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Addition of Group 14 organometallic compounds to C_{60} via photoinduced electron transfer. Direct detection of radical ion pair intermediates[☆]

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Abstract

The carbon–carbon bond formation of C_{60} with Group 14 organometallic compounds is attained through photoinduced electron transfer from Group 14 organometallic compounds acting as electron donors to the triplet excited state of C_{60}. The electron donors employed in this study are ketene silyl acetals and allylic stannanes. When an unsymmetric allylic stannane, e.g. prenyltributyltin ($Me_2C{=}CHCH_2SnBu_3$) is employed, the allylic group is introduced selectively at the α-position to yield C_{60}-1,2-$CH_2CH{=}CMe_2$ under irradiation of the visible light and no γ adduct has been formed. Such regioselectivity is characteristic of the reactions of prenyltributyltin via electron transfer, where the C–C_δ bond formation occurs after cleavage of the Sn–C bond. A comparison of the observed rate constants determined from the dependence of the quantum yields on the concentrations of electron donors, as well as the quenching of the triplet excited state of C_{60} by the electron donors with those predicted for the electron transfer processes, indicates that the photoreduction proceeds via photoinduced electron transfer from the electron donors to the triplet excited state of C_{60}. The radical ion pair generated in the photoinduced electron transfer from ketene silyl acetal to the triplet excited state of C_{60} has been successfully detected as transient absorption spectra in the visible and near-IR region with use of the laser flash photolysis. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Group 14 organometallic compounds; Photoinduced electron transfer; Radical ion pair intermediates

1. Introduction

The carbon–carbon bond formation via photoinduced electron transfer has recently attracted considerable interest from both synthetic and mechanistic viewpoints [1,2]. In particular, the use of the photoexcited state of C_{60} is expected to expand the scope of the reactions with electron donors giving a new way for fullerene functionalization chemistry [3–15]. Since the one-electron reduction potential of the triplet excited state of C_{60} is 1.14 V versus SCE [3], various electron donors having less positive oxidation potentials than 1.14 V can be used for the photoreduction of C_{60}. The authors have previously reported the one-electron oxidation properties of organosilanes that have been frequently used as key reagents for many synthetically important transformations, demonstrating that ketene silyl acetals can act as good electron donors in photoinduced electron transfer reactions [16,17]. Addition of ketene silyl acetals to the triplet excited state of C_{60} has

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[☆] Dedicated to the memory of late Professor Emeritus Rokuro Okawara.

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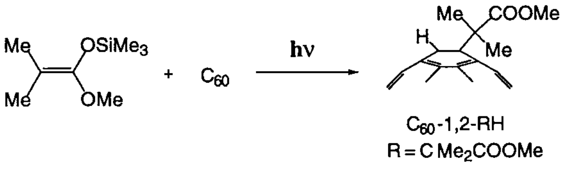
recently been shown to occur efficiently to yield the fullerene with ester functionality [18–20]. Although the kinetic analysis indicates that the photoaddition proceeds via photoinduced electron transfer from ketene silyl acetals to the triplet excited sate of C_{60} [20], the direct observation of a radical ion pair produced upon the photoinduced electron transfer has yet to be confirmed. Other Group 14 organometallic compounds, such as organostannanes, have frequently been used as electron donors in electron transfer reactions [21–30]. Thus, there may still be potential electron donors among other Group 14 organometallic compounds in photoinduced electron transfer reactions of C_{60}, the scope of which remains to be expanded further.

This paper reports that the addition of not only ketene silyl acetals but also allylic stannanes to C_{60} occurs efficiently via photoinduced electron transfer to the triplet excited state of C_{60} [31]. Since the regioselectivity for addition of an unsymmetric allylic stannane, e.g. prenyltributyltin, is reported to be reversed between a polar reaction and an electron transfer pathway [26], it is of interest to examine the regioselectivity for photoaddition of prenyltributyltin to C_{60}. The direct observation of a radical ion pair produced upon the photoinduced electron transfer has been made possible in this study by applying the laser flash photolysis to detect the transient absorption spectra in the near-IR region.

2. Results and discussion

2.1. Transient spectra observed in photoaddition of ketene silyl acetals to C_{60}

Irradiation of a benzene solution containing C_{60} (20 mg) and an excess amount of $Me_2C{=}C(OMe)OSiMe_3$ (three equivalents) with a high-pressure mercury lamp for 60 min gave mainly the mono-adduct, C_{60}-1,2-(H)CMe_2COOMe, in 31% yield, which corresponds to the 50% yield based on the recovered C_{60} (Eq. (1)) [20].



(1)

The initial mono-adduct is further reacted to give bis-adduct at prolonged irradiation time, particularly in a higher concentration of the ketene silyl acetal (ten equivalents) [20]. When an unsubstituted ketene silyl acetal ($H_2C{=}C(OEt)OSiMe_3$) is employed, only the mono-adduct, ethyl-1,2-dihydro[60]fullerene-1-acetate is obtained in the quantitative yield based on recovered C_{60} [20]. No poly-adducts were obtained, even after the prolonged reaction time.

Essentially the same products were obtained in photochemical reactions of C_{60} with ketene silyl acetals in benzonitrile [20]. Since the rate constant for quenching the triplet excited state of C_{60} ($^3C_{60}^*$) by $Me_2C{=}C(OMe)OSiMe_3$ (4.0×10^8 M^{-1} s^{-1}) in benzonitrile is the largest among various ketene silyl acetals examined previously [20], the $Me_2C{=}C(OMe)$–$OSiMe_3$–C_{60} system is chosen for the laser flash photolysis measurements. Fig. 1 shows the transient absorption spectra in the near-IR region obtained by the laser flash photolysis of a deaerated benzonitrile solution containing C_{60} (1.0×10^{-4} M) and $Me_2C{=}C(OMe)OSiMe_3$ (5.0×10^{-3} M) with 532 nm laser light. The transient absorption band at 740 nm appearing immediately after a nanosecond-laser shot is attributed to the triplet–triplet absorption band of $^3C_{60}^*$ [3,4,32,33]. The disappearance of the band due to $^3C_{60}^*$ is accompanied by appearance of a new absorption band at 1080 nm, which is the characteristic band of $C_{60}^{\bullet-}$ [34,35]. The decay rate of $^3C_{60}^*$ coincides with the rate of formation of $C_{60}^{\bullet-}$ obeying the pseudo-first-order kinetics, as shown in Fig. 2. The pseudo-first-order rate constant for the decay of $^3C_{60}^*$ in Fig. 2 is determined to be 6.7×10^6 s^{-1}, which agrees within experimental error with that for the formation of $C_{60}^{\bullet-}$ (7.0×10^6 s^{-1}). Such an agreement between the decay rate of $^3C_{60}^*$ and the rate of formation of $C_{60}^{\bullet-}$ indicates that electron transfer from ketene silyl acetal to $^3C_{60}^*$ occurs to produce the radical cation of ketene silyl acetal and $C_{60}^{\bullet-}$, although no absorption band that can be assigned to the radical cation of ketene silyl acetal can be seen in the visible or near-IR region in Fig. 1.

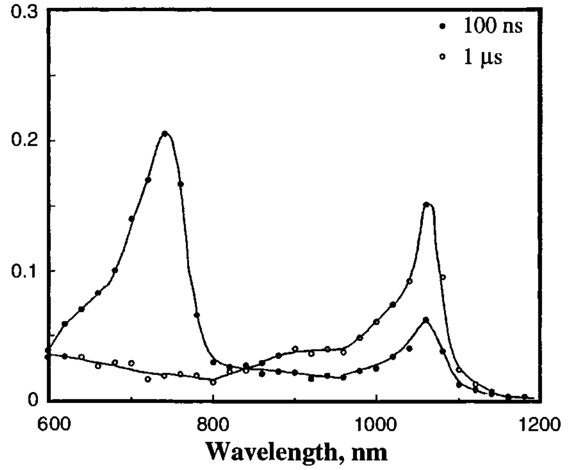
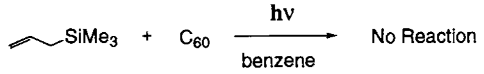


Fig. 1. Transient absorption spectra obtained by laser flash photolysis of C_{60} (1.0×10^{-4} M) in the presence of KSA (5.0×10^{-3} M) in deaerated PhCN: 100 ns (●) and 1 μs (○) after laser excitation at 532 nm.

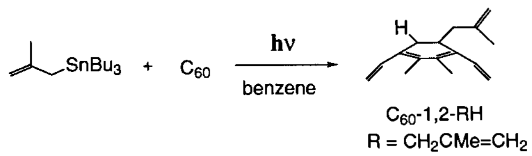
Fig. 2. Time profile at 740 and 1060 nm after 532 nm laser flash photolysis of C_{60} (1.0×10^{-4} M) in the presence of KSA (5.0×10^{-3} M) in deaerated PhCN.

2.2. Photoaddition of allylic stannanes to C_{60}

No photochemical reactions of C_{60} with allyltrimethylsilane have occurred under irradiation with the visible light (Eq. (2)). In contrast, the photoaddition of methallyltributyltin to C_{60} occurs efficiently to yield 1,2-dihydro[60]fullerene-1-(2′-methylprop-2′-ene), C_{60}-1,2-(H)$CH_2CMe{=}CH_2$ selectively in 38% (Eq. (3)).



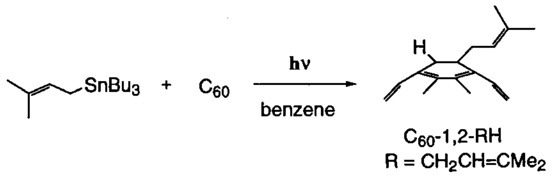
(2)



(3)

The NMR spectrum supports C_s symmetry of the 1,2-adduct to account for an attack on the hexagon–hexagon junction as opposed to the 1,4- and 1,6-adducts (see Section 3). No poly-adducts were obtained after the prolonged reaction time. Since the one-electron oxidation potential of allyltrimethylsilane ($E^\circ_{ox} = 1.50$ V) [16] is significantly higher than that of methallyltributyltin ($E^\circ_{ox} = 1.16$ V) [31], the E°_{ox} values of electron donors that can react with C_{60} photochemically should be lower than 1.3 V, which is compatible with the one-electron reduction potential of the triplet excited state of C_{60} ($E^\circ_{red} = 1.14$ V) [3]. The photochemical reaction of allyltributyltin ($E^\circ_{ox} = 1.06$ V) [31] with C_{60} also occurs in the presence of one equivalent of CF_3COOH to yield 1,2-dihydro[60]fullerene-1-(prop-2′-ene) (18% HPLC yield).

When an unsymmetric allylic stannane, e.g. prenyltributyltin ($Me_2C{=}CHCH_2SnBu_3$) is employed, the allylic group is introduced selectively at the α-position to yield C_{60}-1,2-$CH_2CH{=}CMe_2$ exclusively and no γ-adduct has been formed (Eq. (4)). The product was well-identified from its ^{1}H-NMR spectra (see Section 3).



(4)

Such a regioselective addition of prenyltributyltin at the α-position is reported for the photoreduction of 10-methylacridinium ion ($AcrH^+$) via photoinduced electron transfer from prenyltributyltin to the singlet excited state of $AcrH^+$ in acetonitrile, while the thermal reduction by prenyltributyltin occurs to yield the corresponding γ-adduct exclusively [26]. In a polar reaction, the C–C bond formation should occur prior to the cleavage of Sn–C bond, leading to the γ-addition. In an electron transfer reaction, however, the Sn–C bond may be significantly lengthened in the prenyltributyltin radical cation generated upon the electron transfer [36]. In such a case, the C–C bond formation may occur after the elongation or the cleavage of the Sn–C bond, leading to the more favorable α-addition than the γ-addition because of the steric hindrance of two methyl groups. Thus, the selective α-addition of prenyltributyltin to C_{60} is indicative of the occurrence of electron transfer prior to the C–C bond formation.

2.3. Kinetics and mechanism

Irradiation of the absorption band of C_{60} in PhCN solution containing Group 14 organometallic donors employed in this study results in an increase in the absorbance at $\lambda_{max} = 434$ nm, which is characteristic of the 1,2-mono-adduct of C_{60} (C_{60}-1,2-HR), independent of the nature of R. The quantum yields (Φ) were determined from an increase in absorbance due to the mono-adduct by using a ferrioxalate actinometer [37] under irradiation of mono-chromatized light of $\lambda = 340$ nm. The Φ value for the photoaddition of a Group 14 organometallic donor to C_{60} in PhCN increases with an increase in the concentration of the donor [D] to reach a limiting value (Φ_∞) as shown in Fig. 3, where the results of the photoaddition of allyltributyltin and prenyltributyltin to C_{60} are given as typical examples. In each case, the dependence of quantum yields on [D] is expressed by Eq. (5), which is rewritten as a linear correlation between Φ^{-1} versus $[D]^{-1}$ (Eq. (6)),

$$\Phi = \Phi_\infty K_{obs}[D]/(1 + K_{obs}[D]) \quad (5)$$

$$\Phi^{-1} = \Phi_\infty^{-1}[1 + (K_{obs}[D])^{-1}] \quad (6)$$

where K_{obs} is the quenching constant of the excited state of C_{60} by electron donors. The validity of Eq. (6)

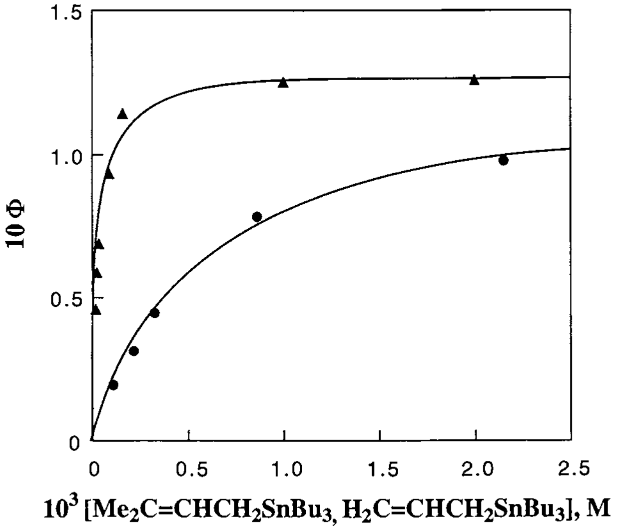


Fig. 3. Dependence of the quantum yields on [$H_2C{=}CHCH_2SnBu_3$] (●) and [$Me_2C{=}CHCH_2SnBu_3$] (▲) for the photoreduction of C_{60} (2.8×10^{-4} M) by $H_2C{=}CHCH_2SnBu_3$ and $Me_2C{=}CHCH_2SnBu_3$ in deaerated PhCN at 298 K, respectively.

is confirmed by the plot of Φ^{-1} versus $[D]^{-1}$ as shown in Fig. 4. From the slope and the intercept, values for the Φ_∞ and K_{obs} are obtained. The K_{obs} ($= k_{obs}\tau_T$) values are converted to the rate constants (k_{obs}) of the reactions of electron donors with the triplet excited state of C_{60} by using the triplet lifetime of $^3C_{60}^*$ in PhCN ($\tau_T = 32$ µs) [20]. The k_{obs} and Φ_∞ values of various Group 14 organometallic compounds are listed in Table 1, together with the free energy change of photoinduced electron transfer from the organometallic donor to $^3C_{60}^*$ [20].

The triplet lifetimes (τ_T) of the transient $^3C_{60}^*$ triplet–triplet (T–T) absorption at $\lambda_{max} = 740$ nm observed by the laser flash photolysis of a deaerated PhCN solution of C_{60} (Fig. 1) are significantly reduced by the presence of electron donors employed in this study. The bimolecular quenching rate constant (k_q) of triplet $^3C_{60}^*$ by the electron donors were determined from the decay kinetics of transient T–T absorption at 740 nm following the laser pulse. A linear plot of the decay rate constant of $^3C_{60}^*$ ($k_d = \tau_T^{-1}$) versus [D] for the quenching of $^3C_{60}^*$ by allyltributylstannane is shown in Fig. 5 as a typical example. The quenching rate constants of various electron donors are listed in Table 1.

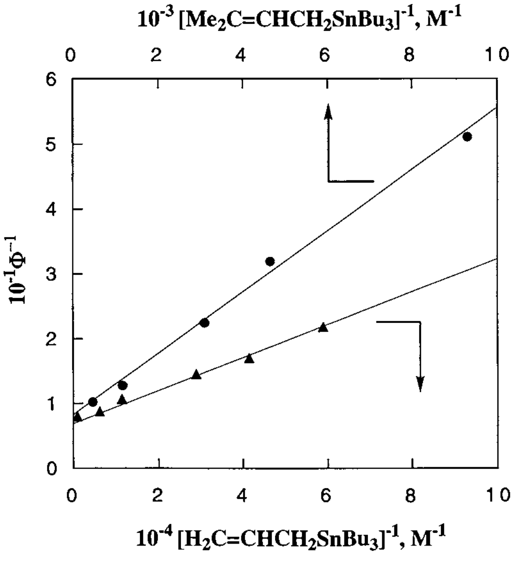


Fig. 4. Plots of Φ^{-1} vs. $[H_2C{=}CHCH_2SnBu_3]^{-1}$ (●) and $[Me_2C{=}CHCH_2SnBu_3]^{-1}$ (▲).

The k_{obs} values of electron donors determined from the dependence of Φ on [D] agree within experimental error with those determined directly from the quenching of $^3C_{60}^*$ (Table 1). Such agreement confirms the essential role of the triplet excited state in the photoaddition reactions of C_{60}.

The free energy change of photoinduced electron transfer from electron donors to $^3C_{60}^*$ (ΔG_{et}°) is given by Eq. (7), where E_{ox}° and E_{red}° are the one-electron oxidation potentials of electron donors and the one-electron reduction potential of $^3C_{60}^*$, respectively.

$$\Delta G_{et}^\circ = F(E_{ox}^\circ - E_{red}^\circ) \qquad (7)$$

The E_{red}° value of $^3C_{60}^*$ has been reported as 1.14 V (versus SCE) [3]. The dependence of the activation free energy of photoinduced electron transfer $\Delta G^{\neq}$ on the free energy change of electron transfer (ΔG_{et}°) has been well-established, as given by the Rehm–Weller free energy relation (Eq. (8)),

$$\Delta G^{\neq} = (\Delta G_{et}^\circ/2) + [(\Delta G_{et}^\circ/2)^2 + (\Delta G_0^{\neq})^2]^{1/2} \qquad (8)$$

where $\Delta G_0^{\neq}$ is the intrinsic barrier that represents the activation free energy when the driving force of electron transfer is zero, i.e. $\Delta G^{\neq} = \Delta G_0^{\neq}$ at $\Delta G_{et}^\circ = 0$ [38]. The $\Delta G^{\neq}$ values are related to the rate constant of electron transfer (k_{et}) as given by Eq. (9)

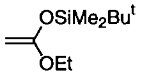
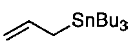
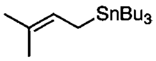
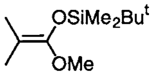
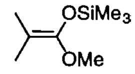
$$\Delta G^{\neq} = 2.3RT \log[Z(k_{et}^{-1} - k_{diff}^{-1})] \qquad (9)$$

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 (5.6×10^9 M^{-1} s^{-1}) [3]. Then, the k_{et} values can be calculated from the ΔG_{et}° and $\Delta G_0^{\neq}$ values [16] by using Eqs. (8) and (9), and they are also listed in Table 1.

The k_{et} values thus evaluated agree reasonably well with the k_q and k_{obs} values as shown in Table 1. The k_{et} value increases with an increase in the one-electron oxidation potentials of donors. Thus, the reactivities of Group 14 organometallic donors in the photoaddition reactions of C_{60} are fully consistent with those of photoinduced electron transfer from the donors to the triplet excited states of C_{60}. Based on the results and discussion described above, the reaction mechanism of photoaddition of ketene silyl acetals to C_{60} may be summarized as shown representatively for the $H_2C{=}C(OEt)OSiMe_3$–C_{60} system in Scheme 1.

Table 1

Free energy change ΔG°_{et} and rate constants k_{et} of photoinduced electron transfer from Group 14 organometallic electron donors to $^3C^*_{60}$, observed rate constants k_{obs}, triplet quenching rate constants k_q and limiting quantum yields Φ_{∞}, in the photoaddition of the donors to C_{60} in PhCN at 298 K

Electron donor	ΔG°_{et} [a] (kcal mol^{-1})	k_{obs} [b] (M^{-1} s^{-1})	k_q (M^{-1} s^{-1})	k_{et} [c] (M^{-1} s^{-1})	Φ_{∞}
	8.3	[d]	[d]	2.3×10^3	[d]
	3.2	2.5×10^6	–	1.3×10^6	0.14
	−1.8	5.0×10^7	7.8×10^7	4.5×10^7	0.13
	−5.8	9.8×10^8	–	1.7×10^9	0.13
	–	2.1×10^8	3.7×10^8	–	0.19
	−5.5	2.2×10^8	4.0×10^8	4.7×108	0.26

[a] Obtained from the E°_{ox} values of electron donors and E°_{red} values of $^3C^*_{60}$ by using Eq. (7).

[b] Obtained from the K_{obs} values ($=k_{obs}\tau_T$) and lifetime of the triplet state of $^3C^*_{60}$ ($\tau_T=32$ μs).

[c] Evaluated by using Eqs. (8) and (9). The $\Delta G^{\neq}_0$ values of the electron transfer are taken from [16].

[d] No reaction.

The triplet excited state $^3C^*_{60}$ generated by the efficient intersystem crossing upon photoexcitation of C_{60} is quenched by electron transfer from the ketene silyl acetal (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 ketene silyl acetal radical cation is nearly localized on the terminal carbon atom [16]. Thus, the ketene silyl acetal radical cation is coupled efficiently with the C_{60} radical anion (k_p) in competition with the back electron transfer to the reactant pair (k_b), to give the zwitterionic intermediate that is eventually converted to the product after the protonation.

Similarly, the reaction mechanism of reductive photoaddition of prenyltributyltin is shown in Scheme 2. Since the allylic group is introduced selectively at the α-position to yield C_{60}-1,2-$CH_2CH{=}CMe_2$ exclusively

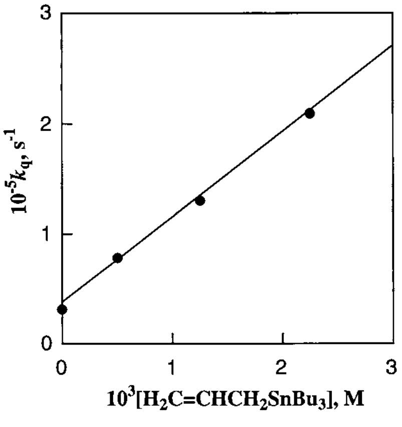
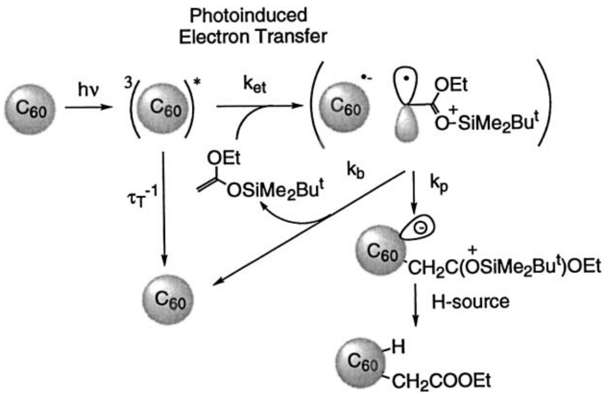
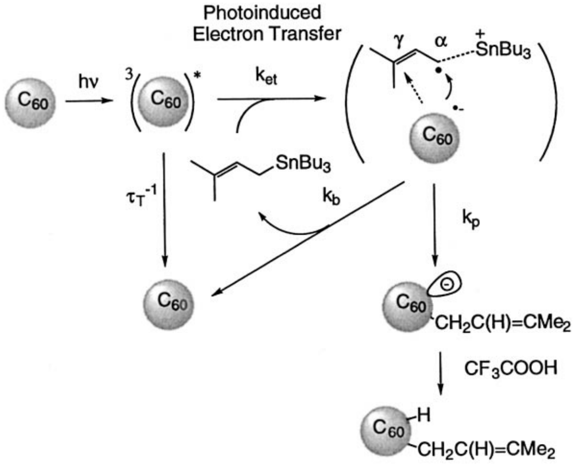


Fig. 5. Plot of k_d vs. [$H_2C{=}CHCH_2SnBu_3$] for the quenching of $^3C^*_{60}$ (3.0×10^{-5} M) in deaerated PhCN at 298 K.



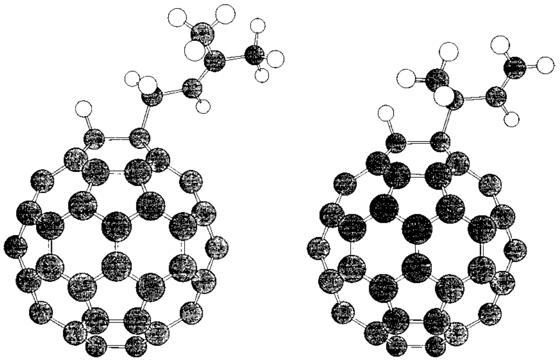
Scheme 1.



Scheme 2.

and no γ-adduct has been formed (Eq. (4)), the Sn–C bond of prenyltributyltin radical cation formed in the photoinduced electron transfer may be nearly cleaved prior to the C–C bond formation with $C_{60}^{\bullet-}$ in the radical ion pair (Scheme 2). The selective γ-addition through the photoinduced electron transfer shows a sharp contrast with the selective γ-addition of prenyltributyltin with 10-methylacridinium ion via a polar mechanism in which the C–C bond formation occurs prior to the cleavage of Sn–C bond [26].

The thermodynamic stabilities of the α- and γ-adducts are evaluated by using the PM3 semiempirical MO method [39]. The optimized structures of the α-adduct (C_{60}-1,2-$CH_2CH{=}CMe_2$) and the γ-adduct (C_{60}-1,2-$CMe_2CH{=}CH_2$) are shown in Fig. 6, where the ΔH_f (heat of formation) values are given. The ΔH_f value of the α-adduct is significantly smaller than that of the γ-adduct. Thus, the α-addition is not only kinetically but also thermodynamically preferred over the γ-addition.


α-Adduct
C_{60}-1,2-$CMe_2CH{=}CH_2$
$\Delta H_f = 774.6$ kcal mol^{-1}

γ-Adduct
C_{60}-1,2-$CH_2CH{=}CMe_2$
$\Delta H_f = 786.8$ kcal mol^{-1}

Fig. 6. Optimized structures of C_{60}-1,2-$CH_2CH{=}CMe_2$ and C_{60}-1,2-$CMe_2CH{=}CH_2$ with the ΔH_f values calculated by using the PM3 method.

By applying the steady-state approximation to the reactive species, $^3C_{60}^*$ and the radical ion pair in Schemes 1 and 2, the dependence of Φ on the donor concentration [D] can be derived, as given by Eq. (11), which agrees with the observed dependence of Φ on [D] (Eq. (5)).

$$\Phi = [k_p/(k_p + k_b)]k_{et}\tau_T[D]/(1 + k_{et}\tau_T[D]) \quad (11)$$

The limiting quantum yields Φ_∞ corresponds to $k_p/(k_p + k_b)$. Thus, the Φ_∞ values being smaller than unity in Table 1 may be ascribed to the competition of the radical coupling process (k_p) with the back electron transfer process (k_b).

3. Experimental

3.1. General Procedure

^{1}H- and ^{13}C-NMR spectra were measured on a Varian EM390 (90 MHz) or GEMINI 300 (300 MHz), JEOL GSX-400 (400 MHz) and JEOL GSX-500 (500 MHz) spectrometers. Chemical shifts of ^{1}H-NMR were expressed in ppm down-field from tetramethylsilane as an internal standard ($\delta = 0$). Chemical shifts of ^{13}C-NMR were expressed in ppm in $CDCl_3$ as an internal standard ($\delta = 77.1$). IR spectra were measured on a JASCO FT/IR-5000 spectrometer. FAB MS spectra were obtained with JEOL JMS-AXSOSH. The UV–vis spectra were measured on a Shimadzu UV-2200 spectrometer. The light source used for the 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 glass plates pre-coated 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. THF was distilled from sodium benzophenone ketyl immediately prior to use. Dichloromethane was freshly distilled over CaH_2. Benzonitrile (PhCN; 99.9%) was purchased from Aldrich, and used as-received. Benzene was distilled from sodium under argon atmosphere. Preparations of ketene silyl acetals are described elsewhere [19,20]. Allylic stannanes are prepared according to the literature method [40].

3.2. Synthesis of C_{60} adducts of allylic stannanes

Typically, to a solution of C_{60} (20 mg, 0.028 mmol) in deaerated benzene (20 ml), metallylstannane (0.56 mmol) was added, and irradiated with high-pressure mercury lamp for 9 h. After evaporation under reduced pressure, 1,2-dihydro[60]fullerene-1-(2′-methylprop-2′-ene) was obtained in 38% HPLC yield (36% NMR yield with dibenzyl as an internal standard). ^{1}H-NMR (300 MHz, C_6D_6/CS_2): δ 2.23 (s (br), 3H, C_{60}-$CH_2C(C\mathit{H}_3){=}CH_2$), 3.96 (s, 2H, C_{60}–$C\mathit{H}_2C(CH_3){=}CH_2$), 5.37 (m, 1H, $CH_2C(CH_3){=}C\mathit{H}_2$), 5.47 (s (br), 1H, $CH_2C(CH_3){=}C\mathit{H}_2$), 6.47 (s, 1H, C_{60}–H). ^{13}C-NMR (125 MHz, C_6D_6/CS_2 with $Cr(acac)_3$ as relaxation agent): δ sp^2-carbons for the C_{60} skeleton: 156.36 (2C), 154.30 (2C), 147.75 (1C), 147.59 (1C), 147.32 (2C), 146.73 (2C), 146.70 (2C), 146.56 (3C), 146.50 (2C), 146.11 (2C), 145.79 (1C), 145.77 (3C), 145.72 (3C), 145.05 (2C), 144.91 (2C), 143.63 (2C), 142.94 (4C), 142.38 (2C), 142.33 (2C), 142.20 (2C), 142.01 (2C), 141.98 (3C), 141.71 (2C), 140.61 (2C), 140.49 (2C), 136.50 (2C), 135.96 (2C); sp^3-carbons for the C_{60} skeleton: 58.93 (1C), 55.43 (1C); allyl part: 142.51 (1C), 118.64 (1C), 30.38 (1C), 24.97 (1C).

3.2.1. 1,2-Dihydro[60]fullerene-1-(prop-2′-ene)

^{1}H-NMR (300 MHz, C_6D_6/CS_2): δ 3.91 (dm, $J = 7.2$ Hz, 2H, C_{60}–$C\mathit{H}_2CH{=}CH_2$), 5.58 (ddt, $J = 1.7$, 10.1, 0.9 Hz, 1H, $CH_2CH = C\mathit{H}_2$), 5.67 (dq, $J = 17.0$, 1.5 Hz, 1H, $CH_2CH{=}C\mathit{H}_2$), 6.27 (s, 1H, C_{60}–H), 6.65 (ddt, $J = 10.1$, 17.0, 7.2 Hz, 1H, $CH_2C\mathit{H}{=}CH_2$).

3.2.2. 1,2-Dihydro[60]fullerene-1-(3′-methylbut-2′-ene)

^{1}H-NMR (300 MHz, C_6D_6/CS_2): δ 1.98 (s, 6H, C_{60}–$CH_2C(H){=}C(C\mathit{H}_3)_2$), 3.99 (dm, $J = 7.2$ Hz, 2H, $C\mathit{H}_2C(H){=}C(CH_3)_2$), 6.18 (tm, $J = 7.2$ Hz, 1H, $CH_2C(\mathit{H}){=}C(CH_3)_2$), 6.25 (s, 1H, C_{60}–H). ^{13}C-NMR (75 MHz, C_6D_6/CS_2 with $Cr(acac)_3$ as relaxation agent): δ 156.22 (2C), 154.311 (2C), 147.78, 147.65, 147.37 (2C), 147.78, 147.65, 147.37 (2C), 146.77 (2C), 146.74 (2C), 146.66 (2C), 146.60 (2C), 146.55 (2C), 146.42, 146.18 (2C), 145.08 (2C), 144.98 (2C), 143.64 (2C), 143.34 (2C), 142.96 (3C), 142.58 (2C), 142.41 (2C), 142.34 (2C), 142.02 (2C), 140.67, 140.63 (2C), 140.56 (2C), 138.33 (2C), 136.78 (2C), 136.31 (2C), 127.86 ($CH{=}\mathit{C}Me_2$), 119.74 ($\mathit{C}H{=}CMe_2$), 65.39, 59.37, 45.57 (C_{60}–$\mathit{C}H_2$), 26.55, 18.96.

3.3. Laser flash photolysis

The measurements of transient absorption spectra of $^3C_{60}^*$ and $C_{60}^{\bullet-}$ in the photochemical reaction of ketene silyl acetal with C_{60} were performed according to the following procedures. A deaerated benzonitrile solution containing C_{60} (1.0×10^{-4} M) and ketene silyl acetal (5.0×10^{-3} M) was excited by a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns FWHM) at 532 nm with the power of 7 mJ. A pulsed xenon flash lamp (Tokyo Instruments, XF80-60, 15 J, 60 ms FWHM) was used for the probe beam, which was detected with a Ge-APD module (Hamamatsu, C5331-SPL) after passing through the photochemical quartz vessel (10×10 mm^2) and a monochromator. The output from Ge-APD module was recorded with a digitizing oscilloscope (HP 54510B, 300 MHz). Since the purple solution of C_{60} in benzonitrile disappeared by each laser shot (532 nm; 7 mJ) in the presence of ketene silyl acetal, the transient spectra were recorded using fresh solutions in each laser excitation. All experiments were performed at 295 K.

For the quenching experiments of $^3C_{60}^*$ by electron donors, 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} (2.8×10^{-5} M) and electron donors at various concentrations. 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 electron donors. The Stern–Volmer relationship was obtained for the triplet decay rate constants (k_d) in the absence and presence of electron donors, and the concentrations of electron donors [D]. The quenching rate constants k_q were determined from the slope of a linear plot of k_d versus [D].

3.4. Quantum yield determinations

A standard actinometer (potassium ferrioxalate) [37] was used for the quantum yield determination of the photoreduction of C_{60} by electron donors. Square quartz cuvettes (10 mm i.d.) that contained a deaerated PhCN solution (3.0 cm^3) of C_{60} (3.0×10^{-4} M) with electron donors at various concentrations were irradiated with monochromatized light of $\lambda = 340$ nm from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, the actinometer and C_{60} absorbed essentially all the incident light of $\lambda = 340$ nm. The light intensity of monochromatized light of $\lambda = 340$ 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 reduced C_{60} adducts at 434 nm. In order to avoid the contribution of light absorption of the products, only the initial rates were determined for determination of the quantum yields.

3.5. Theoretical calculations

The theoretical studies were performed using the PM3 molecular orbital method [39]. The calculations were performed by using the MOL-GRAPH program Ver. 2.8 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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