text{H}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$	$\ll 1 \times 10^7$	8.3×10^5	<i>b</i>	<i>b</i>

^a Evaluated by using eqs 6 and 7, see text. ^b No reaction.

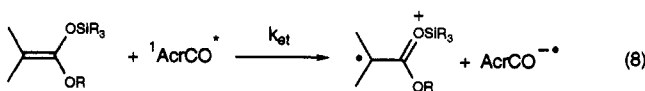
by the Rehm-Weller Gibbs energy relation (eq 6),¹² where ΔG^*_0 is the intrinsic barrier that represents the activation

$$\Delta G^* = (\Delta G^0_{\text{et}}/2) + [(\Delta G^0_{\text{et}}/2)^2 + (\Delta G^*_0)^2]^{1/2} \quad (6)$$

Gibbs energy when the driving force of electron transfer is zero, i.e., $\Delta G^* = \Delta G^*_0$ at $\Delta G^0_{\text{et}} = 0$. The ΔG^*_0 values of ketene silyl acetals have previously been reported as a constant, 4.6 kcal mol⁻¹.³ On the other hand ΔG^* values are related to the rate constant of electron transfer (k_{et}) as given by eq 7, where Z is the collision frequency that

$$\Delta G^* = 2.3RT \log [Z(k_{\text{et}}^{-1} - k_{\text{diff}}^{-1})] \quad (7)$$

is taken as $1 \times 10^{11} \text{M}^{-1} \text{s}^{-1}$, and k_{diff} is the diffusion rate constant in MeCN ($2.0 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$).¹² Then, the k_{et} values can be calculated from the ΔG^0_{et} and ΔG^*_0 values by using eqs 6 and 7. The k_{et} values thus obtained are also listed in Table I, where the k_{et} values agree well with the observed k_q values. The k_{et} value of $\text{H}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ ($8.0 \times 10^5 \text{M}^{-1} \text{s}^{-1}$) is too small to quench the singlet excited state with a short lifetime (8.7 ns), since the quenching efficiency in the presence of 1 M of $\text{H}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ is expected to be only 0.7%. Thus, the fluorescence quenching of ¹AcrCO* by β,β -dimethyl-substituted ketene silyl acetals may occur via photoinduced electron transfer from ketene silyl acetals to ¹AcrCO* (eq 8).



The intersystem crossing (ISC) from the singlet excited state of AcrCO to the triplet excited state is known to be rapid particularly in a nonpolar solvent such as benzene.¹³ The triplet excitation energy is determined as 2.70 eV from the phosphorescence maximum (475 nm).¹⁴ The ΔG^0_{et} values of the triplet excited state are also evaluated by using eq 5, and the corresponding k_{et} values calculated by using eqs 6 and 7 are listed in Table II. Since the triplet lifetime (29 μs in MeCN)⁵ is much longer than the singlet lifetime (8.7 ns), the quenching efficiency of the triplet state by electron transfer with 0.1 M $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ is as large as 99.6%. Thus, photoinduced electron transfer from β,β -dimethyl-substituted ketene silyl acetals to the triplet excited state ³AcrCO* is expected to be more efficient than that to the singlet excited state ¹AcrCO* at low concentrations of the ketene silyl acetals.

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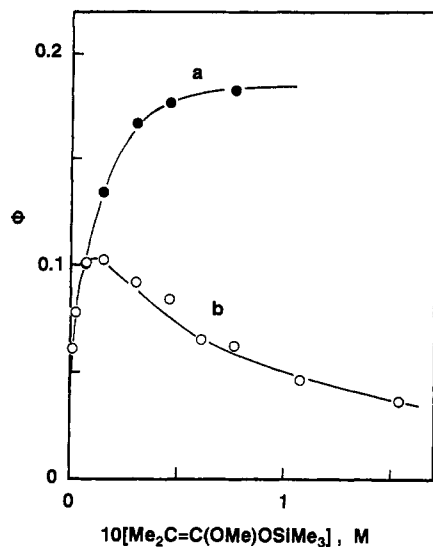


Figure 3. Dependence of the quantum yields (Φ) on $[\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3]$ for the photoreduction of AcrCO (5.7×10^{-4} M) by $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ in (a) deaerated benzene (\bullet) and (b) MeCN (\circ) at 298 K.

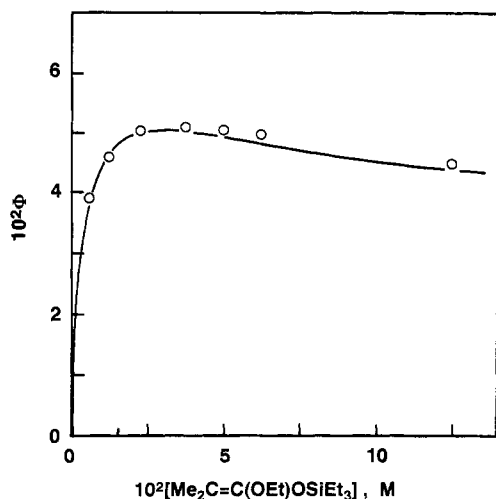
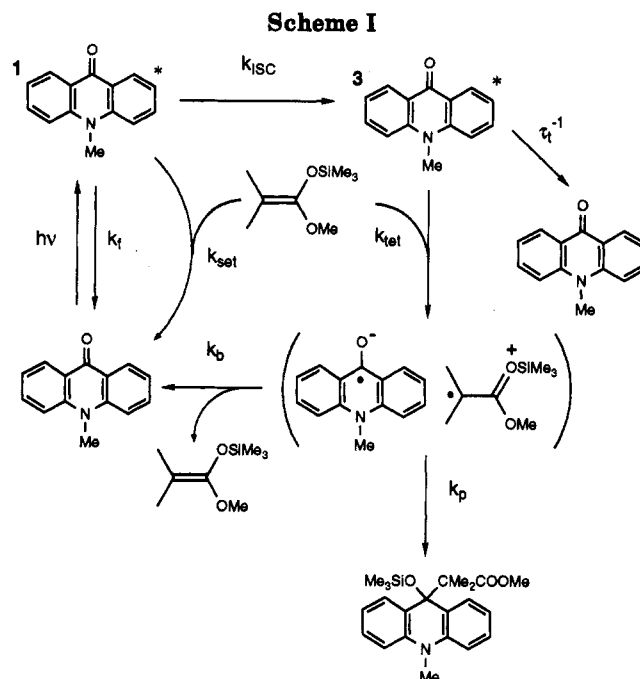


Figure 4. Dependence of the quantum yields (Φ) on $[\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3]$ for the photoreduction of AcrCO (5.7×10^{-4} M) by $\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ in deaerated MeCN at 298 K.

Photoinduced Electron Transfer Mechanism. The quantum yields (Φ) were determined from the decrease in absorbance due to AcrCO ($\lambda = 362$ nm, $\epsilon = 3.5 \times 10^3$ M $^{-1}$ cm $^{-1}$) by using a ferrioxalate actinometer (see Experimental Section). The Φ value for the photoaddition reaction of $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ with AcrCO in benzene increases with an increase in the concentration $[\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3]$ to reach a limited value (Φ_∞) as shown in Figure 3a. When the photochemical reaction is carried out in MeCN, however, the Φ value decreases at the high concentration region (Figure 3b), where the fluorescence quenching by electron transfer from $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ to $^1\text{AcrCO}^*$ (eq 8) becomes dominant. The absence of a retarding effect of $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ in the high concentration region in benzene (Figure 4) may be ascribed to the short lifetime of $^1\text{AcrCO}^*$ (1.2 ns)¹⁵ as compared to that in MeCN (8.7 ns). The dependence of quantum yields on the concentrations of ketene silyl acetals may well be explained by the reaction mechanism shown



representatively for the $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ -AcrCO system in Scheme I (*vide infra*). The singlet excited state is efficiently converted to the triplet excited state by the intersystem crossing (k_{ISC}) in competition with the fluorescence decay to the ground state (k_f) and the quenching by electron transfer from $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ to $^1\text{AcrCO}^*$ (k_{set}). The triplet state $^3\text{AcrCO}^*$ is efficiently quenched by electron transfer from $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ (k_{tet}) to give the radical ion pair in competition with the back electron transfer to the ground state (k_b). It has previously been disclosed that the spin density of the radical cation is nearly localized on the terminal carbon atom,³ which is coupled with the radical anion to yield the 1,2-adduct (Scheme I). The quenching of the singlet excited state $^1\text{AcrCO}^*$ by electron transfer from $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ in MeCN (k_{set} , eq 8) may mostly result in the back electron transfer to the ground state judging from the strong retarding effect of $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ at the high concentration region (Figure 3b).

By applying the steady-state approximation to the reactive species, $^1\text{AcrCO}^*$, $^3\text{AcrCO}^*$, and the radical ion pair in Scheme I, the dependence of Φ on the concentration of the electron donor, $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$, $[\text{D}]$ can be derived as given by eq 9. When the singlet quenching

$$\Phi = \left\{ \frac{k_p}{k_p + k_b} \right\} \left\{ \frac{k_{\text{ISC}}}{k_f + k_{\text{ISC}} + k_{\text{set}}[\text{D}]} \right\} \left\{ \frac{k_{\text{tet}}\tau_t[\text{D}]}{1 + k_{\text{tet}}\tau_t[\text{D}]} \right\} \quad (9)$$

process can be neglected, i.e., $k_{\text{set}}[\text{D}] \ll k_f + k_{\text{ISC}}$ as is the case of the reaction in benzene, eq 9 is reduced to eq 10,

$$\Phi = \Phi_\infty k_{\text{tet}}\tau_t[\text{D}] / (1 + k_{\text{tet}}\tau_t[\text{D}]) \quad (10)$$

where $\Phi_\infty = [k_{\text{ISC}} / (k_f + k_{\text{ISC}})] [(k_p / (k_p + k_b))]$. Equation 10 is rewritten by eq 11 which predicts a linear correlation

$$\Phi^{-1} = \Phi_\infty^{-1} [1 + (k_{\text{tet}}\tau_t[\text{D}])^{-1}] \quad (11)$$

between Φ^{-1} and $[\text{D}]^{-1}$. The validity of eq 11 is confirmed by the plot of Φ^{-1} vs $[\text{D}]^{-1}$ for the photoaddition of $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ to AcrCO in benzene as shown in Figure 5. From the slope and the intercept are obtained

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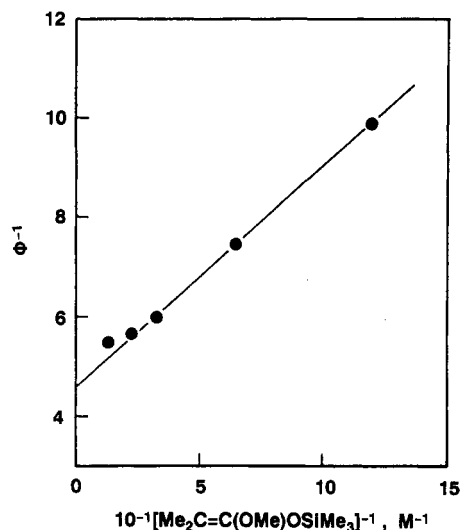


Figure 5. Plot of Φ^{-1} vs $[\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3]^{-1}$ for the photoreduction of AcrCO (5.7×10^{-4} M) by $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ in deaerated benzene at 298 K.

Table II. Observed Triplet Quenching Rate Constants k_{tet} in the Photoreduction of AcrCO by Ketene Silyl Acetals, Electron Transfer Rate Constant k_{et} from Ketene Silyl Acetals to $^3\text{AcrCO}^*$, and the Limiting Quantum Yields Φ_∞ via the Triplet Quenching at 298 K

ketene silyl acetal	solvent	k_{tet}^a $\text{M}^{-1} \text{s}^{-1}$	k_{et}^b $\text{M}^{-1} \text{s}^{-1}$	Φ_∞
$\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$	MeCN	1.6×10^7	2.9×10^6	0.15
$\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$	MeCN	8.9×10^6	6.0×10^6	0.065
$\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$	C_6H_6	7.3×10^6		0.22
$\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$	C_6H_6	8.9×10^6		0.073

^a The k_{tet} values are derived from the quantum yield data according to eq 11. ^b Evaluated by using eqs 6 and 7, see text.

the Φ_∞ and k_{tet} values in benzene ($\tau_t = 14 \mu\text{s}$),⁵ which are listed in Table II. Under the conditions that the triplet quenching efficiency reaches close to 100%, i.e., $k_{\text{tet}}\tau_t[\text{D}] \gg 1$, eq 9 is reduced to eq 12, where $\tau_s^{-1} = k_{\text{ISC}} + k_f$. Equation 12 is rewritten by eq 13 which predicts a linear

$$\Phi = \Phi_\infty / (1 + k_{\text{set}}\tau_s[\text{D}]) \quad (12)$$

$$\Phi^{-1} = \Phi_\infty^{-1}(1 + k_{\text{set}}\tau_s[\text{D}]) \quad (13)$$

correlation between Φ^{-1} and $[\text{D}]$. The validity of eq 13 is confirmed as shown in Figure 6, where the Φ^{-1} values in MeCN at high $[\text{D}]$ region in Figure 3b are plotted against $[\text{D}]$. From the slope and intercept in Figure 6 is obtained the k_{set} value as $2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table I). The k_{set} value agrees well with the quenching rate constant ($k_q = 2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) in Table I, demonstrating the validity of Scheme I.

By using the k_{set} value thus obtained together with the known τ_t value in MeCN ($29 \mu\text{s}$),⁵ the simulation of the dependence of Φ on $[\text{D}]$ in MeCN was performed based on eq 9 with the k_{tet} and Φ_∞ values being variable parameters. The best fit was achieved when the k_{tet} and Φ_∞ values are $1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and 0.15, respectively (Table II). The simulated curve (solid line in Figure 3b) agrees well with the experimental results. The comparison of the k_{tet} value with the calculated k_{et} value ($2.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) for electron transfer from to $^3\text{AcrCO}^*$ in Table II also supports the electron transfer mechanism in Scheme I, although the k_{tet} value is somewhat larger than the calculated k_{et} value probably because of the error in estimation of the triplet excitation energy as well as the

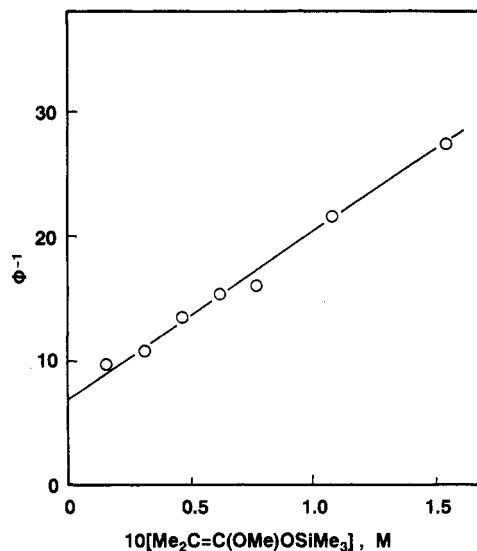
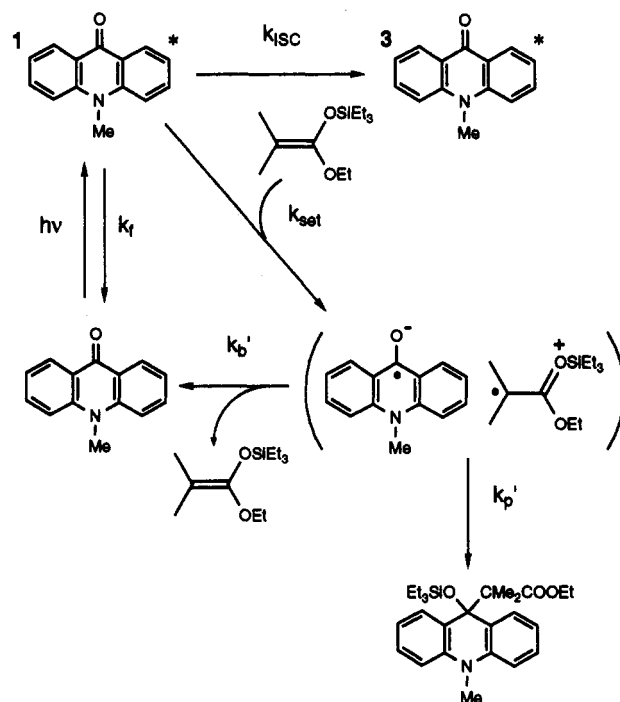


Figure 6. Plot of Φ^{-1} vs $[\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3]$ for the photoreduction of AcrCO (5.7×10^{-4} M) by $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ in deaerated MeCN at 298 K.

Scheme II



possible difference in the $\Delta G^{\ddagger*}$ value of the triplet state as compared to that of the singlet state.³ Since no significant interaction is required for the electron transfer process as compared to an alternative nucleophilic process, the electron transfer process should be preferred when it is energetically feasible (*vide supra*).

In the case of $\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$, the retarding effect at the high concentration in Figure 4 is less apparent than that observed for the photoaddition reaction of $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ in MeCN (Figure 3b). In such a case, the electron transfer to the singlet excited state $^1\text{AcrCO}^*$ may also result in the formation of adduct in competition with the back electron transfer to the ground state as shown in Scheme II. By combining Schemes I and II, the dependence of Φ on the concentration of the electron donor, $\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$, $[\text{D}]$ can be derived as given by eq 14, where $\Phi_\infty' = k_p' / (k_p' + k_b')$. As is the case of

$$\Phi = \left\{ \frac{\Phi_{\infty}}{1 + k_{\text{set}}\tau_s[\text{D}]} \right\} \left\{ \frac{k_{\text{tet}}\tau_t[\text{D}]}{1 + k_{\text{tet}}\tau_t[\text{D}]} \right\} + \frac{\Phi_{\infty}' k_{\text{set}}\tau_s[\text{D}]}{1 + k_{\text{set}}\tau_s[\text{D}]} \quad (14)$$

$\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ (*vide supra*), the simulation of the dependence of Φ on $[\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3]$ in MeCN (Figure 4) was performed based on eq 14 with the k_{set} , k_{tet} , Φ_{∞} , and Φ_{∞}' values being variable parameters. The best fit values are also listed in Tables I and II. The k_{set} value of $\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ ($1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) agrees well with the quenching rate constant ($1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) which is also in agreement with the calculated rate constant of electron transfer (Table I), demonstrating the validity of Scheme II. The comparison of the Φ_{∞}' values of $\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ (0.034) and $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ (ca. 0) in Table I indicates that the competition between the bond-forming step (k_p') and the back electron transfer step (k_b') derived from the singlet excited state $^1\text{AcrCO}^*$ is highly sensitive to the substitution of the alkoxy and siloxy groups. On the other hand, no drastic difference is observed for the Φ_{∞} values ($= [k_{\text{ISC}}/(k_f + k_{\text{ISC}})] [(k_p/(k_p + k_b))]$) derived from the triplet excited state $^3\text{AcrCO}^*$, although the Φ_{∞} value of $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ (0.15) is somewhat larger than that of $\text{Me}_2\text{C}=\text{C}(\text{OEt})\text{OSiEt}_3$ (0.065) as shown in Table II. Thus, the competition between the bond-forming step and the back electron transfer step is also dependent on the spin multiplicity of the excited state of AcrCO, although the origin of such difference in the Φ_{∞}' value is not clear at present.

Generation of Radical Ion Pair in Benzene. It should be noted that the k_{tet} values in benzene are as large as those in MeCN (Table II). The photoinduced electron transfer reactions are usually performed in polar solvents such as MeCN, in which the Coulombic barrier to separation is greatly reduced compared to less polar solvents. Although many product-forming reactions have been reported in nonpolar solvents,^{16,17} these reactions have usually been believed to proceed via exciplexes and not separated ion pairs. Unfortunately, however, no exciplex formation has been detected in the present case as is often the case for the reactions which have been claimed to proceed via exciplex formation.¹⁶ Thus, in order to evaluate the contribution of electron transfer step (or formation of emissionless exciplex which may correspond to the radical ion pair) the energetics of electron transfer from ketene silyl acetals to the triplet excited state $^3\text{AcrCO}^*$ in benzene is estimated by taking account of the difference in the solvation and the Coulombic interaction of the radical ion pair (*vide infra*).

The solvation energy (ΔG_s) for $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ attendant upon the electron transfer oxidation is given by the difference between the adiabatic ionization potential in the gas phase (I_a) and the electron transfer oxidation in solution (E_{ox}^0) as shown in eq 15,^{18,19} where C is a

$$\Delta G_s/F = E_{\text{ox}}^0 - I_a + C \quad (15)$$

constant (4.40 V vs SCE)²⁰ that includes the potential of the reference electrode on the absolute scale together with the liquid junction potential. The ΔG_s value of the radical cation of $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ in MeCN obtained in this manner is $-47 \text{ kcal mol}^{-1}$, as reported previously.³ Then, the ΔG_s value in benzene can be estimated by taking into account the solvent-induced change in ΔG_s , which is derived from the modified Born equation,²¹ as given by eq 16,²² where ϵ and ϵ_0 are the dielectric constants of benzene

$$\Delta G_s \text{ (in benzene)} = [(1 - \epsilon^{-1})/(1 - \epsilon_0^{-1})] \Delta G_s \text{ (in MeCN)} \quad (16)$$

(2.28) and MeCN (37.5), respectively.²³ The estimated ΔG_s value in benzene is $-27 \text{ kcal mol}^{-1}$, which significantly reduced as compared to the value in MeCN ($-47 \text{ kcal mol}^{-1}$). Such a difference in the ΔG_s values in benzene and MeCN results in a significant positive shift (0.86 V) in the E_{ox}^0 value (1.76 V) in benzene as compared to the value in MeCN (0.90 V).³ On the other hand, the ΔG_s value attendant upon the electron transfer reduction of AcrCO is given by eq 17, where E_A is the electron affinity

$$\Delta G_s/F = E_A - E_{\text{red}}^0 - C \quad (17)$$

of AcrCO in the gas phase. The E_A value is estimated as 0.92 eV from the difference in the heat of formation (ΔH_f°) between the neutral form and the radical anion with the optimized structure using the PM3 method (see Experimental Section).^{9,10} In the same manner as employed to estimate the E_{ox}^0 value in benzene, the E_{red}^0 value of AcrCO in benzene can be evaluated as -2.57 V , which is by 0.66 V more negative than the value in MeCN (-1.91 V). Thus, the ΔG_{et}^0 value for the photoinduced electron transfer from $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ to $^3\text{AcrCO}^*$ in benzene is 1.52 eV larger than that in MeCN provided that the Coulombic interaction of the radical ion pair in Scheme I is neglected. The Coulombic interaction energy which corresponds to the work term w_p required to bring the radical cation and anion to the mean separation r of the radical ion pair in a solvent with dielectric constant ϵ is given by eq 18.²² The

$$w_p = -e^2/4\pi\epsilon r \quad (18)$$

w_p value may well be neglected in MeCN having a large dielectric constant (37.5). In a nonpolar solvent such as benzene the w_p value can no more be neglected. The difference of 1.52 eV in the ΔG_{et}^0 values between benzene and MeCN may well be canceled by the large Coulombic interaction in benzene, since the w_p value with the mean separation of 4.15 Å is equal to 1.52 eV. In fact such a distance is typical for the mean separation of the charge transfer complexes.²⁴ Thus, the photoinduced electron transfer from $\text{Me}_2\text{C}=\text{C}(\text{OMe})\text{OSiMe}_3$ to $^3\text{AcrCO}^*$ in benzene is expected to be as efficient as that in MeCN.

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