Comparison between Electron Transfer and Nucleophilic Reactivities of Ketene Silyl Acetals with Cationic Electrophiles

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The products and kinetics for the reactions of ketone silyl acetals with a series of *p*-methoxy-substituted trityl cations have been examined, and they are compared with those of outer−sphere electron transfer reactions from 10,10′-dimethyl-9,9′, 10, 10′- tetrahydro-9,9′-biacridine [$(AcrH)_2$] to the same series of trityl cations as well as other electron acceptors. The C-C bond formation in the reaction of β,β-dimethyl-substituted ketene silyl acetal (**1:** $(Me_2C{=}C(OMe)OSiMe_3)$ with trityl cation salt ($Ph_3C^+ClO_4^-$) takes place between **1** and the carbon of para-positon of phenyl group of Ph_3C^+, whereas a much less sterically hindered ketene silyl acetal (**3**: $H_2C{=}C(OEt)OSiEt_3$) reacts with Ph_3C^+ at the central carbon of Ph_3C^+. The kinetic comparison indicates that the nucleophilic reactivities of ketene silyl acetals are well correlated with the electron transfer reactivities provided that the steric demand at the reaction center for the C−C bond formation remains constant.

Carbon−carbon bond formation reactions of organosilanes have found considerable interest in organic synthesis.[1−4] The nucleophilic reactivities of organosilanes in polar reactions have been evaluated extensively based on the rate constants for the reactions with carbocations.[5−7] On the other hand, the electron-transfer reactivities of organosilanes have been determined based on the rate constants for the electron-transfer reactions with one-electron oxidants.[8−10] The importance of electron-transfer processes has now been well recognized in many areas of chemistry.[11−13] It has previously been shown that nucleophilic reactivities are largely correlated with the one-electron oxidation potentials of nucleophiles, which are one of the most important factors to determine the electron-transfer reactivities.[14] However, the nucleophilic reactivity is often affected by the steric demand at the reaction center.[8] In the case of ketene silyl acetals, β-methyl-substitution increases the electron-transfer reactivity whereas an increase in the steric demand would affect the nucleophilic reactivity.[8] Thus, an exact comparison between the nucleophilic and electron-transfer reactivities of ketene silyl acetals should be made by using the same series of electrophiles or electron acceptors in order to keep the steric demand at the reaction center constant.

This study reports products and kinetics for the reactions of β,β-dimethyl-substituted ketene silyl acetal and a much less sterically hindered ketene silyl acetal with a series of *p*-methoxy-substituted trityl cations [$(MeOC_6H_4)_x(C_6H_5)_{(3-x)}C^+$] ($x$ = 0−3), and these data are directly compared with those of outer-sphere electron-transfer reactions from 10,10′-dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridine [$(AcrH)_2$][15] to the same series of trityl cations as well as other electron acceptors. The present study provides valuable insight into the electron transfer vs nucleophilic reactivities of ketene silyl acetals.

Results and Discussion

The reactions of β,β-dimethyl-substituted ketene silyl acetal (**1**) with less sterically hindered benzhydryl cation

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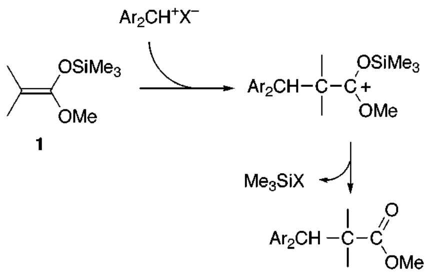
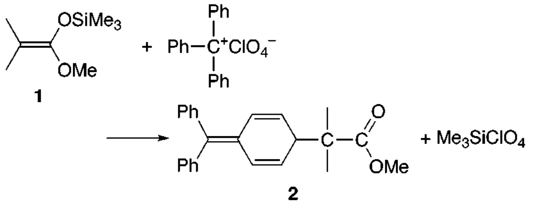
Scheme 1

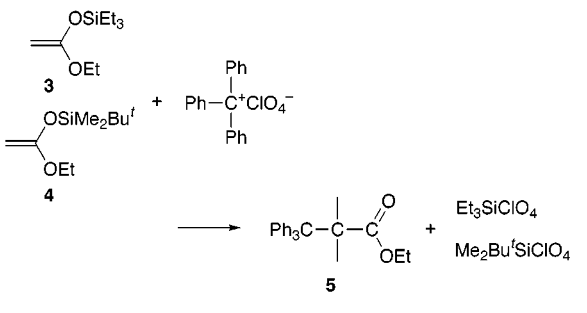


salts $Ar_2CH^+X^-$ (X = BF_4 or OTf) as compared to trityl cation are known to produce the corresponding esters in which the central carbon of benzhydryl cation is connected to **1** via nucleophilic addition of **1** to benzhydryl cation followed by the facile desilylation of the intermediate siloxy-substituted carbenium ion as shown in Scheme 1.[5,6] In contrast, we have found that C−C bond formation in the reaction of **1** with trityl cation salt ($Ph_3C^+ClO_4^-$) takes place between **1** and the carbon of *para*-position of phenyl group of Ph_3C^+ (see Experimental Section) rather than the central carbon to yield a different type of ester **2** (eq 1).



(1)

When **1** is replaced by a much less sterically hindered ketene silyl acetal (**3**: $H_2C{=}C(OEt)OSiEt_3$), C−C bond formation occurs at the central carbon of Ph_3C^+ (eq 2).[8] Thus, the steric demand at the reaction center for the C−C bond formation results in a change in the type of products. To examine the contribution of an electron-transfer pathway in the reactions of ketene silyl acetals with trityl cations, the rates were determined by using a stopped-flow technique, and the observed rate constants are compared with those of outer-sphere electron-transfer reactions from $(AcrH)_2$ to the same series of trityl cations as well as other electron acceptors.



(2)

The reactions of $(AcrH)_2$ with various electron acceptors including trityl cations are known to occur via an outer-sphere electron transfer from $(AcrH)_2$ to the acceptors, followed by the facile C−C bond cleavage to produce $AcrH^•$ which can rapidly transfer an electron to the acceptors to yield two equivalents of $AcrH^+$ and trityl radical (eq 3).[15]

Trityl radical produced was detected by the ESR spectrum. The electron-transfer rates were determined from the appearance of absorbance due to $AcrH^+$ (λ_{max} = 358 nm, ϵ_{max} = 18000 M^{-1} cm^{-1}) as reported previously.[15] The rates obey second-order kinetics, showing first-order dependence on each reactant concentration. The observed second-order rate constants (k_{obs}) of electron transfer from $(AcrH)_2$ to a variety of one-electron oxidants are listed in Table 1. The free energy change of electron transfer (ΔG^0_{et} in eV) was determined from the one-electron oxidation potential of $(AcrH)_2$ (E^0_{ox} = 0.62 V vs SCE)[15] and the one-electron reduction potentials (E^0_{red} vs SCE) of a series of trityl cations. The E^0_{red} values of a series of trityl cations are determined by the fast scanning cyclic voltammograms which show reversible redox waves as shown in Figure 1.

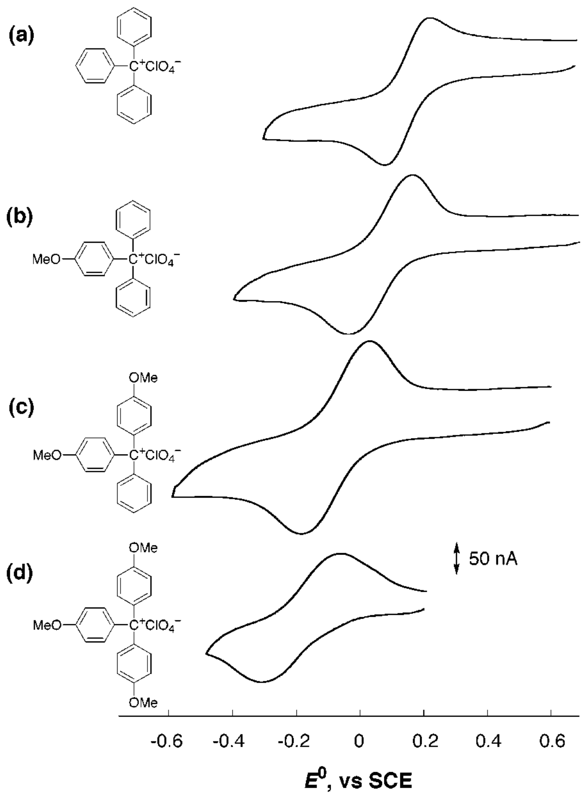
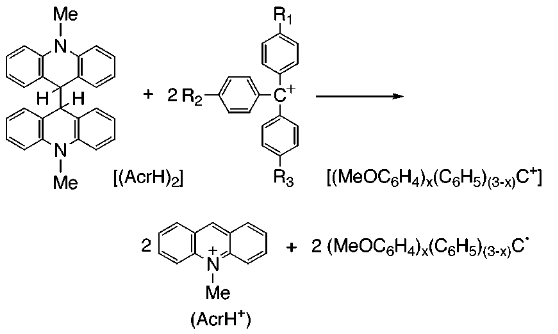


Figure 1. Cyclic voltammograms of (a) $Ph_3C^+ClO_4^-$, (b) $(MeOC_6H_4)Ph_2C^+ClO_4^-$, (c) $(MeOC_6H_4)_2PhC^+ClO_4^-$, (d) $(MeOC_6H_4)_3C^+ClO_4^-$ (2.0×10^{-2} M) in deaerated MeCN containing $Bu_4NClO_4^-$ (0.10 M) with a gold microelectrode at 298 K; sweep rate 100 V s^{-1}.



(3)

The observed rate constants (log k_{obs}) are plotted against ΔG^0_{et} as shown in Figure 2a, which exhibits typical dependence of log k_{obs} vs ΔG^0_{et} for an endergonic outer-sphere electron transfer, i.e., log k_{obs} increases linearly with increasing ΔG^0_{et} with a slope of $-1/2.3kT$ (= −16.9 at 298 K, k is the Boltzmann constant).

Table 1. One-Electron Reduction Potentials of Various Oxidants, Free Energy Changes of Electron Transfer (ΔG^0_{et}), and Rate Constants (k_{obs}) in the Reaction of Trityl Cation Derivatives with $(AcrH)_2$ in Deaerated MeCN at 298 K

no.	oxidant	E^0_{red} vs SCE, V	reductant	ΔG^0_{et}, eV	k_{obs}, $M^{-1}\,s^{-1}$
1a	$[Fe(C_5H_5)_2]^+$	0.37[a]	$(AcrH)_2$	0.25	2.3×10^5 [a]
2a	$[Fe(C_5H_5)(HgClC_5H_4)]^+$	0.36[a]	$(AcrH)_2$	0.26	2.8×10^5 [a]
3a	$[(TPP)Co]^+$	0.35[a]	$(AcrH)_2$	0.27	1.8×10^5 [a]
4a	$[Fe(C_5H_5)(\textit{tert}\text{-amyl}C_5H_4)]^+$	0.32[a]	$(AcrH)_2$	0.30	1.1×10^5 [a]
5a	$[Fe(C_5H_5)(BuC_5H_4)]^+$	0.31[a]	$(AcrH)_2$	0.31	8.1×10^4 [a]
6a	2,3-dicyano-*p*-benzoquinone	0.28[a]	$(AcrH)_2$	0.34	1.1×10^4 [a]
7a	$[Fe(MeC_5H_4)_2]^+$	0.26[a]	$(AcrH)_2$	0.36	2.1×10^4 [a]
8a	$[Fe(BuC_5H_4)_2]^+$	0.25[a]	$(AcrH)_2$	0.37	2.0×10^4 [a]
9a	TCNE	0.22[a]	$(AcrH)_2$	0.40	3.8×10^3 [a]
10a	Ph_3C^+	0.21[a]	$(AcrH)_2$	0.41	4.2×10^3
11a	TCNQ	0.19[a]	$(AcrH)_2$	0.43	3.8×10^3 [a]
12a	$(p\text{-}MeOC_6H_4)Ph_2C^+$	0.05	$(AcrH)_2$	0.57	1.9
13a	*p*-chloranil	0.01[a]	$(AcrH)_2$	0.61	2.4[a]
14a	*p*-bromanil	0.00[a]	$(AcrH)_2$	0.62	2.3[a]
15a	$(p\text{-}MeOC_6H_4)_2PhC^+$	−0.07	$(AcrH)_2$	0.69	9.0×10^{-2}
16a	$(p\text{-}MeOC_6H_4)_3C^+$	−0.21	$(AcrH)_2$	0.83	$<10^{-3}$
10b	Ph_3C^+	0.21	1	0.69	4.2×10^4
12b	$(p\text{-}MeOC_6H_4)Ph_2C^+$	0.05	1	0.85	3.3×10^3
15b	$(p\text{-}MeOC_6H_4)_2PhC^+$	−0.07	1	0.97	7.9
16b	$(p\text{-}MeOC_6H_4)_3C^+$	−0.21	1	1.11	6.1×10^{-2}
15c	$(p\text{-}MeOC_6H_4)_2PhC^+$	−0.07	3	1.37	5.0×10^2
16c	$(p\text{-}MeOC_6H_4)_3C^+$	−0.21	3	1.51	1.9×10
10c	Ph_3C^+	0.21	4	1.07	3.4×10^4
16c	$(p\text{-}MeOC_6H_4)_3C^+$	−0.21	4	1.49	2.1×10

[a] Taken from ref 15b.

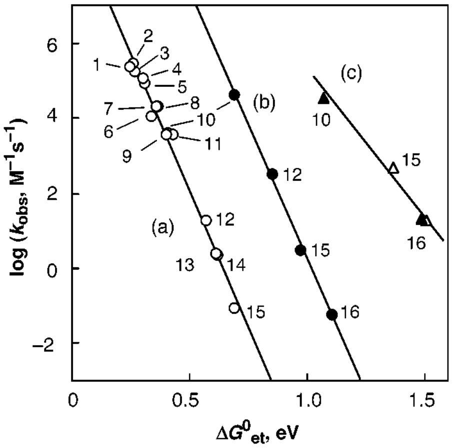


Figure 2. Plots of log k_{obs} vs ΔG^0_{et} for the reaction of (a) $(AcrH)_2$ (○), (b) $(CH_3)_2C{=}C(OMe)OSiMe_3$ (●), (c) $CH_2{=}C(OEt)OSiEt_3$ (△), $CH_2{=}C(OEt)OSiMe_2Bu^t$ (▲) with the various oxidants at 298 K. 1 Fc^+, 2 $(1\text{-HgCl})Fc^+$, 3 $[(TPP)Co]^+$, 4 (1-*tert*-amyl)Fc^+, 5 1-BuFc^+, 6 2,3-dicyano-*p*-benzoquinone, 7 1,1′-Me_2Fc^+, 8 1,1′-Bu_2Fc^+, 9 tetracyanoethylene, 10 Ph_3C^+, 11 7,7′,8,8′-tetracyano-*p*-quinodimethane, 12 $(MeOC_6H_4)(C_6H_5)_2C^+$, 13 *p*-chloranil, 14 *p*-bromanil, 15 $(MeOC_6H_4)_2(C_6H_5)C^+$, 16 $(MeOC_6H_4)_3C^+$. Fc = ferrocene, TPP^{2-} = the dianion of tetraphenylporphyrin.

The rates of reactions of ketene silyl acetals with trityl cations were determined from the disappearance of absorbance due to trityl cations (e.g., $Ph_3C^+ClO_4^-$; λ_{max} = 400 nm, ϵ_{max} = 3800 $M^{-1}\,cm^{-1}$) as shown in Figure 3. The disappearance rate obey pseudo-first-order kinetics in the presence of large excess ketene silyl acetal (see inset in Figure 3) and the pseudo-first-order rate constants increases linearly with increasing ketene silyl acetal concentration. The observed second-order rate constants determined from the slope of plots of the pseudo-first-order rate constant vs ketene silyl acetal concentration are also listed in Table 1.

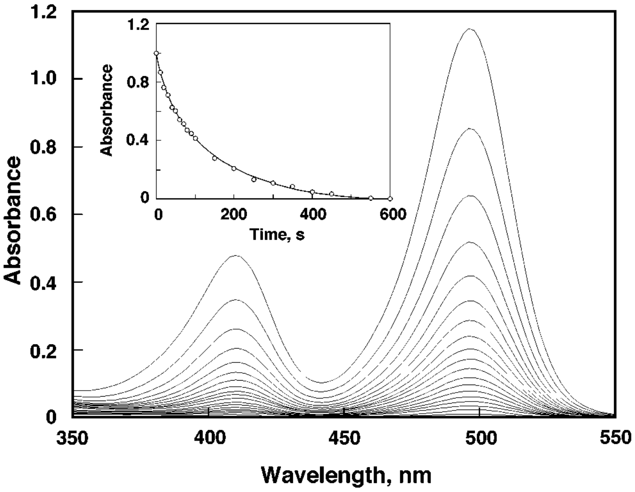


Figure 3. Visible spectral change observed in the reaction of $(p\text{-}MeOC_6H_4)_2PhC^+ClO_4^-$ (3.0×10^{-5} M) with $(CH_3)_2C{=}C(OMe)OSiMe_3$ (**1**: 2.4×10^{-3} M) in deaerated MeCN at 298 K (20 s interval). Inset: Plots of time dependence of the decay in absorbance at 496 nm due to $(p\text{-}MeOC_6H_4)_2PhC^+$.

The ΔG^0_{et} values for electron transfer from ketene silyl acetals to trityl cations were determined from the E^0_{ox} values of ketene silyl acetals[8b,16] and the E^0_{red} values of trityl cations. A plot of log k_{obs} vs ΔG^0_{et} for the reactions of **1** with trityl cations shown in Figure 2b has a good parallel linear correlation with the plot for outer-sphere electron-transfer reactions from $(AcrH)_2$ to trityl cations (Figure 2a). The slope is almost identical between these two different types of reactions: one is the addition of **1** to trityl cations, and the other is the outer-sphere electron transfer. However, it is unlikely that the addition of **1** to trityl cations proceeds via an outer-sphere electron transfer, since the k_{obs} values are at least by a five orders magnitude larger than those expected from the outer-sphere electron-transfer reactions. Thus, there should be an orbital interaction (the difference in 10^5 in k_{obs}

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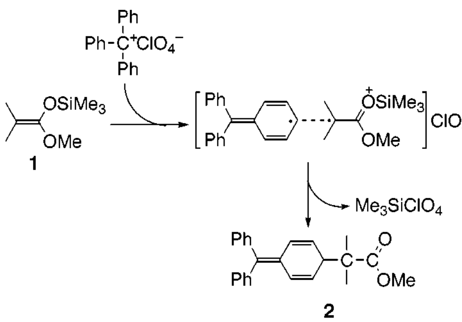
(16) The E^0_{ox} values have been estimated based on free energy relationsships for outer-sphere electron-transfer reactions of ketene silyl acetals.[8b]

Scheme 2



corresponds to the energy of ca. 7 kcal mol^{-1}) in the radical pair which would be produced by the electron-transfer reaction. Such a reaction may be best described as an inner-sphere electron transfer from **1** to trityl cation, followed by the C−C bond formation leading to the formal nucleophilic addition of **1** to trityl cation as shown in Scheme 2. It has not been strictly ruled out that the reaction of **1** with trityl cation simply is an ionic reaction at the least hindered position of the trityl cation, since the charge may be delocalized into the aromatic ring, In such a case, however, it would be difficult to account for a good parallel linear correlation between the reactions of **1** with trityl cations and the outer-sphere electron-transfer reactions in Figure 2.

In the case of a less sterically hindered ketene silyl acetal **3**, however, the type of product in the reaction of trityl cation is different from that obtained in the reaction with a sterically hindered ketene silyl acetal (eq 1). The k_{obs} values of the reactions of **3** with trityl cations (Figure 2c) are by more than 10^{12} larger than those expected from the outer-sphere electron-transfer correlation. The much larger reactivity of **3** as compared to **1** in the nucleophilic addition to trityl cations shows sharp contrast with the reversed reactivity in the electron-transfer reactions in which the reactivity of **3**, which has the more positive E^0_{ox} value (1.30 V),[8b] is expected to be much smaller than **1** (0.83 V).[8b]

In conclusion, the nucleophilic reactivities of ketene silyl acetals vary significantly depending on the steric demand at the reaction center, but they are well correlated with the electron-transfer reactivities when the steric demand at the reaction center for the C−C bond formation remains constant (Figure 2).

Experimental Section

Materials. Trityl cation derivatives were prepared by the corresponding triphenylmethyl chloride or triphenylmethanol with perchloric acid in acetic anhydride.[17] The purity of trityl cation derivatives thus obtained was checked by elemental analysis and ^{1}H NMR spectra. ^{1}H NMR measurements were performed with a JNM-GSX-400 (400 MHz) NMR spectrometer. Anal. Calcd for $C_{19}H_{15}O_4Cl$, $Ph_3C^+ClO_4^-$; C, 66.58; H, 4.41. Found: C, 65.78; H, 7.15. Anal. Calcd for $C_{20}H_{17}O_5Cl$, $(MeOC_6H_4)Ph_2C^+ClO_4^-$; C, 64.44; H, 4.60. Found: C, 64.15; H, 4.54. Anal. Calcd for $C_{21}H_{19}O_6Cl$, $(MeOC_6H_4)_2PhC^+ClO_4^-$; C, 62.62; H, 4.75. Found: C, 61.20; H, 4.68. Anal. Calcd for $C_{22}H_{21}O_7Cl$, $(MeOC_6H_4)_3C^+ClO_4^-$; C, 61.05; H, 4.89. Found: C, 60.52; H, 4.81. ^{1}H NMR (CD_3CN, 400 MHz) δ (Me_4Si, ppm) $Ph_3C^+ClO_4^-$, 7.2−8.3 (m, 15H); $(MeOC_6H_4)Ph_2C^+ClO_4^-$, 4.22 (s, 3H), 7.4−8.1 (m, 14H); $(MeOC_6H_4)_2PhC^+ClO_4^-$, 4.12 (s, 6H), 7.3−8.1 (m, 13H); $(MeOC_6H_4)_3C^+ClO_4^-$, 4.07 (s, 9H), 7.2−8.1 (m, 12H). Methyl trimethylsilyl dimethylketene acetal ($Me_2C{=}C(OMe)OSiMe_3$, **1**) was were obtained commercially from Aldrich. 2-Ethoxy-2-butenyldimethyl-*tert*-butylsilane ($CH_2{=}C(OEt)OSiMe_2Bu^t$ and 2-ethoxy-2-butenyltriethylsilane ($CH_2{=}C(OEt)OSiEt_3$, **3**) were prepared as described in the literature.[18] The silicon reagents were purified by vacuum distillation. 10,10′-Dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridine [$(AcrH)_2$] was prepared from the reduction of 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$) with $Me_3SnSnMe_3$ in MeCN at 333 K and purified by recrystallization from the mixture of acetonitrile and chloroform. Anal. Calcd for $C_{28}H_{24}N_2$; C, 86.56; H, 6.23; N, 7.21. Found: C, 86.56; H, 6.29; N, 7.15. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (Me_4Si, ppm) 3.08 (s, 6H), 3.95 (s, 2H), 6.5−7.3 (m, 16H). 10-methylacridinium iodide ($AcrH^+I^-$) was prepared by the reaction of acridine with methyl iodide in acetone,[19] and it was converted to the perchlorate salt ($AcrH^+ClO_4^-$) by the addition of magnesium perchlorate to the iodide salt and purified by recrystallization from methanol.[20] Acetonitrile and dichloromethane used as solvent were purchased from Wako Pure Chemical Ind. Ltd., Japan, and distilled over P_2O_5 prior to use.[21] *p*-Benzoquinones were purchased from Tokyo Kasei Organic Chemicals and purified by the standard methods.[21] Acetonitrile-d_3 and chloroform-*d* were obtained from EURI SO-TOP, CEA, France. Trifluoroacetic acid was also obtained commercially. Tetrabutylammonium perchlorate (TBAP), obtained from Fluka Fine Chemical, was recrystallized from ethanol and dried in vacuo prior to use.

Spectral and Kinetic Measurements. The reactions of the trityl cation derivatives with the various nucleophiles in deaerated MeCN were monitored with a Hewlett-Packard 8452 diode array spectrophotometer when the rates were slow enough to be determined accurately. The rates were determined from appearance of the absorbance due to $AcrH^+$ ($\lambda_{max} = 358$ nm, $\epsilon_{max} = 1.8 \times 10^4$ M^{-1} cm^{-1}) or the trityl cation derivatives (e.g., $Ph_3C^+ClO_4^-$, $\lambda_{max} = 400$ nm, $\epsilon_{max} = 3.8 \times 10^3$ M^{-1} cm^{-1}). The kinetic measurements for faster reactions such as the reaction of $Ph_3C^+ClO_4^-$ with $(AcrH)_2$ were carried out with a Union RA-103 stopped-flow spectrophotometer which was thermostated at 298 K under deaerated conditions. The concentration of the trityl cation derivatives or the various nucleophiles was maintained at more than 15-fold excess of the other reactant to attain pseudo-first-order conditions. Pseudo-first-order rate constants were determined by a least-squares curve fit using an NEC microcomputer. The first-order plots of $\ln(A_\infty - A)$ vs time (A_∞ and A are the final absorbance and the absorbance at the reaction time, respectively) were linear for three or more half-lives with the correlation coefficient, $\rho > 0.999$. In each case, it was confirmed that the rate constants derived from at least five independent measurements agreed within an experimental error of ±5%.

Reaction Procedure. Typically, $Ph_3C^+ClO_4^-$ (1.0×10^{-2} M) and $Me_2C{=}C(OMe)OSiMe_3$ (1.0×10^{-2} M) were added to an NMR tube which contained deaerated CD_3CN solution (0.60 cm^3) under an atmospheric pressure of argon. The products of was identified by the ^{1}H NMR spectra by comparing with those of authentic samples. The ^{1}H NMR measurements were performed using a JNM-GSX-400 (400 MHz) NMR spectrometer. **2**: ^{1}H NMR (CD_3CN, 298 K, 400 MHz); δ(Me_4Si, ppm): 1.17 (s, 6H), 3.50 (tt, 1H, $J = 4.4$ and 2.2 Hz), 3.67 (s, 3H), 5.72 (td, 2H, $J = 10.6$ and 1.8 Hz), 6.54 (qd, 2H, $J = 10.6$ and 1.8 Hz), 7.11−7.36 (m, 10H). The assignment was confirmed by an NOE experiment in which the signal at 3.50 ppm is coupled with that at 1.17 ppm. *p*-Methoxy-substituted **2**: 1.16

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(s, 6H), 3.46 (m, 1H), 3.76 (s, 3H), 4.21 (s, 3H), 6.37−6.56 (m, 4H), 6.80−7.38 (m, 9H).

Electrochemical Measurements. Electrochemical measurements of trityl cation derivatives were performed on a BAS 100B electrochemical analyzer in deaerated acetonitrile containing 0.10 M $Bu^n_4NClO_4$ as a supporting electrolyte at 298 K. The gold working microelectrode (i.d. = 10 μm, BAS) was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire (BAS). The measured potentials were recorded with respect to the $Ag/AgNO_3$ (1.0×10^{-2} M) reference electrode. The E^0_{red} values (vs Ag/Ag^+) are converted to those vs SCE by adding 0.29 V.[22]

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