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Addition of Ketene Silyl Acetals to the Triplet Excited State of C_{60} via Photoinduced Electron Transfer Leading to the Fullereneacetates

Koichi Mikami,*,[†] Shoji Matsumoto,[†] Akito Ishida,[‡] Setsuo Takamuku,[‡] Tomoyoshi Suenobu,[§] and Shunichi Fukuzumi*,[§]

Contribution from the Department of Chemical Technology, Faculty of Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan, The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan, and Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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Abstract: The photochemical carbon−carbon bond formation of C_{60} with ketene silyl acetals is described to give a new way for fullerene functionalization chemistry. The photoaddition of ketene silyl acetals to C_{60} occurs efficiently under irradiation of the visible light in benzene as well as benzonitrile to yield the fullereneacetates. 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 quenching of triplet excited state of C_{60} by ketene silyl acetals with those predicted for the electron transfer processes indicates that the photoaddition proceeds via photoinduced electron transfer from ketene silyl acetals to the triplet excited state of C_{60}. The negative shift in the one-electron reduction potentials by the adduct formation of C_{60} is examined by the cyclic voltammetry measurements. The factors to control the formation of mono- and bisadducts of C_{60} are clarified based on the rates of photoinduced electron transfer from ketene silyl acetals to the triplet excited states of C_{60} and the adducts.

Introduction

Since the preparation of buckminsterfullerene (C_{60}) in synthetically useful quantities,[1] much attention has been focused on its functionalization with nucleophiles, radicals, reducing agents, dienes, dipoles, zero-valent transition metals, oxygen, and also electrophiles.[2] Ester-derived ketene silyl acetals (KSAs) may be regarded as attractive nucleophiles for the functionalization of C_{60}, since KSAs can be used as storable enolate equivalents in the Aldol[3] and Michael[4] processes for C−C bond formation to yield the adducts with ester functionality. However, no "silatropic ene reaction",[5] in other words, [1,5]-silyl transfer from KSAs to C_{60} has observed[6] in contrast with the analogous "prototropic ene reaction", an intermolecular [1,5]-hydrogen transfer process.[7] On the other hand, electron transfer oxidation of KSAs has recently received increasing attention in both thermal and photochemical reactions because of its synthetic utility for the C−C bond formation.[8,9] The use of the excited state of a substrate is of particular interest, since it has recently been reported that addition of KSA to 10-methylacridone proceeds efficiently via the photoinduced electron transfer from KSA to the triplet excited state of 10-methylacridone under neutral conditions without acid or base catalysts under irradiation of the visible light.[10] The one-electron reduction potential of the triplet excited state of C_{60} (1.14 V vs SCE) reported by Foote *et al.*[11] is more positive than that of 10-methylacridone (0.88 V vs SCE).[10] Thus, the

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[†] Tokyo Institute of Technology.

[‡] The Institute of Scientific and Industrial Research, Osaka University.

[§] Faculty of Engineering, Osaka University.

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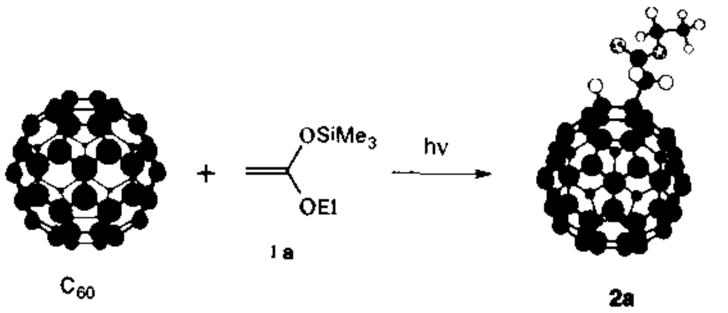
photoinduced electron transfer from KSAs to the triplet excited state $^3C_{60}{}^*$ is energetically feasible.[11,12] However, the valuable role of photoinduced electron transfer processes of C_{60} for its functionalization has remained to be explored. We report herein the photoinduced electron transfer process from KSAs to $^3C_{60}{}^*$ [6,13] to give the fullerene with ester functionality,[14,15] which is useful for further elaboration to fullerene amide and peptide of biological importance.[16] The rates of photoinduced electron transfer from various KSAs to the triplet excited states of C_{60} and its derivatives have been determined from the dependence of quantum yields on the KSA concentrations as well as the quenching of the triplet excited states by KSAs, providing valuable insight into the mechanistic viability and the fine control of degree of the functionalization of C_{60}.

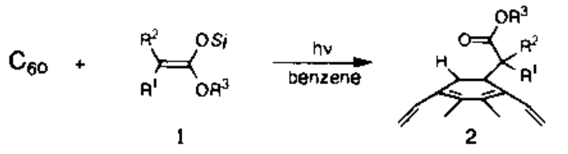
Results and Discussion

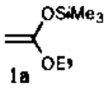
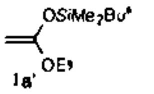
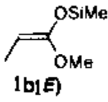
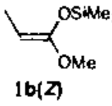
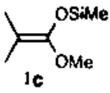
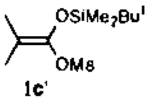
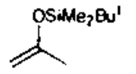
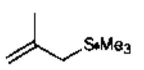
Photoaddition of Ketene Silyl Acetals. C_{60} (20 mg) and an excess amount of ethyl acetate-derived KSA **1a** ($H_2C{=}C(OEt)OSiMe_3$) (20 equiv) in benzene (20 mL) were photolyzed with a high-pressure mercury lamp (eq 1).[17] The color of the solution changed from purple to dark brown within 2 h. In the dark, however, no reaction has occurred even at 200 °C. Purification through flash column chromatography on silica gel (hexanes and then mixtures of hexanes and ethyl acetate) afforded the product, ethyl 1,2-dihydro[60]fullerene-1-acetate **2a** in 71% yield which corresponds to the quantitative yield based on recovered C_{60} (no homocoupling products derived from **1a** have been obtained). No polyadducts were obtained even after the prolonged reaction time (Table 1, entry 1). The more facile reaction was found with β,β-dimethyl substituted KSA (**1c**), ($Me_2C{=}C(OMe)OSiMe_3$) (entries 6−8). The initial photoproduct is identified as C_{60}-1,2-(H)CMe_2COOMe (**2c**). In this case, however, the initial monoadduct is further reacted to yield the bisadduct (**3c**: λ_{max} = 432 nm) at prolonged irradiation time particularly in higher concentration (1.5×10^{-2} M) of the KSA **1c** (entry 6). Short time irradiation leads to the drastic increase in the yield of **2c** based on recovered C_{60} (entry 7). The addition of *tert*-butyldimethylsilyl KSA (**1c'**) was found to be relatively slow (entry 9). Unfortunately, the silyl enol ether of acetone and allylic silanes did not undergo the addition reaction (entries 10 and 11).



(1)

Table 1. Photoinduced C−C Bond Formation of C_{60} with Ketene Silyl Acetals



entry	Si-Nu	Equiv.	Time (min)	Product	Yield of monoadduct^a (%)
1	 **1a**	20	90	**2a**	71 (100)
2		10	30		44 (100)
3	 **1a'**	10	120	**2a**	63 (100)
4	 **1b(*E*)**	10	90	**2b**	37 (51)
5	 **1b(*Z*)**	10	90	**2b**	36 (58)
6	 **1c**	10	30	**2c**	16 (24)^b
7		10	10		26 (60)
8		3	60		31 (50)
9	 **1c'**	10	30	**2c**	28 (46)
10		10	120	-	0
11		10	60	-	0

^{a} Value in parentheses is based on recovered C_{60}. ^{b} Because of the formation of bisadduct.

Essentially the same products are obtained in photochemical reactions of C_{60} with KSAs in benzonitrile as well. No photochemical reactions of C_{60} with benzyltrimethylsilane and allyltrimethylsilane have occurred under irradiation with the visible light. Judging from the reported values of one-electron

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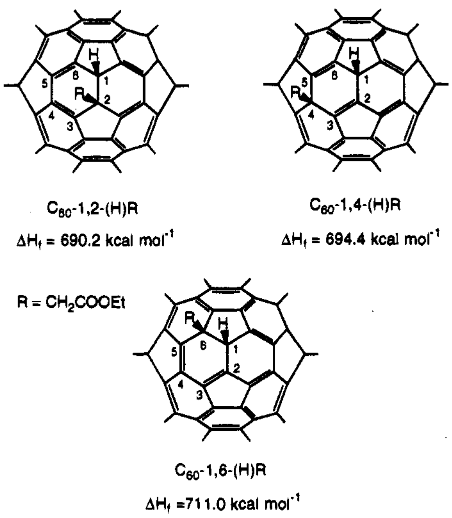
(17) The ketene silyl acetal **1a** was found to isomerize to the corresponding α-silylated or desilylated ester tautomers, of which the enol forms may act as a proton source for C_{60}-*H*, under irradiation of the visible light in the presence of C_{60} but not in the absence of C_{60}. The isomerization mechanism will be reported elsewhere.

oxidation potentials (E^0_{ox}) of organosilanes in acetonitrile,[8] the E^0_{ox} values of organosilanes which can react with C_{60} is *ca.* ≤ 1.3 V.

The thermodynamic stabilities of the 1,2-, 1,4-, and 1,6-isomers of monoadducts are evaluated by using the PM3 semiempirical MO method.[18] The final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The ΔH_f (heat of formation) value of C_{60}-1,6-(H)CH_2COOEt is significantly larger than those of the corresponding 1,2- and 1,4-isomers. The smaller ΔH_f value of the 1,2-isomer than that of the 1,4-isomer suggests that the 1,2-isomer would be preferred over the 1,4-isomer.[19]

As suggested by the PM3 calculations, the NMR spectrum of **2a** supports Cs symmetry of the 1,2-adduct at the hexagon−hexagon (symmetrical) junction rather than the unsymmetrical 1,4- and 1,6-adducts. The ^{13}C NMR spectrum of **2a**, C_{60}-1,2-(H)CH_2COOEt shows 30 signals for the C_{60} skeleton. This is the appropriate number and ratio of peak intensities for the symmetrical 1,2-adduct (the total of 64 carbons). Although the resonances of the two sp^3-hybridized carbons of the fullerene at $\delta = 65.94$ and 61.39 are at low field, the downfield shift is probably caused by the anisotropy effect of C_{60}. The ^1H NMR spectrum of **2a** shows one singlet at 6.79 ppm and one singlet at 4.46 ppm for the C_{60}-*H* and C_{60}-CH_2CO_2Et protons of Cs symmetrical adduct, respectively. The downfield shift of CH_2CO_2Et protons is also caused by the ring current. The IR spectrum clearly shows the presence of the ester functionality at 1738 cm^{-1}. The UV−vis spectra agree with those of 1,2-adducts, fullerene-carboxylic esters.[14]



Quenching of Triplet Excited State. Irradiation of the absorption band of C_{60} in deaerated benzonitrile (PhCN) solution containing KSA (**1c′**: 1.2×10^{-2} M) results in an increase in the absorbance at $\lambda_{max} = 434$ nm which is characteristic of the adduct, fullereneacetate (**2c**), as shown in Figure 1. Similar spectral change was observed in the photochemical reactions of other KSAs with C_{60}. When the photochemical reaction is carried out under an atmospheric pressure of oxygen, however, the reaction is strongly inhibited by oxygen as shown in Figure 2. Essentially the same results were obtained when the photochemical reaction was performed in benzene instead of PhCN. Since oxygen is a well-known triplet quencher,[20] the photoaddition of KSA to C_{60} may proceed via the triplet excited state of C_{60} which is quenched by oxygen to retard the photoaddition. The singlet excited state of C_{60} produced initially upon irradiation is known to be efficiently converted to the triplet excited state by the fast intersystem crossing.[21] In fact the transient $^3C_{60}$* triplet−triplet (T−T) absorption at 740 nm is observed by the laser flash photolysis of a deaerated PhCN solution of C_{60} as shown in Figure 3. Under the experimental conditions where triplet−triplet annihilation is negligible, the triplet lifetime of $^3C_{60}$* in PhCN at 298 K is determined as 32

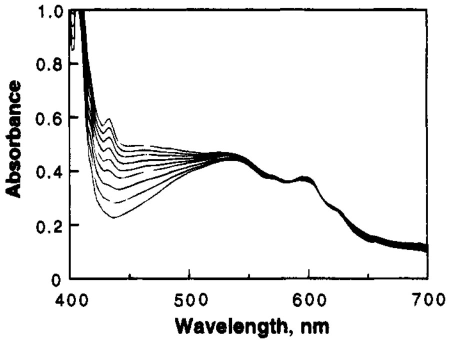


Figure 1. Electronic absorption spectra observed in photoaddition of **1c** (1.3×10^{-3} M) to C_{60} (3.0×10^{-4} M) in deaerated PhCN at 298 K (60 s interval).

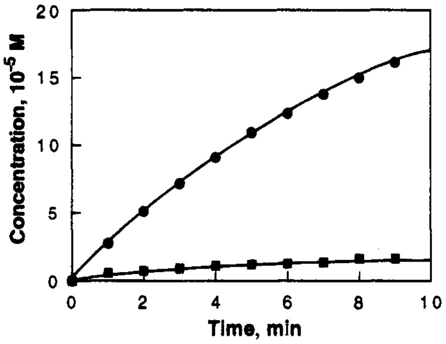


Figure 2. Time dependence of formation of the monoadduct in photoaddition of **1c** (3.3×10^{-3} M) to C_{60} (3.0×10^{-4} M) in deaerated (●) and O_2-saturated (■) PhCN at 298 K.

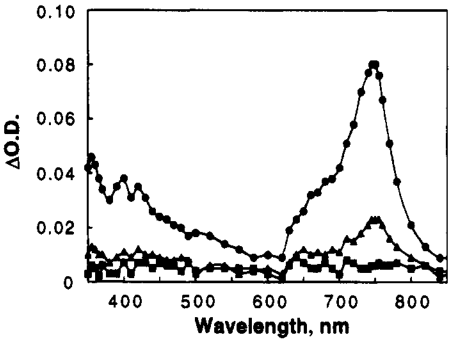


Figure 3. Transient absorption spectra obtained by laser flash photolysis of C_{60} (3.0×10^{-5} M) in PhCN: (●) 3.4×10^{-6} s, (▲) 1.5 $\times 10^{-5}$ s, (■) 4.4×10^{-5} s after laser excitation at 355 nm.

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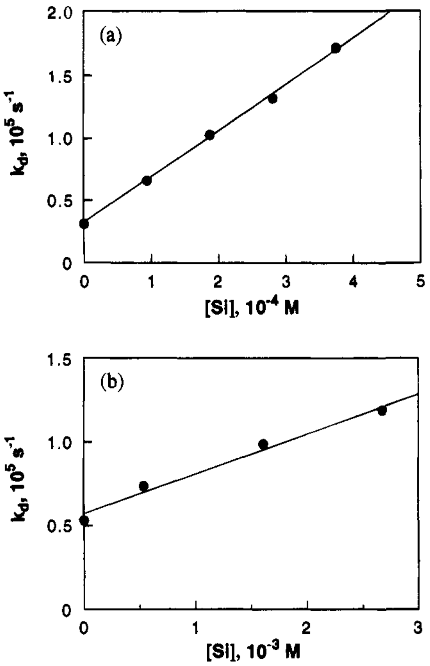

Figure 4. Plots of k_d vs [Si] for the quenching of (a) $^3C_{60}^*$ (3.0×10^{-5} M) and (b) ^{3}**2c*** (3.0×10^{-5} M) by **1c′** in deaerated PhCN at 298 K.

μs.[22] The triplet lifetimes are significantly reduced by the presence of KSA in PhCN. The quenching rate constants of triplet $^3C_{60}^*$ by KSAs were determined from the decay kinetics of transient T−T absorption at 740 nm following excitation at 355 nm. In each case, the quenching of $^3C_{60}^*$ by KSA obeys eq 2, where k_d is the observed first-order decay rate constant of

$$k_d = k_T + k_q[\mathrm{Si}] \qquad (2)$$

$^3C_{60}^*$, k_T is the rate constant without quencher, k_q is the bimolecular quenching rate constant, and [Si] is the concentration of KSA. A linear plot of k_d vs [Si] for the quenching of $^3C_{60}^*$ by **1** is shown in Figure 4 (part a), where the intercept agrees well with the k_T value in the absence of quencher, demonstrating the validity of the triplet lifetime of $^3C_{60}^*$.

Essentially the same T−T absorption at 740 nm was observed for the isolated initial product in the photochemical reaction of **1c′** with C_{60}, i.e., monoadduct (**2c**). The triplet lifetime of ^{3}**2c*** was also determined as 19 μs, which is somewhat shorter than that of $^3C_{60}^*$ (32 μs).[23] The triplet excited state of ^{3}**2c*** is further quenched by **1c′** as shown in Figure 4 (part b), in consonant with the further reaction of **2c** to yield the bisadduct (**3c**) at prolonged irradiation time (*vide supra*). The quenching rate constant (k_q) is determined from the slope in the plot of k_d vs [Si]. The k_q value for the quenching of the triplet excited state of ^{3}**2c*** (2.3×10^7 M^{-1} s^{-1}) is significantly smaller than that of $^3C_{60}^*$ (2.1×10^8 M^{-1} s^{-1}). The diminished reactivity of the monoadduct (**2c**) as compared with the original C_{60} may be related to the negative shift in the one-electron reduction potential (E^0_{red}) of **2c**. Figure 5 shows the cyclic voltammograms of C_{60} and the monoadduct (**2c**) in PhCN. The E^0_{red} values (vs SCE) of **2c** and **2c**$^{\bullet-}$ (−0.56 and −0.97 V, respectively) are uniformly shifted to the negative direction (*ca.* −0.1 V) as compared with those of C_{60} and $C_{60}^{\bullet-}$ (−0.43 and −0.87 V, respectively).[24]

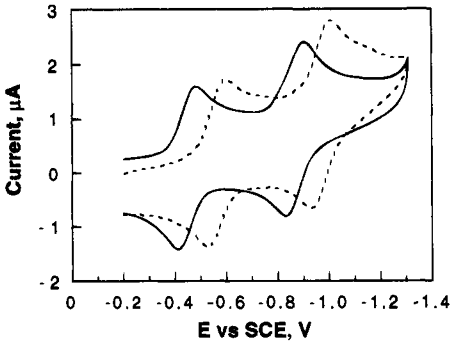

Figure 5. Cyclic voltammograms of C_{60} (—, 3.0×10^{-4} M) and the monoadduct **2c** (– –, 3.0×10^{-4} M) in deaerated PhCN at 298 K.

Photoinduced Electron Transfer Mechanism. The quantum yields (Φ) were determined from the increase in absorbance due to the adducts by using a ferrioxalate actinometer under irradiation of monochromatized light of $\lambda = 340$ nm. The Φ values for the photoaddition reaction of KSAs to C_{60} in PhCN increases with an increase in the concentration of KSA [Si] to reach a limiting value (Φ_∞) as shown in Figure 6 (parts a−c for photoaddition of **1c′** and **1a′** to C_{60} and that of the monoadduct **2c**, respectively). In each case, the dependence of quantum yields on the concentrations of KSAs is expresed by eq 3, which is rewritten as a linear correlation between Φ^{-1}

$$\Phi = \Phi_\infty K_{obs}[\mathrm{Si}]/(1 + K_{obs}[\mathrm{Si}]) \qquad (3)$$

vs $[\mathrm{Si}]^{-1}$ as eq 4, where K_{obs} is the quenching constant of the excited state of C_{60} by KSAs. The validity of eq 4 is confirmed

$$\Phi^{-1} = \Phi_\infty^{-1}[1 + (K_{obs}[\mathrm{Si}])^{-1}] \qquad (4)$$

by the plot of Φ^{-1} vs $[\mathrm{Si}]^{-1}$ as shown in Figure 7 (parts a−c which corresponds to parts a−c in Figure 6, respectively). From the slope and the intercept are obtained the Φ_∞ and K_{obs} values as listed in Table 2. The quenching constant K_{obs} ($= k_{obs}\tau_T$) is converted to the rate constant (k_{obs}) of the reaction of KSAs with the triplet excited state of C_{60} by using the triplet lifetimes of $^3C_{60}^*$ and the monoadduct ^{3}**2c*** (Table 2). The k_{obs} values of KSAs determined from the dependence of Φ on [Si] agree reasonably well with those determined directly from the triplet quenching of $^3C_{60}^*$ and the monoadduct ^{3}**2c***.[25] Such agreement confirms the essential role of the triplet excited state in the photoaddition of KSAs to C_{60}. When the reactivities of KSAs toward $^3C_{60}^*$ are compared, the k_{obs} values of β,β-dimethyl substituted KSAs (2.2×10^8 and 2.1×10^8 M^{-1} s^{-1} for **2c** and **2c′**, respectively) are significantly larger than that of nonsubstituted counterpart (2.5×10^6 M^{-1} s^{-1} for **1a′**). Such a drastically diminished reactivity of the nonsubstituted KSA as compared to the β,β-dimethyl substituted KSAs is reminiscent of the significant difference in their reactivities for the electron transfer reactions.[8] The one-electron oxidation potential (E^0_{ox}) of **1c** (0.90 V) is *ca.* 0.4 V less positive than that of **1a** (1.28

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[22] This value is slightly smaller than the reported value (49 μs) of $^3C_{60}^*$ in benzene.[21] However, it is well known that the triplet lifetimes depend greatly on measurement conditions such as the triplet concentration and solvents, which affect the triplet-triplet annihilation.[21]

[23] The similar shortened lifetime of the triplet excited state of dihydrofullerene as compared to that of C_{60} has recently been reported; see: Anderson, J. L.; An, Y.-Z.; Rubin, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 9763.

[24] The similar but somewhat larger negative shift has recently been reported for the E^0_{red} values of the dimethyl adduct C_{60}-1,2-Me_2 and the radical anion (−0.58 and −1.00 V, respectively), see: Caron, C.; Subramanian, R.; D'Souza, F.; Kim, J.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 8505.

[25] The somewhat smaller k_{obs} values of **2c** and **2c′** than those of k_q values may be ascribed to the decrease in the apparent triplet lifetime of $^3C_{60}^*$ due to the larger concentration of C_{60} employed in determining the quantum yields than those in laser-flash photolysis measurements (see Experimental Section).

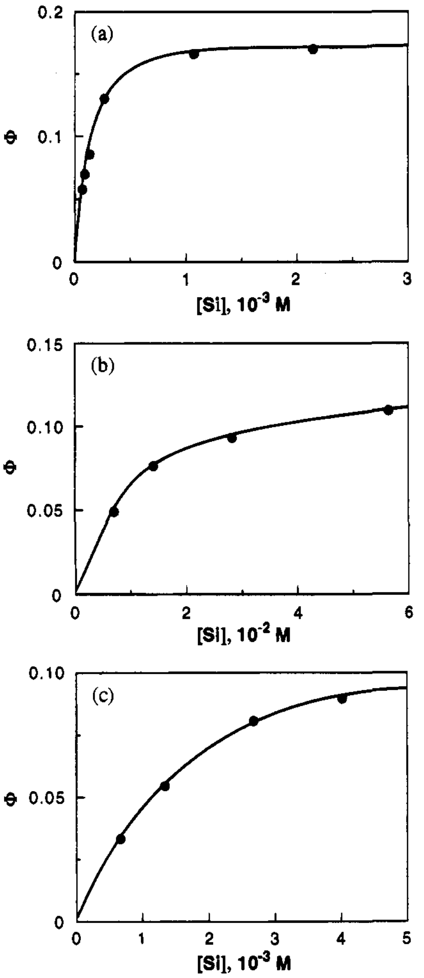

Figure 6. Dependence of the quantum yields (Φ) on the concentration of KSAs ([Si]) for photoaddition of (a) **1c**' and (b) **1a**' to C_{60} (3.0×10^{-4} M) and (c) that of **1c**' to **2c** (7.4×10^{-5} M) in deaerated PhCN at 298 K.

V).[8] The free energy change of photoinduced electron transfer from KSAs to $^3C_{60}^*$ (ΔG^0_{et}) is given by eq 5, where E^0_{ox} and

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

E^0_{red} are the one-electron oxidation potentials of KSAs[8,26] and the one-electron reduction potential of $^3C_{60}^*$, respectively. The E^0_{red} value of $^3C_{60}^*$ has been reported as 1.14 V (vs SCE).[11] The ΔG^0_{et} values of **2c** and **2c**′ thus evaluated by using eq 5 is negative (−5.5 kcal mol^{-1}), while that of **1a**′ is positive (= 3.2 kcal mol^{-1}). The dependence of the activation free energy of photoinduced electron transfer $\Delta G^{\ddagger}$ on the free energy change of electron transfer (ΔG^0_{et}) has well been established as given by an empirical free energy relation (eq 6), where $\Delta G^{\ddagger}_0$ is the intrinsic barrier that represents the activation free energy

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

when the driving force of electron transfer is zero, *i.e.*, $\Delta G^{\ddagger} = \Delta G^{\ddagger}_0$ at $\Delta G^0_{et} = 0$.[27] The $\Delta G^{\ddagger}_0$ values of **1c** and **1a** have previously been reported as 5.2 and 4.8 kcal mol^{-1}, respectively.[8] On the other hand, the $\Delta G^{\ddagger}$ values are related to the rate constant of electron transfer (k_{et}) as given by eq 7, where Z is the collision frequency that is taken as 1×10^{11} M^{-1} s^{-1}, F is the Faraday constant, and k_{diff} is the diffusion rate constant

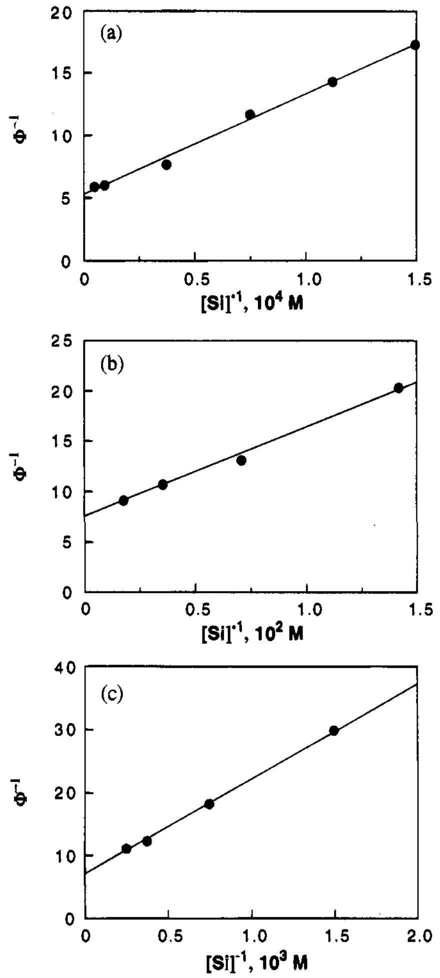

Figure 7. Plots of Φ^{-1} vs $[\mathrm{Si}]^{-1}$ for photoaddition of (a) **1c**′ and (b) **1a**′ to C_{60} (3.0×10^{-4} M) and (c) that of **1c**′ to **2c** (7.4×10^{-5} M) in deaerated PhCN at 298 K.

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

(2.0×10^{10} M^{-1} s^{-1}).[8] Then, the k_{et} values can be calculated from the ΔG^0_{et} and $\Delta G^{\ddagger}_0$ values by using eqs 6 and 7.

The k_{et} values thus obtained for **1c** and **1c**′ (3.7×10^8 M^{-1} s^{-1}) agree reasonably well with the k_q values (4.0×10^8 and 3.7×10^8 M^{-1} s^{-1} for **1c** and **1c**′, respectively).[28] The diminished reactivity of an unsubstituted KSA (**1a**′: $k_{obs} = 2.5 \times 10^6$ M^{-1} s^{-1}) as comapred with that of *β,β*-dimethyl substituted KSAs (**1c** and **1c**′) is also well explained by the much smaller k_{et} value of **1a**′ (1.3×10^6 M^{-1} s^{-1}).[29] Moreover, the smaller k_{obs} value for the further photoaddition of **1c**′ to the monoadduct **2c** (2.6×10^7 M^{-1} s^{-1}) than that for the initial photoaddition of **1c**′ to C_{60} (2.1×10^8 M^{-1} s^{-1}) is consistent with the expected decrease in the k_{et} value for the photoinduced electron transfer from **1c**′ to $^3C_{60}^*$ (3.7×10^8 M^{-1} s^{-1}) as compared with that to ^{3}**2c*** (8.4×10^7 M^{-1} s^{-1}) due to the positive shift (0.12 V) in the one-electron reduction potential

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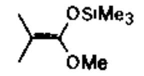
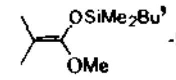
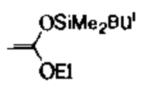
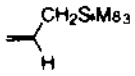
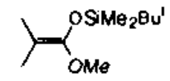
[26] The reported E^0_{ox} values of KSAs in acetontirile at 298 K[8] have been used as those in benzonitrile in evaluation of ΔG^0_{et} for photoinduced electron transfer from KSAs to $^3C_{60}^*$ in benzonitrile at 298 K, since benzonitrile (ϵ = 25.2) is as polar as acetonitrile (ϵ = 37.5).

[27] Rehm, A.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834. Rehm, A.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[28] The E^0_{ex} and $\Delta G^{\ddagger}_0$ values of **1c**' are assumed to be the same as those of **1c**.[8]

[29] The E^0_{ox} and $\Delta G^{\ddagger}_0$ values of **1a**' ($H_2C{=}C(OEt)OSiMe_2Bu^t$) are also assumed to be the same as those of **1a**.[8] Judging from the experimental errors in estimation of the E^0_{ex} and $\Delta G^{\ddagger}_0$ values the agreement between k_{obs} and k_{et} values within a factor of two is remarkable.

Table 2. Free Energy Change ΔG^0_{et} and Rate Constants k_{et} for Photoinduced Electron Transfer from KSAs to $^3C_{60}$* and ^{3}2c*, Observed Quenching Constants K_{obs}, Rate Constants k_{obs}, and Limiting Quantum Yields Φ_∞, and Triplet Quenching Rate Constants k_q in the Photoaddition of KSAs to C_{60} and 2c in PhCN at 298 K

excited state	KSA	ΔG^0_{et},[a] kcal mol^{-1}	K_{obs}, M^{-1}	k_{obs},[b] M^{-1}s^{-1}	k_q, M^{-1}s^{-1}	k_{et},[c] M^{-1}s^{-1}	Φ_∞
$^3C_{60}$*		-5.5	7.0×10^3	2.2×10^8	4.0×10^8	3.7×10^8	0.26
		-5.5	6.7×10^3	2.1×10^8	3.7×10^8	3.7×10^8	0.19
		3.2	8.1×10	2.5×10^8	—	1.3×10^6	0.14
		8.3	d	d	—	2.3×10^3	d
^{3}**2c***		-2.8	4.9×10^2	2.6×10^7	2.3×10^7	8.4×10^7	0.14

[a] Obtained from the E^0_{ox} values of KSAs and E^{0*}_{red} values of $^3C_{60}$* and ^{3}2c* by using eq 5. [b] Obtained from the K_{obs} values ($= k_{obs}\tau_T$) and lifetime of the triplet state of $^3C_{60}$*(τ_T = 32 μs) and ^{3}2c* (τ_T = 19 μs). [c] Evaluated by using eqs 6 and 7. The $\Delta G^\ddagger_0$ values of the electron transfer are taken from ref 8. [d] No reaction.

(E^0_{red}) of the monoadduct (*vide supra*).[30] The k_{et} value of allyltrimethylsilane calculated based on the more positive E^0_{ox} value (1.50 V)[8] than those of KSAs is 2.3×10^1 M^{-1} s^{-1}, which is too small to quench $^3C_{60}$*, agreeing with no photochemical reaction observed in the case of allyltrimethylsilane (*vide supra*).

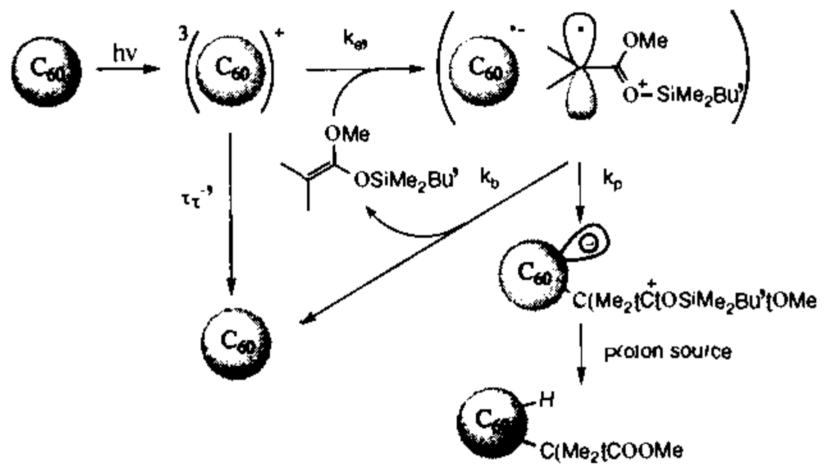
The Marcus theory provides the quantitative basis to predict the rates of electron transfer reactions using eq 8, where the reorganization energy λ corresponds to $4\Delta G^\ddagger_0$.[31] Since the application of the Marcus equation is restricted to the normal region, i.e., $\Delta G^0_{et} > -\lambda$ for forward intermolecular electron

$$\Delta G^\ddagger = (\lambda/4)(1 + \Delta G^0_{et}/\lambda)^2 \qquad (8)$$

transfer reactions, the photoinduced electron transfer reactions of ketene silyl acetals including the inverted region, $\Delta G^0_{et} < -\lambda$, have been analyzed using an empirical free energy relation (eq 6).[8] However, the k_{et} values calculated by using eqs 7 and 8 also predict well the change in the reactivities of organosilanes in Table 1.[32] Thus, the reactivities of various organosilanes in the photochemical reactions with C_{60} and the adducts are fully consistent with those of photoinduced electron transfer from organosilanes to the triplet excited states of C_{60} and the adducts.

Based on the results and discussion described above, the reaction mechanism of photoaddition of KSAs to C_{60} may be summarized as shown representatively for the **1c**'-C_{60} system in Scheme 1. The triplet excited state $^3C_{60}$* generated by the efficient intersystem crossing upon photoexcitation of C_{60} is

Scheme 1



quenched by electron transfer from KSA (k_{et}) to give the radical ion pair in competition with the decay to the ground state ($k_T = \tau_T^{-1}$). It has previously been disclosed that the spin density of the KSA radical cation is nearly localized on the terminal carbon atom.[8] Thus, the triplet radical ion pair initially produced by electron transfer from KSA to $^3C_{60}$* may be converted to the singlet radical ion pair by a fast intersystem crossing through a nucleus-electron hyperfine interaction of KSA radical cation.[33] Then, the KSA radical cation in the singlet radical ion pair is coupled efficiently with the $C_{60}^{\bullet-}$ to give the zwitterionic intermediate which is eventually converted to the product **2** after the protonation.[34–36] The product formation step (k_p) may compete well with the back electron transfer step to the reactant pair (k_b).

By applying the steady-state approximation to the reactive species, $^3C_{60}$* and the radical ion pair in Scheme 1, the dependence of Φ on the KSA concentration [Si] can be derived as given by eq 9, which agrees with the observed dependence of Φ on [Si] in eq 3. The limiting quantum yields Φ_∞

$$\Phi = [k_p/(k_p + k_b)]k_{et}\tau_T[\mathrm{Si}]/(1 + k_{et}\tau_T[\mathrm{Si}]) \qquad (9)$$

corresponds to $k_p/(k_p + k_b)$. Thus, the Φ_∞ values being smaller than unity in Table 2 may be ascribed to the competition of the product formation process (k_p) with the back electron transfer process (k_b).

The photoinduced electron transfer reactions are usually performed in polar solvent such as acetonitrile and benzonitrile, in which the solvation energy of free ions is greatly reduced compared to much less polar solvents such as benzene. Such a difference in the solvation energy of the KSA radical cation (**1c**$^{\bullet+}$) in benzene and PhCN has previously been estimated as 0.86 eV.[8,26] On the other hand, the difference in the solvation energy of $C_{60}^{\bullet-}$ in benzene and PhCN may be negligible because of highly delocalized negative charge.[26,37] The overall difference in the free energy change of electron transfer to produce

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(30) The E^0_{red} value of ^{3}**2c*** is estimated as 1.02 V from that of $^3C_{60}$* (1.14 V) by assuming that the triplet excitation energy is the same between C_{60} and the monoadduct. However, the somewhat smaller k_{obs} value than the corresponding k_{et} value calculated based on the estimated E^0_{red} value of ^{3}**2c*** suggests the slight decrease in the triplet excitation energy of the monoadduct due to the larger increase in the HOMO level than the LUMO level by the reductive alkylation.

(31) Marcus, R. A. *Ann. Rev. Phys. Chem.* **1964**, *15*, 155.

(32) The calculated k_{et} values of **1c** and **1c'** (8.2×10^8 M^{-1} s^{-1}) are much larger than that of **1a'** (1.6×10^6 M^{-1} s^{-1}). However, the k_{et} values obtained using eq 8 are somewhat different from those obtained using eq 7, since the λ values were originally determined based on eq 7 in ref 8.

(33) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369.

(34) The hydrogen in C_{60}-*H* may come from the adventitious water. Indeed, no adduct was obtained in the presence of MS 4A to trap the water. However, upon addition of D_2O (large excess) in the reaction mixture, we did not observe any deuterated **2c**. See ref 17.

(35) No radical coupling species of free KSA radical cation escaped from the radical ion pair cage has been observed, indicating the efficiency of the C–C bond formation in the radical ion pair in Scheme 1.

(36) Alternatively a triplet biradical may be formed by an ion coupling of silyl cation of KSA radical cation with $C_{60}^{\bullet-}$ to give the silyl adduct which is converted to the final product after the desilylation. In such a case, however, the steric hindrance of the silyl group may result in formation of the 1,4-adduct instead of the 1,2-adduct.

(37) The E^0_{red} value of C_{60} has been reported to be rather insensitive to the solvent polarity because of the highly delocalized negative charge. For example, the E^0_{red} value in PhCN (−0.40 V vs SCE) is about the same as that in benzene (−0.36 V vs SCE). The slight differnce in the E^0_{red} value is also caused by the difference in the supporting electrolyte. See: Dubois, D.; Moninot, G.; Kutner, W.; Jones, T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.

free ions in benzene and PhCN is thereby estimated as 0.86 eV. The Coulombic interaction energy which corresponds to the work term w_p required to bring $\mathbf{1c}^{\bullet+}$ and $C_{60}^{\bullet-}$ to the mean separation r of the radical ion pair in a solvent with dielectric constant ϵ is given by eq 10. The w_p value may well be

$$w_p = -e^2/4\pi\epsilon r \qquad (10)$$

neglected in PhCN having a large dielectric constant (25.2) as compared to the value of benzene (2.27).[27] The difference of 0.86 eV in the $\Delta G^0{}_{et}$ values between benzene and PhCN may well be canceled by the large Coulombic interaction in benzene, since the difference in the w_p values in benzene and PhCN with the mean separation of 6.7 Å is equal to 0.86 eV. In fact such a distance is typical for the radical ion pair (6.5 Å).[38] Moreover, the solvent reorganization energy in benzene may be smaller than that in PhCN. Thus, the photoinduced electron transfer from KSAs to $^3C_{60}{}^*$ in benzene may also be expected to be as efficient as that in benzonitrile. The efficient C−C bond formation between the KSA radical cation and $C_{60}^{\bullet-}$ in the radical ion pair following the photoinduced electron transfer (Scheme 1) leads eventually to the fullerene with ester functionality, which is useful for further elaboration to fullerene amide and peptide of biological importance.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were measured on a Varian EM 390 (90 MHz) or GEMINI 300 (300 MHz) and a JEOL GSX-500 (500 MHz) spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$). Chemical shifts of ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard ($\delta = 77.1$). IR spectra were measured on a JASCO FT/IR-5000 spectrometer. FAB mass spectra were obtained with JEOL JMS-AX505H. The UV−vis spectra were measured on a Shimadzu UV-2200 spectrometer. The light source used for high-pressure mercury lamp was a Riko UVL-100P (100 W), and the irradiation was performed through a Pyrex vessel. Analytical thin layer chromatography (TLC) were performed on a glass plates precoated with silica gel (Merck Kieselgel 60 F_{254}, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$, and phosphomolybdic acid. All experiments were carried out under nitrogen or argon atmosphere. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately prior to use. Dichloromethane was freshly distilled over CaH_2. Benzene was distilled from sodium under argon atmosphere.

Preparation of Silyl Nucleophiles: 1-Ethoxy-1-[(trimethylsilyl)oxy]ethene (1a). To a solution of diisopropylamine (2.22 g, 22 mmol) in THF (20 mL) was added 1.6 M hexane solution of *n*-butyllithium (13.8 mL, 22 mmol) at 0 °C and stirred for 20 min at that temperature. To the mixture was added ethyl acetate (1.95 mL, 20 mmol) at −78 °C. After stirring for 30 min, to the mixture was added trimethylsilyl chloride (3.0 mL, 24 mmol) at that temperature. After stirring for additional 30 min, the mixture was warmed up to room temperature. After stirring for 1 h, the reaction mixture was poured into a solution of hexane (80 mL) and water (40 mL). The organic layer was washed with brine and dried over $MgSO_4$. After evaporation under reduced pressure, the residue was distilled under reduced pressure (50 °C/75 mmHg) to give 1-ethoxy-1-[(trimethylsilyl)oxy]ethene in 70% yield (C−*Si*/O−*Si* = 75:25): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 9H), 1.30 (t, J = 7.0 Hz, 3H), 3.05 (d, J = 2.5 Hz, 1H), 3.20 (d, J = 2.5 Hz, 1H), 3.75 (q, J = 7.0 Hz, 2H).

1-[(*tert*-Butyldimethylsilyl)oxy]-1-ethoxyethene (1a′). To a solution of diisopropylamine (1.47 mL, 10.5 mmol) in THF (25 mL) was added 1.71 M hexane solution of *n*-butyllithium (6.1 mL, 10.4 mmol) and DMPU (*N,N′*-dimethylpropylene-urea) (5.0 mL) at 0 °C and stirred for 20 min at that temperature. To the mixture was added ethyl acetate (0.98 mL, 10.0 mmol) at −78 °C. After stirring for 30 min, to the mixture was added a solution of *tert*-butyldimethylsilyl chloride (1.50 g, 10.0 mmol) in THF (2 mL) at that temperature. After stirring for an additional 30 min, the mixture was warmed up to room temperature. After stirring for 1 h, the reaction mixture was poured into a solution of hexane (80 mL) and water (40 mL). The organic layer was washed with brine and dried over $MgSO_4$. After evaporation under reduced pressure, the residue was distilled under reduced pressure (60−63 °C/10 mmHg) to give 1-[(*tert*-butyldimethylsilyl)oxy]-1-ethoxyethene in 89% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 6H), 0.92 (s, 9H), 1.29 (t, J = 7.1 Hz, 3H), 3.05 (d, J = 2.4 Hz, 1H), 3.21 (d, J = 2.4 Hz, 1H), 3.74 (q, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.6, 14.3, 18.1, 25.6, 60.4, 63.4, 161.5.

(*E*)-1-Methoxy-1-[(trimethylsilyl)oxy]-1-propene (1b). The titled compound was prepared in 34% yield (*E*/*Z* = 85:15) according to the procedure as described for 1-ethoxy-1-[(trimethylsilyl)oxy]ethene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 9H), 1.53 (d, J = 7.4 Hz, 3H), 3.54 (s, 3H), 3.68 (q, J = 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.3, 9.3, 54.8, 78.9, 154.1; bp 70 °C/55 mmHg.

(*Z*)-1-Methoxy-1-[(trimethylsilyl)oxy]-1-propene (1b). To a solution of diisopropylamine (10.8 mL, 77 mmol) in THF (50 mL) was added 1.55 M hexane solution of *n*-butyllithium (49.5 mL, 77 mmol) at 0 °C under an argon atmosphere. After stirring for 30 min, to the solution was added HMPA (12 mL), and it was then cooled to −78 °C. To the solution was added a solution of methyl propionate (6.5 mL, 70 mmol) in THF (10 mL) over 10 min period. After stirring for 2 h at that temperature, to the mixture was added trimethylsilyl chloride (10.1 mL, 80 mmol) at −78 °C. After stirring for 30 min at that temperature, the mixture was warmed up to room temperature, and then the reaction mixture was poured into a solution of ice water (200 mL) and hexane (100 mL). The organic layer was washed with brine and dried over Na_2SO_4. After filtration and evaporation, the residue was distilled under reduced pressure (68−69 °C/70 mmHg) to give (*Z*)-1-methoxy-1-[(trimethylsilyl)oxy]-1-propene in 35% yield (*E*/*Z* = 5:95): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.19 (s, 9H), 1.50 (d, J = 6.9 Hz, 3H), 3.48 (s, 3H), 3.52 (q, J = 6.9 Hz, 1H). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 0.2, 9.5, 54.6, 70.6, 157.1.

1-Methoxy-2-methyl-1-[(trimethylsilyl)oxy]-1-propene (1c). The titled compound was prepared in 58% yield according to the procedure as described for 1-ethoxy-1-[(trimethylsilyl)oxy]ethene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 9H), 1.48 (s, 3H), 1.53 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.1, 16.0, 16.7, 56.5, 90.9, 149.5; bp 45 °C/12 mmHg.

1-Methoxy-2-methyl-1-[(*tert*-butyldimethylsilyl)oxy]-1-propene (1c′). The titled compound was prepared in 77% yield according to the procedure as described for 1-[(*tert*-butyldimethylsilyl)oxy]-1-ethoxyethene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 6H), 0.95 (s, 9H), 1.52 (s, 3H), 1.56 (s, 3H), 4.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.5, 16.4, 17.0, 18.2, 25.8, 57.1, 91.4, 149.7; bp 52 °C/2 mmHg.

2-[(*tert*-Butyldimethylsilyl)oxy]-1-propene. To a solution of *tert*-butyldimethylsilyl trifluoromethanesulfonate (8.3 mL, 36 mmol) and triethylamine (4.2 mL, 30 mmol) in CH_2Cl_2 (30 mL) was added acetone (2.2 mL, 30 mmol) at 0 °C. After stirring for 1 h, the reaction mixture was poured into a solution of hexane (80 mL) and water (40 mL). The organic layer was washed with brine and dried over $MgSO_4$. After evaporation under reduced pressure, the residue was distilled under reduced pressure (70 °C/30 mmHg) to give 2-[(*tert*-butyldimethylsilyl)oxy]-1-propene in 85% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.15 (s, 6H), 0.92 (s, 9H), 1.77 (s, 3H), 4.04 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.6, 18.1, 22.8, 25.7, 91.3, 156.3.

General Procedure for the Photochemical Reaction: Ethyl 1,2-Dihydro[60]fullerene-1-acetate (2a). To a solution of C_{60} (14.5 mg, 0.020 mmol) in deaerated benzene (15 mL) was added 1-ethoxy-1-[(trimethylsilyl)-oxy]ethene (63 mg, 0.39 mmol), and the solution was irradiated with high-pressure mercury lamp for 90 min. After evaporation under reduced pressure, the residue was separated by silica-gel chromatography (hexane and then hexane/ethyl acetate = 10:1) to give ethyl 1,2-dihydro[60]fullerene-1-acetate in 71% yield and recovered

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C_{60}: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (t, J = 7.0 Hz, 3H, $CO_2CH_2CH_3$), 4.46 (s, 2H, C_{60}-CH_2CO_2Et), 4.57 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 6.79 (s, 1H, C_{60}-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.83 (CO), 154.31 (2C), 153.64 (2C), 147.74, 147.48, 147.15 (2C), 146.59 (2C), 146.54 (2C), 146.39 (2C), 146.35 (2C), 146.03 (2C), 145.89 (2C), 145.74 (2C), 145.61 (2C), 145.54 (4C), 144.97 (2C), 144.70 (2C), 143.40 (2C), 142.75 (2C), 142.71 (2C), 142.41 (2C), 142.25 (2C), 142.12 (2C), 141.86 (2C), 141.78 (4C), 140.39 (2C0, 140.30 (2C), 136.85 (2C), 136.55 (2C), 65.94, 61.39, 59.46 (OCH_2), 49.79 (CH_2CO), 14.65 (CH_3). IR (CCl_4) 2964, 2930, 2860, 1738, 1462, 1255, 1102, 1038, 527 cm^{-1}; UV−vis (λ_{max}, hexane) 431, 327, 249, 215 nm; (λ_{max}, benzonitrile) 434, 335 nm; FAB-MS m/z = 809 ([M + H]$^+$), 808 ([M]$^+$), 807 ([M − H]$^+$), 721 ([M − $C_4H_7O_2$]$^+$), 720 ([M − $C_4H_8O_2$]$^+$).

Methyl 1,2-dihydro[60]fullerene-1-(2′-propionate) (2b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (d, J = 7.2 Hz, 3H, C_{60}-$CH(CH_3)CO_2Me$), 4.07 (s, 3H, CO_2CH_3), 4.43 (q, J = 7.2 Hz, 1H, C_{60}-$CH(CH_3)CO_2Me$), 6.94 (s, 1H, C_{60}-H); IR (CCl_4) 2962, 2930, 2860, 1738, 1460, 1263, 1197, 1125, 1077 cm^{-1}; FAB-MS m/z = 809 ([M + H]$^+$), 808 ([M]$^+$), 721 ([M − $C_4H_7O_2$]$^+$), 720 ([M − $C_4H_8O_2$]$^+$).

Methyl 1,2-dihydro[60]fullerene-1-(2′-isobutyrate) (2c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 6H, C60-$C(CH_3)_2CO_2Me$), 4.10 (s, 3H, CO_2CH_3), 6.69 (s, 1H, C_{60}-H). IR (CCl_4) 2964, 2932, 2860, 1734, 1433, 1263 cm^{-1}; UV−vis (λ_{max}, benzonitrile) 434, 335 nm.

Laser Flash Photolysis. Typically, a solution containing C_{60} or its derivative in PhCN (3.0×10^{-5} M) was irradiated with a laser flash at room temperature. A flash at 355 nm was obtained by the third-harmonic oscillation from a Nd:YAG laser (Quantel Model Brilliant). The single laser flash has a diameter of 0.5 cm, 5 ns duration, 30 mJ pulse^{-1} measured by a pyroelectric power meter (Gentec ED-500). The probe beam was obtained from a 450 W Xe-lamp (Osram, XBO-450) which was operated by a large current pulse-power supply. The probe beam was passed through an iris with a diameter of 0.2 cm and sent into the sample solution with perpendicular intersection of the laser beam. The probe beam is focused to a computer controlled monochrometer (CVI Laser, Digikrom-240) by two lenses and four mirrors. The output of monochrometer is monitored by a PMT (photomultiplier tube; Hamamatsu Photonix, R1417 or R2497). The signal from the PMT is recorded on a transient digitizer (Tektronix, 7912AD with plug-ins, 7A19 and 7B92A). Total system control is carried out with a microcomputer (Sharp, X-98000) which is connected to all measurement components with a GP-IB interface. To avoid pyrolysis of sample solution by the probe beam, a suitable cut-off filter was used. At large concentrations of $^3C_{60}$*, the decay of the transient triplet−triplet absorption obeyed the second-order kinetics due to the triplet−triplet annihilation. At lower concentrations of $^3C_{60}$*, however, the decay rates folloewed the first-order kinetics, from which the decay rate constants were determined.

For the quenching experiments of $^3C_{60}$* by KSAs, the irradiation laser wavelength of C_{60} was 355 nm which excites C_{60} selectively. The solution was deoxygenated by argon purging for 10 min prior to the measurements. Relative intensities of triplet−triplet absorption spectrum at maxima (740 nm) were measured for PhCN solutions containing C_{60} (3.0×10^{-5} M) or **2c** (3.0×10^{-5} M) with ketene silyl acetals at various concentrations (1.0×10^{-4}−2.7×10^{-3} M). There was no change in the shape, but there was a change in the lifetime of the T−T absorption spectrum by the addition of ketene silyl acetals. The Stern−Volmer relationship (eq 2) was obtained for the triplet decay rate constants (k_d) in the absence and presence of KSAs and the concentrations of KSAs [Si]. The quenching rate constants k_q were determined from the slope of a linear plot of k_d vs [Si] according to eq 2.

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[39] was used for the quantum yield determination of the photoreduction of C_{60} or its adduct by ketene silyl acetals. Square quartz cuvettes (10 mm i.d.) which contained a deaerated PhCN solution (3.0 cm^3) of C_{60} (3.0×10^{-4} M) or **2c** (7.4×10^{-5} M) with ketene silyl acetals at various concentrations (1×10^{-4}−5.8×10^{-2} M) were irradiated with monochromatized light of λ = 340 nm from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, the actinometer, C_{60} and C_{60} derivative absorbed essentially all the incident light of λ = 340 nm. The light intensity of monochromatized light of λ = 340 nm was determined as 6.91×10^{-9} einstein s^{-1} with the slit width of 10 nm. The photochemical reaction was monitored using a Hewlett Packard 8452A diode-array spectrophotometer. The quantum yields were determined from the increase in absorbance due to the C_{60} adducts at 434 nm (ϵ_{max} = 2.29×10^3 and 1.96×10^3 M^{-1} cm^{-1} for **2c** and **2a**, respectively). In order to avoid the contribution of light absorption of the products, only the initial rates were determined for determination of the quantum yields.

Cyclic Voltammetry. The cyclic voltammetry measurements were performed on a BAS 100B electrochemical analyzer in deaerated PhCN containing 0.1 M Bu_4NClO_4 as a supporting electrolyte at 298 K. The platinum working electrode (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/$AgNO_3$ (0.01 M) reference electrode. The E^0_{red} and E^0_{ox} values (vs Ag/Ag$^+$) are converted to those vs SCE by adding 0.29 V.[40] The cyclic voltammograms of C_{60} and **2c** exhibit the reversible cathodic and anodic waves.

Theoretical Calculations. The theoretical studies were performed using the PM3 molecular orbital method.[18] The calculations were performed by using the MOL-GRAPH 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.

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