Stepwise Bond Formation in Photochemical and Thermal Diels−Alder Reactions of C_{60} with Danishefsky's Dienes

Koichi Mikami,*,[†] Shoji Matsumoto,[†] Yasutaka Okubo,[†] Mamoru Fujitsuka,[‡] Osamu Ito,*,[‡] Tomoyoshi Suenobu,[§] and Shunichi Fukuzumi*,[§]

Contribution from the Department of Chemical Technology, Faculty of Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8552, Japan, Institute for Chemical Reaction Science, Tohoku University, Aoba-ku, Sendai 980-8577, Japan, and Department of Material and Life Science, Graduate School of Engineering, Osaka University, CREST, Suita, Osaka 565-0871, Japan

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Abstract: Mechanisms of both the photochemical and thermal Diels−Alder reactions of C_{60} with Danishefsky's dienes are studied on the basis of product stereochemistry, kinetics, and the detection of radical intermediates. A stereochemically defined (1*E*,3*Z*)-1-methoxy-2-methyl-3-[(trimethylsilyl)oxy]-penta-1,3-diene (**1a**) is used as a stereochemical probe in the Diels−Alder reactions with C_{60}. The major Diels−Alder product is *trans*-adduct (**3**) rather than *cis*-adduct (**4**) in both the photochemical and thermal Diels−Alder reactions. Such stereochemistry indicates that the Diels−Alder reactions proceed by a stepwise mechanism rather than a concerted mechanism. The transient spectra of $C_{60}^{\bullet-}$ formed in photoinduced electron transfer from **1a** to the triplet excited state of C_{60} ($^3C_{60}^*$) have been detected successfully in laser flash photolysis of the **1a**-C_{60} system. The observed rate constants determined from the dependence of the quantum yields on the concentrations of Danishefsky's dienes agree well with those for the photoinduced electron transfer from Danishefsky's dienes to $^3C_{60}^*$. Such an agreement together with the formation of *trans*-adduct (**3**) indicates that the photochemical Diels−Alder reaction proceeds via stepwise bond formation in the radical ion pair produced in the photoinduced electron transfer from Danishefsky's dienes to $^3C_{60}^*$. On the other hand, the rate constants for the thermal Diels−Alder reactions of Danishefsky's dienes are 10^{16} times larger than those expected for outer-sphere electron transfer from Danishefsky's dienes to C_{60}. Thus, a strongly unsymmetrical orbital interaction is required for the thermal Diels−Alder reaction to yield *trans*-adduct (**3**) which would not be produced by a concerted pathway.

Introduction

Since the preparation of fullerene (C_{60}) in synthetically useful quantities was established,[1] the chemistry of C_{60} has been rapidly explored to show a wide variety of reactivities.[2] Particularly, Diels−Alder reactions of C_{60} with Danishefsky's dienes[3] have been well-examined[4] for fullerene functionalization.[2] The Diels−Alder reactions of C_{60} are generally believed to proceed via a thermally allowed concerted (suprafacial) process or a photochemical concerted (antarafacial) process.[5] On the other hand, an alternative stepwise (open-shell) mechanism for the Diels−Alder reaction has recently merited increasing attention.[6−8] There have been some reports on an electron transfer with formation of radical ion pairs as primary step of the Diels−Alder reactions, followed by stepwise bond formation.[9,10] In particular Sustmann et al.[11] have reported stereochemical studies and observation of radical ions for [4+2]-cycloadditions of strong electron donor−acceptor pairs. There has been considerable interest in photocycloadditions via photoinduced electron transfer as a new potentially important pathway for controlling synthetic processes which cannot be exploited using a classical concerted pathway.[12,13] However, there has so far been no report on a thermal or photoinduced electron-transfer pathway in the

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* Author for correspondence.

[†] Tokyo Institute of Technology.

[‡] Tohoku University.

[§] Osaka University.

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solution phase fullerene Diels−Alder reaction. Although we have recently reported a solid-state photoinduced electron transfer in the fullerene Diels−Alder reaction with anthracenes,[14] the energetics for the photoinduced electron transfer in the solid state is quite different from that in solution where the solvent plays an important role.

We report herein the first definitive evidence for stepwise bond formation in both the photochemical and thermal Diels−Alder reactions of C_{60} with Danishefsky's diene (**1a**)[15] as a vinylogue of ketene silyl acetal (KSA).[16] In the case of the photochemical Diels−Alder reaction, the stepwise bond formation via a photoinduced electron transfer can be unequivocally shown by detection of the transient absorption spectrum of $C_{60}^{\bullet -}$ in the visible and near-IR region using laser flash photolysis combined with dependence of the quantum yields on the concentrations of Danishefsky's dienes. The fundamental electron-transfer properties of Danishefsky's dienes such as the one-electron oxidation potentials (E^0_{ox}) and the intrinsic barrier for the electron-transfer oxidation are also determined for the first time in this study. These data provide the energetic basis to evaluate the rate constants of thermal outer-sphere electron transfer from Danishefsky's dienes to C_{60}. Comparison of the rate constants for the thermal Diels−Alder reactions of C_{60} with Danishefsky's dienes and those expected for the outer-sphere electron transfer from Danishefsky's dienes to C_{60} provides valuable insight into stepwise bond formation in the thermal Diels−Alder reactions.

Results and Discussion

Photochemical Diels−Alder Reaction. The fullerene Diels−Alder reaction was examined with a stereochemically defined (1*E*,3*Z*)-1,4-disubstituted Danishefsky's diene (**1a**)[17] as a stereochemical probe. A mixture of C_{60} and **1a** in deaerated benzene was irradiated with high-pressure mercury lamp for 9 h at −30 °C when no thermal reaction would occur in the dark. Formation of the Diels−Alder adduct **2** was monitored on TLC [$R_f = 0.8$ (hexane/ethyl acetate = 4:1)]. After the treatment with triethylamine/SiO_2 suspension and purification by column chromatography, two desilylated adducts (**3** and **4**) were obtained through the Diels−Alder adduct (**2**) in 20 and 14% yield, respectively (Scheme 1). The product (**3**) was identified as *trans* with respect to the 1,4-substituents on the basis of the NOEs between MeO/H^4 (+5.2%) and MeO/Me (−2.4%). The other product (**4**) was deduced to be *cis* by the NOE between H^4/H^1 (+8.9%) (Scheme 1). The boat conformations of **3** and **4** were fully optimized by PM3 semiempirical calculations[18] (see Supporting Information). The 1,2-relationships of **3** and **4** were thus deduced to be *cis* and *trans* from the coupling constants, $^3J_{H1,H2} = 2.7$ and 11.4 Hz, respectively. The boat conformations of fullerene Diels−Alder products were determined by X-ray analysis.[19] The same *trans* product (**3**) was obtained as a single isomer in the photochemical reaction of C_{60} with **1a** after a short irradiation time when the thermal reaction was negligible (Table 1). This indicates that the *cis* adduct (**4**) obtained at the prolonged irradiation time may be formed via the isomerization from the *trans* adduct (**3**) (Table 1). When a mixture of C_{60} and **1a** in benzene was stirred for 6h, **3** and **4** were obtained in 36 and 33% yield, respectively, after treatment with triethylamine/SiO_2 suspension and purification by flash column chromatography

Scheme 1

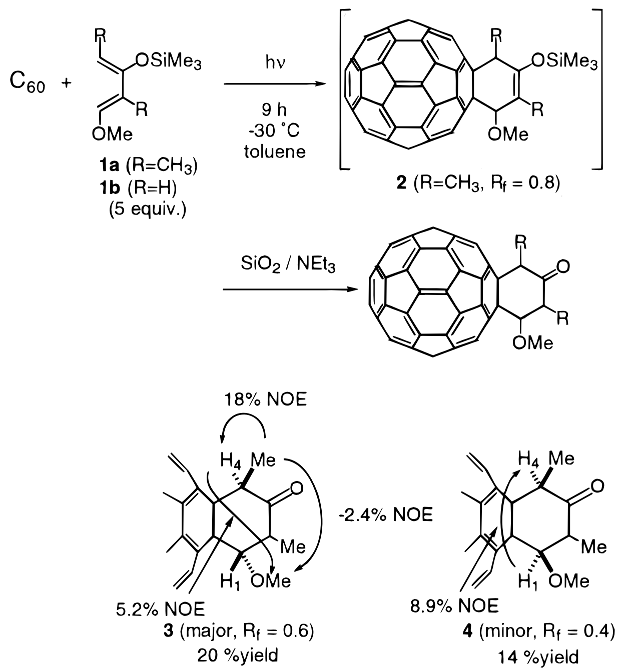

Table 1. Fullerene Diels−Alder Reaction with Danishefsky's Dienes

substrate	condition	time	**3** (major)[a]	**4** (minor)[a]
1a (R = Me)	dark, rt	30 min	5	1
		1 h	13 (27)	3 (6)
		6 h	36 (46)	33 (43)
	hν, rt	10 min	10	
		30 min	18 (27)	
	dark, -30 °C[b]	9 h	no reaction	
	hν, -30 °C[b]	9 h	20 (26)	14 (18)
1b (R = H)	dark, rt	6 h	24 (32)	
	hν, rt	6 h	19 (24)	

[a] Values in parentheses are based on recovery of C_{60}. [b] Toluene used as a solvent.

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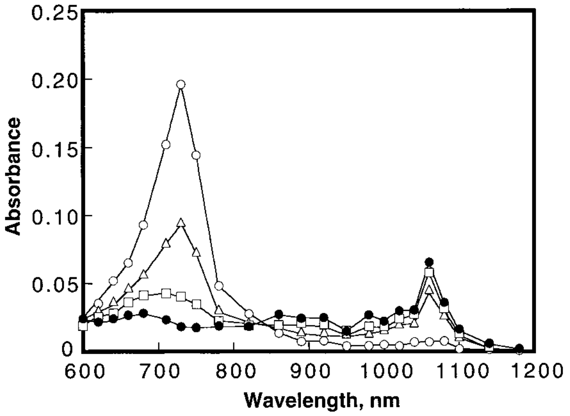

Figure 1. Transient absorption spectra observed in the photochemical Diels–Alder reaction of C_{60} (1.0×10^{-4} M) with **1a** (2.0×10^{-2} M) at 100 ns, 1 μs, 2 μs, and 4 μs after laser excitation in deaerated benzonitrile. Note that there is a clean isosbestic point with which the yield of $C_{60}^{\bullet-}$ can be obtained accurately.

(Table 1). Essentially the same products were obtained in reactions of C_{60} and **1a** in benzonitrile as well.

The transient absorption spectra of $C_{60}^{\bullet-}$ in the visible and near-IR region are observed by the laser flash photolysis of a deaerated benzonitrile solution of C_{60} in the presence of **1a** as shown in Figure 1, where the triplet–triplet absorption band of the triplet excited state of C_{60} ($^3C_{60}^*$) at 740 nm[20] appearing immediately after nanosecond laser exposure decays, accompanied by concomitant appearance of a new absorption band at 1080 nm which is diagnostic of $C_{60}^{\bullet-}$ as shown in Figure 1.[21]

The decay of the absorbance at 740 nm due to the triplet–triplet absorption of $^3C_{60}^*$ obeys pseudo-first-order kinetics, coinciding with a rise of the absorbance at 1080 nm due to $C_{60}^{\bullet-}$ as shown in Figure 2. The pseudo-first-order rate constant (k_d) for the decay of $^3C_{60}^*$ increases linearly with an increase in the concentration of **1a** (Figure 3).

These results show unequivocally that an electron transfer occurs from **1a** to $^3C_{60}^*$ to produce $C_{60}^{\bullet-}$.[22] The rate constant of electron transfer from **1a** to $^3C_{60}^*$ is determined from the linear plot of k_d vs [**1a**] as 3.6×10^7 M^{-1} s^{-1}.

The $C_{60}^{\bullet-}$ in the triplet radical ion pair produced in the photoinduced electron transfer from **1a** to $^3C_{60}^*$ is stable within the examined time scale in Figure 2. This indicates that the spin conversion is required prior to the back-electron transfer from $C_{60}^{\bullet-}$ to $\mathbf{1a}^{\bullet+}$ in the triplet radical ion pair to the singlet ground state.

One-Electron Oxidation Properties of Danishefsky's Dienes. Since direct electrochemical measurements of Danishefsky's dienes are complicated by the irreversible behavior seen with other organosilanes,[23] we have examined the rates of outer-sphere electron-transfer oxidation from which the fundamental one-electron oxidation properties can be deduced.

A number of rate constants (k_{et}) for photoinduced electron transfer from Danishefsky's dienes (**1a** and **1b**) to the singlet excited states of electron acceptors (9,10-dicyanoanthracene, 1-cyanonaphthalene, naphthalene, triphenylene, phenanthrene, and pyrene) and the triplet excited state of C_{60} are determined by fluorescence quenching and triplet quenching in deaerated acetonitrile and benzonitrile at 298 K, respectively. The k_{et} values and the known values of the one-electron reduction potentials (E^0_{red}) of the excited states[20,24] are listed in Table 2. The k_{et} values for both 1,4-disubstituted Danishefsky's diene **1a** (R=CH$_3$) and the parent Danishefsky's diene **1b** (R=H) in Table 2 increase with an increase in the E^0_{red} value of the oxidant reaching a diffusion-limited value, a typical feature of photoinduced electron-transfer processes.[25,26]

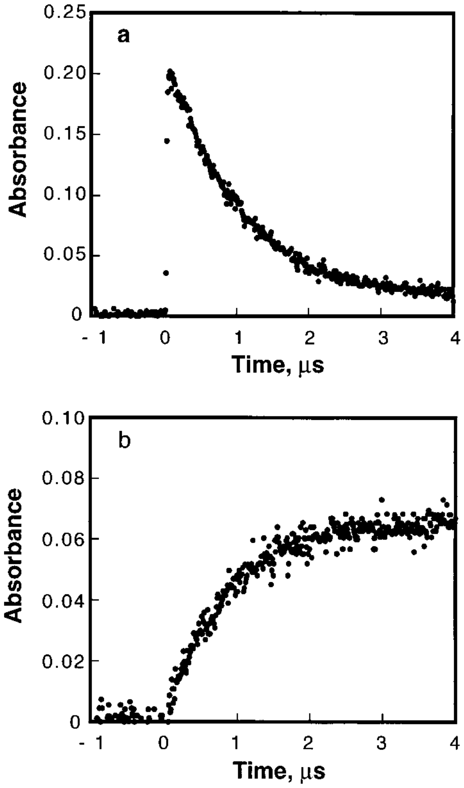

Figure 2. (a) Decay of the absorbance at 740 nm due to $^3C_{60}^*$ and (b) the rise of the absorbance at 1080 nm due to $C_{60}^{\bullet-}$ observed in the photochemical Diels–Alder reaction of C_{60} (1.0×10^{-4} M) with **1a** (2.0×10^{-2} M) after laser excitation in deaerated benzonitrile.

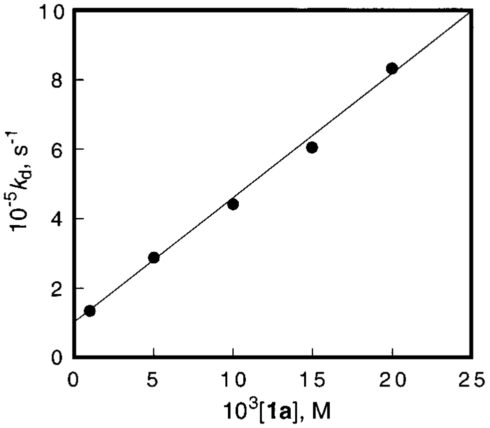

Figure 3. Plot of the pseudo-first-order rate constant (k_d) for the decay of $^3C_{60}^*$ vs [**1a**].

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Table 2. Observed Second-Order Rate Constants (k_{obs}) for Electron-Transfer Oxidation of **1a** and **1b** with One-Electron Oxidants in MeCN at 298 K, Maximum Fluorescence Wavelength (λ_{em}), Fluorescence Lifetime (τ), and One-Electron Reduction Potentials (E^0_{red}) of Oxidants[a]

no.	oxidant	λ_{em}, nm	τ, ns	E^0_{red} vs SCE, V	k_{obs}, $M^{-1}\ s^{-1}$	
					1a	**1b**
1	9,10-dicyanoanthracene*	442	15.3	1.91	1.4×10^{10}	1.3×10^{10}
2	1-cyanonaphthalene*	348	8.7	1.73	1.2×10^{10}	1.1×10^{10}
3	naphthalene*	338	105	1.46	5.4×10^{9}	3.5×10^{9}
4	triphenylene*	400	37	1.40	3.5×10^{9}	1.8×10^{9}
5	phenanthrene*	367	61	1.28	4.3×10^{8}	8.0×10^{7}
6	pyrene*	394	475	1.23	1.4×10^{8}	2.2×10^{7}
7[b]	$^3C_{60}$*		3.2×10^{4}	1.14	2.8×10^{7}	4.1×10^{6}

[a] Asterisk (*) denotes the excited state. [b] In PhCN.

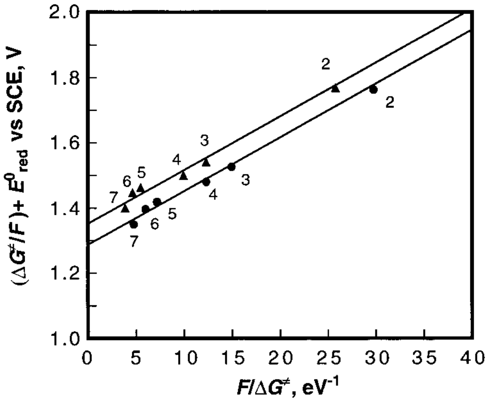

Figure 4. Plots of ($\Delta G^{\ddagger}/F$)+ E^0_{red} vs (F /$\Delta G^{\ddagger}$) for electron-transfer oxidation of Danishefsky's dienes **1a** (●) and **1b** (▲) with various photoexcited-state oxidants: (2) 1-cyanonaphtharene, (3) naphthalene, (4) triphenylene, (5) phenanthrene, (6) pyrene, and (7) C_{60} in deaerated acetonitrile (2−6) or benzonitrile (7) at 298 K.

The Gibbs activation energy of electron transfer ($\Delta G^{\ddagger}$) is obtained from the k_{et} value by eq 1

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

where Z is the collision frequency, taken as $1 \times 10^{11}\ M^{-1}\ s^{-1}$, k_{diff} is the diffusion rate constant taken as $2.0 \times 10^{10}\ M^{-1}\ s^{-1}$ in acetonitrile, and the other notations are conventional.[25,26] The dependence of $\Delta G^{\ddagger}$ on the Gibbs energy change of electron transfer (ΔG^0_{et}) has been well-established as given by eq 2[25]

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

where $\Delta G^{\ddagger}_0$ is the intrinsic barrier that represents the Gibbs activation energy when the driving force of electron transfer is zero, that is, $\Delta G^{\ddagger} = \Delta G^{\ddagger}_0$ at $\Delta G^0_{et} = 0$. On the other hand, the ΔG^0_{et} value is obtained from the one-electron oxidation potential of the Danishefsky's diene donor (E^0_{ox}) and the one-electron reduction potential of the excited state of the acceptor (E^0_{red}) by using eq 3, where F is the Faraday constant. From eqs 2 and 3 is derived a linear relation between $\Delta G^{\ddagger} + E^0_{red}$ and $(\Delta G^{\ddagger})^{-1}$ as shown in eq 4.[27]

$$\Delta G^0_{et} = F(E^0_{ox} - E^0_{red}) \qquad (3)$$

$$(\Delta G^{\ddagger}/F) + E^0_{red} = E^0_{ox} + (\Delta G^{\ddagger}_0/F)^2/(\Delta G^{\ddagger}/F) \qquad (4)$$

Figure 4 shows such linear plots of $\Delta G^{\ddagger} + E^0_{red}$ vs $(\Delta G^{\ddagger})^{-1}$ for photoinduced electron-transfer reactions of Danishefsky's dienes (**1a** and **1b**). According to eq 4, the intercept corresponds to the E^0_{ox} value of Danishefsky's diene and the $\Delta G^{\ddagger}_0$ value can be obtained from the slope. Thus, the unknown values of E^0_{ox} and $\Delta G^{\ddagger}_0$ can be determined from the intercept and slope of the plots of $\Delta G^{\ddagger} + E^0_{red}$ vs $(\Delta G^{\ddagger})^{-1}$ by using eq 4, respectively. The E^0_{ox} value of **1a** (1.29 V) is less positive than that of **1b** (1.36 V) due to the electron-donating effect of the methyl group of **1a**. The $\Delta G^{\ddagger}_0$ values (2.9 kcal mol^{-1}) of **1a** and **1b** are the same.

The ΔG^0_{et} value for photoinduced electron transfer from **1a** to $^3C_{60}$* is determined as 3.5 kcal mol^{-1} using eq 3. The equilibrium constant (K_{et}) for the photoinduced electron transfer at 298 K is then determined as 2.7×10^{-3} using the relation, $\Delta G^0_{et} = -RT \ln K_{et}$. Although the photoinduced electron transfer is endergonic ($K_{et} < 1$), the yield of $C_{60}^{\bullet-}$ in the presence of excess **1a** (2.0×10^{-2} M) is evaluated from the K_{et} value (2.7×10^{-3}) as 87 ± 9%,[28,29] which is consistent with the nearly quantitative formation of $C_{60}^{\bullet-}$ in Figure 2.

Stepwise Bond Formation via Photoinduced Electron Transfer. The quantum yields (Φ) were determined from an increase in absorbance due to the adduct formation by using a ferrioxalate actinometer[30] under irradiation of monochromatized light of $\lambda = 546$ nm. The Φ values for the photocycloaddition reaction of Danishefsky's dienes (**1a** and **1b**) to C_{60} in benzonitrile increases with an increase in the concentration of Danishefsky's dienes [**1**], reaching a limiting value (Φ_∞) as shown in Figure 5. In each case, the dependence of quantum yields on the concentrations of **1** is expressed by eq 5

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

which is rewritten as a linear correlation between Φ^{-1} vs $[\mathbf{1}]^{-1}$ (eq 6)

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

where K_{obs} is the quenching constant of the excited state of C_{60} by Danishefsky's dienes. The validity of eq 6 is confirmed by the plot of Φ^{-1} vs $[\mathbf{1}]^{-1}$ as shown in Figure 6. From the slope and the intercept are obtained the Φ_∞ and K_{obs} values: $\Phi_\infty = 0.042 \pm 0.004$ and 0.032 ± 0.003, $K_{obs} = (9.1 \pm 1.8) \times 10^2$ M^{-1} and $(1.3 \pm 0.3) \times 10^2$ M^{-1} for **1a** and **1b**, respectively.

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(26) (a) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425. (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(27) Fukuzumi, S.; Tanaka, T. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, pp 578−635.

(28) The yield of $C_{60}^{\bullet-}$ ($\alpha = [C_{60}^{\bullet-}]/[^3C_{60}^*]$) is obtained by the equilibrium equation, $K_{et}(1 - \alpha)[\mathbf{1a}]/[^3C_{60}^*] = \alpha^2$. The $[^3C_{60}^*]$ value is determined using the molar absorption coefficient ($\epsilon_{max} = 20\,200 \pm 2000$ M^{-1} cm^{-1}) reported by Bensasson et al.[29]

(29) Bensasson, R. V.; Hill, T.; Lambert, C.; Land, E. J.; Leach, S.; Truscott, T. G. *Chem. Phys. Lett.* **1993**, *201*, 326.

(30) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

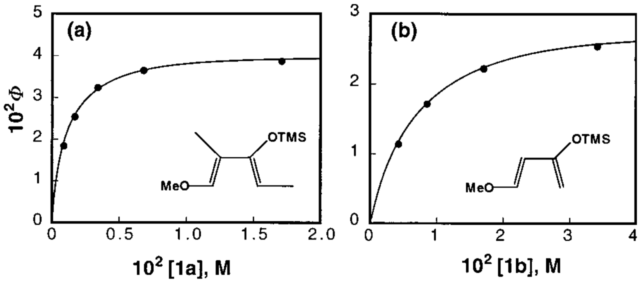

Figure 5. Dependence of the quantum yields (Φ) on the concentration of Danishefsky's dienes (a) [**1a**] and (b) [**1b**] for the photochemical Diels−Alder reaction of C_{60} (1.3×10^{-4} M) with Danishefsky's dienes (**1a** and **1b**) in deaerated benzonitrile at 298 K.

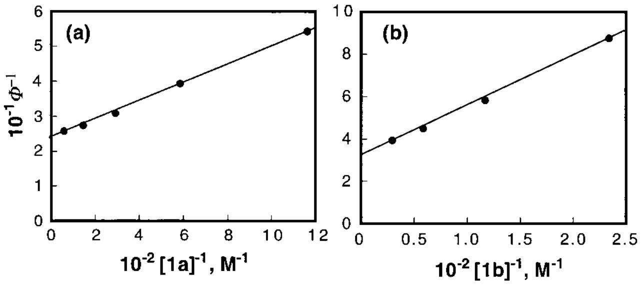

Figure 6. Plots of Φ^{-1} vs (a) [**1a**]$^{-1}$ and (b) [**1b**]$^{-1}$ for the photochemical Diels−Alder reaction of C_{60} (1.3×10^{-4} M) with Danishefsky's dienes (**1a** and **1b**) in deaerated benzonitrile at 298 K.

The quenching constant $K_{\rm obs}$ (= $k_{\rm obs}\tau_{\rm T}$) is converted to the corresponding rate constant ($k_{\rm obs}$) for the reaction of **1a** and **1b** with $^3C_{60}{}^*$ by using the triplet lifetime ($\tau_{\rm T}$) of $^3C_{60}{}^*$ (32 μs).[16b,31] The $k_{\rm obs}$ values thus obtained are given in Table 2. The $k_{\rm obs}$ value of **1a** ($(2.8 \pm 0.6) \times 10^7$ M^{-1} s^{-1}) agrees within experimental error with the $k_{\rm et}$ value ($(3.6 \pm 0.4) \times 10^7$ M^{-1} s^{-1}) determined directly by the decay of $^3C_{60}{}^*$ and the formation of $C_{60}{}^{\bullet-}$ (Figure 2). In addition, the $k_{\rm obs}$ value of **1a** fits in the linear plot for the photoinduced electron-transfer reactions of **1a** in Figure 4. The $k_{\rm obs}$ value of **1b** also fits in the plot for the photoinduced electron-transfer reactions of **1b** in Figure 4. Thus, the photochemical Diels−Alder reaction proceeds via photoinduced electron transfer from **1** to $^3C_{60}{}^*$ as shown in Scheme 2.

The photoinduced electron transfer from **1a** to $^3C_{60}{}^*$ ($k_{\rm et}$) gives the triplet radical ion pair (**A**) in competition with the decay to the ground state ($k_{\rm T} = \tau_{\rm T}{}^{-1}$). The triplet radical ion pair then provides the singlet radical ion pair to give a diradical intermediate (**B**) or a zwitterionic intermediate (**C**) ($k_{\rm p}$) in competition with the back-electron transfer to the reactant pair ($k_{\rm b}$). The PM3 semiempirical calculation of **1a**$^{\bullet+}$ with the full structural optimization indicates that the positive charge density is the largest on the carbon (C-1) next to the methoxy group and that the unpaired electron density is the largest on the terminal carbon (C-4). Thus, in the case of the diradical pathway (**B**) in Scheme 2, the initial C−C bond formation should occur between C-1 carbon of **1a**$^{\bullet+}$ and $C_{60}{}^{\bullet-}$, while it occurs between C-4 of **1a**$^{\bullet+}$ and $C_{60}{}^{\bullet-}$ in the case of the zwitterion pathway (**C**). At present, however, it is difficult to distinguish the two pathways. In any case, the bond formation occurs stepwise, and thus there is no symmetry restriction for bond formation. The PM3 calculation gave the heat of formation of **3** (705.9 kcal mol^{-1}*), which is about the same as that of* **4** (706.2 kcal mol^{-1}) as shown in the Supporting Information. Thus, both *trans*-adduct **3** and *cis*-adduct **4** were obtained as the final products.

Stepwise Bond Formation in the Thermal Diels−Alder Reaction. The *trans* product is also obtained as the primary product in the thermal reaction, while the *trans*/*cis* ratio decreases with prolonged reaction time in the dark (Table 1). The *trans* product (**3**) could have arisen only via a stepwise bond formation, since it *cannot* be obtained in a thermal concerted process because of the orbital symmetry constraint. Formation of the same *trans* product (**3**) in the thermal reaction as that obtained in the photochemical reaction (Scheme 2), suggests that the thermal reaction also proceeds via electron transfer from **1** to C_{60}. The rate constant for electron transfer from **1** to C_{60} can be estimated from the Gibbs energy relation between log $k_{\rm et}$ and $\Delta G^0{}_{\rm et}$ as shown in Figure 7, which includes the data in Table 2. The solid line in Figure 7 is based on eqs 1 and 2. The $\Delta G^0{}_{\rm et}$ values for electron transfer from **1a** and **1b** to C_{60} are obtained from the $E^0{}_{\rm ox}$ values of **1a** (1.29 V) and **1b** (1.36 V), both of which are determined from the plots in Figure 4 and the $E^0{}_{\rm red}$ value of C_{60} (−0.43 V)[32] using eq 3. The $\Delta G^{\ddagger}{}_0$ value for the electron self-exchange reaction of $C_{60}/C_{60}{}^{\bullet-}$ has recently been determined as 3.7 kcal mol^{-1}.[33] The $\Delta G^{\ddagger}{}_0$ values for photoinduced electron transfer from **1a** and **1b** to the excited states of aromatic compounds are 2.9 kcal mol^{-1} as determined in the plots in Figure 4. Then, the $\Delta G^{\ddagger}{}_0$ value for electron transfer from **1** to C_{60} can be obtained as the average of these two values, that is, 3.3 kcal mol^{-1}. From these $\Delta G^0{}_{\rm et}$ and $\Delta G^{\ddagger}{}_0$ values are calculated the rate constant of electron transfer ($k_{\rm et}$) from **1a** and **1b** to C_{60} using eqs 1 and 2 as 5.2×10^{-19} and 3.4×10^{-20} M^{-1} s^{-1}, respectively. Such small $k_{\rm et}$ values indicate that essentially no thermal electron transfer from **1a** or **1b** to C_{60} occurs.

The rates of thermal Diels−Alder reactions of **1a** and **1b** with C_{60} were determined by monitoring the increase in the adduct absorbance. The rates obey pseudo-first-order kinetics under experimental conditions where the diene concentration is greater than a 10-fold excess of the C_{60} concentration. The pseudo-first-order rate constants (k_1) increase proportionally with increasing the diene concentration (Figure 8). The second-order rate constants of **1a** and **1b** ($k_{\rm obs}$) are obtained from the slopes of the linear plots as 4.7×10^{-2} and 4.1×10^{-2} M^{-1} s^{-1}, respectively. These $k_{\rm obs}$ values are more than 10^{16} times larger than the predicted $k_{\rm et}$ values for electron transfer from **1a** and **1b** to C_{60} as shown in Figure 7. Such a huge difference between the $k_{\rm obs}$ and $k_{\rm et}$ values clearly indicates that the thermal Diels−Alder reaction proceeds by a strong orbital interaction between Danishefsky's dienes and C_{60} rather than by the electron transfer in which little interaction is required. The question that must be addressed is why the *trans*-adduct **3**, which would not be produced by a concerted HOMO−LUMO interaction, is obtained as the primary product.

The optimized geometry and the HOMO orbital are calculated with density functional theory at the Becke3LYP/6-31G* level[34,35] which has been successfully used to predict geometries and energies for some Diels−Alder reactions.[8] The result is shown in Figure 9 where the two double bonds of **1a** are twisted (part a) and the two pπ HOMO orbitals at C1 and C4 positions are not coplanar (part b, where the angle between the two pπ HOMO orbitals is 41°). The corresponding torsion angle of **1b** becomes slightly smaller (33.2°). Essentially the same result

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[31] Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **1998**, *120*, 8060.

[32] Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.

[33] Fukuzumi, S.; Nakanishi, I.; Suenobu, T.; Kadish, K. M. *J. Am. Chem. Soc.* **1999**, *121*, 3468.

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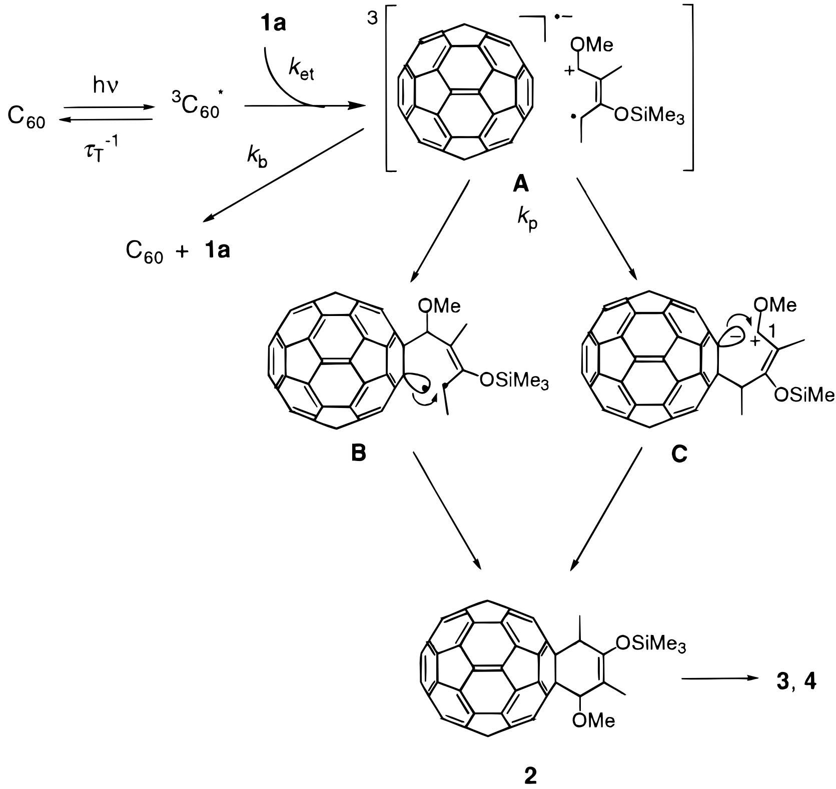
[35] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

Scheme 2



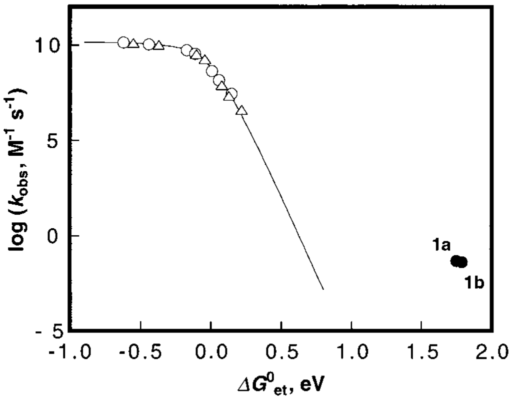


Figure 7. Dependence of log k_{obs} on ΔG^0_{et} for the electron-transfer oxidation of Danishefsky's dienes **1a** (○) and **1b** (△) with various one-electron oxidants as compared to the thermal Diels–Alder reaction of **1a** and **1b** (●) with C_{60} in deaerated acetonitrile or benzonitrile at 298 K. The solid line is drawn according to eqs 1 and 2, using the E^0_{ox} values and the averaged $\Delta G^{\ddagger}_0$ value (2.9 kcal mol^{-1}).

was obtained by a PM3 calculation.[36] It is therefore not surprising that there is a strongly unsymmetrical orbital interaction between Danishefsky's dienes and C_{60}, resulting in stepwise bond formation to yield the *trans*-adduct (**3**) as well as the *cis*-adduct (**4**).

Summary

In summary, we have shown a stepwise bond-forming process via an electron transfer in the fullerene [60] Diels–Alder reaction with Danishefsky's diene which has so far been generally regarded as a concerted process. A stereochemically defined (1*E*,3*Z*)-1,4-disubstituted Danishefsky's diene **1a** (R=

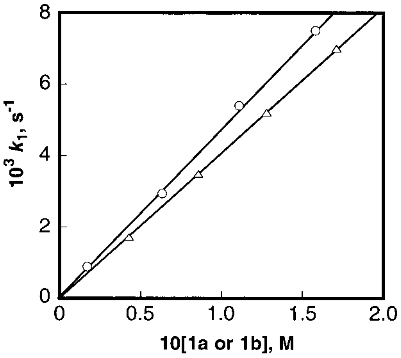


Figure 8. Plots of pseudo-first-order rate constant (k_1) vs [**1a** or **1b**] in the thermal Diels–Alder reaction of C_{60} (1.3×10^{-4} M) with **1a** (○) or **1b** (△) in deaerated benzonitrile at 298 K.

CH_3) was used as a stereochemical probe in both thermal and photochemical Diels–Alder reactions. The major Diels–Alder adduct is the *trans*-diastereomer (**3**), thus indicating that the Diels–Alder reactions proceed by a stepwise mechanism, which is likely to involve electron transfer from **1a** to C_{60} under photochemical conditions. The transient spectra of $C_{60}^{\bullet -}$, formed in the photoinduced electron transfer from **1a** to the triplet excited state of C_{60} ($^3C_{60}^*$) have been detected successfully in a laser flash photolysis of the **1a**-C_{60} system. The observed rate constant agrees well with the predicted rate constant on the basis of the electron-transfer mechanism. More significantly, the rate constants for the thermal Diels–Alder reactions of Danishefsky's dienes are 10^{16} times larger than those expected for ground-state electron transfer from Danishefsky's dienes to C_{60}. Thus, a strongly unsymmetrical orbital interaction is required for the stepwise thermal Diels–Alder reaction to yield *trans*-adduct (**3**), which would not be expected from a concerted pathway.

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(36) The angle between the two pπ HOMO orbitals of **1a** calculated by the PM3 method becomes even larger (70°) as compared to the DFT calculation.

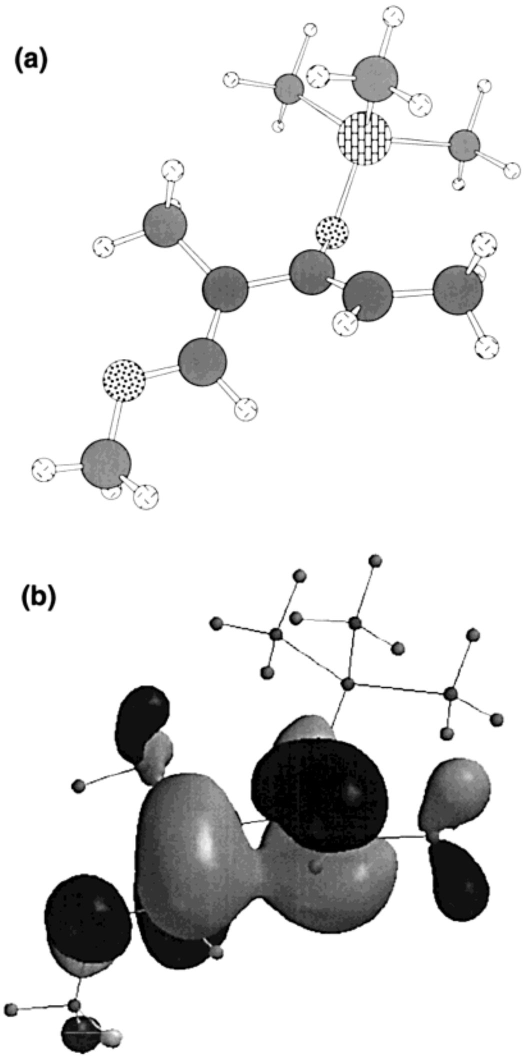
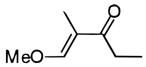


Figure 9. (a) Becke3LYP/6-31G* optimized structure of **1a** and (b) the HOMO orbital.

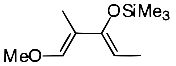
Experimental Section

General. ^{1}H and ^{13}C NMR spectra were measured on a Varian GEMINI 300 (300 MHz) spectrometers. 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) was performed on a glass plate precoated with silica gel (Merck Kieselgel 60 F_{254}, layer thickness 0.25 mm). Silica gel chromatography was performed on a Silica Gel 60 (70−230 mesh) purchased from Kanto Chemical Co., Inc. All experiments were carried out under nitrogen or argon atmosphere unless otherwise noted. Hexane and ethyl acetate were purchased from Kanto Chemical Co., Inc. Benzene was distilled from sodium benzophenone ketyl under argon atmosphere.

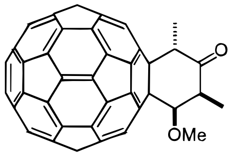
Preparation of Danishefsky's Diene (1a). (*E*)-1-Methoxy-2-methyl-1-penten-3-one. A 1-L, three necked, round-bottomed flask equipped with a mechanical stirrer, calcium sulfate drying tube, and 100-mL dropping funnel was charged with benzene (280 mL), 55% NaH dispersion (13.3 g, 305 mmol) and MeOH (0.3 mL, 7.4 mmol). The flask was immersed in an ice bath, and the dropping funnel was charged with a mixture of 3-pentanone (31.9 mL, 300 mmol) and ethyl formate (24.1 mL, 300 mmol). The mixture was added dropwise to the cooled, stirred suspension over 1.5 h. During the addition, there was a visible evolution of gas, and a paste-like precipitate formed. After stirring for 1 h at room temperature, the reaction mixture was then diluted with Et_2O. The suspension was filtered and washed with Et_2O to give crude sodium salt of 1-hydroxy-2-methyl-1-penten-3-one. Then, the solution of sodium salt obtained as above in water (225 mL) was acidified to pH = 5 by dropwise addition of concentrated HCl. The resultant two-phase mixture was separated and extracted with Et_2O. The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure to give crude 1-hydroxy-2-methyl-1-penten-3-one. To a solution of 1-hydroxy-2-methyl-1-penten-3-one in benzene (150 mL) was added a 60:40 mixture of benzene/MeOH (75 mL) and *p*-toluenesulfonic acid monohydrate (140 mg, 0.74 mmol). The dropping funnel was charged with a 60:40 benzene/MeOH (75 mL). The stirred solution was warmed to a gentle reflux at which time the solution began to darken to a light brown color. The distillation temperature was raised to 59 °C (the boiling point of the benzene/MeOH azeotrope) and stabilized. The distillate volume was monitored throughout the course of the reaction. When 40 mL of distillate was collected, the reaction vessel was replenished with 40 mL of fresh benzene/MeOH mixture. This cycle was repeated until the starting material was consumed. At this time any residual benzene/MeOH mixture in the dropping funnel was discarded, and the funnel was charged with benzene (75 mL). The reaction volume was maintained by the addition of benzene as the boiling point of the distillate rose to 79 °C. In this way, a total of 120 mL of benzene was distilled out of the reaction mixture as the reaction was driven to completion. The reaction mixture was allowed to cool to room temperature and quenched by the addition of aqueous $NaHCO_3$ solution. The resultant two-phase mixture was separated and extracted with Et_2O. The combined organic layer was dried over Na_2SO_4 and distilled under reduced pressure (62 °C/6 mmHg) to give (*E*)-1-methoxy-2-methyl-1-penten-3-one in 63% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (t, $J = 7.4$ Hz, 3H), 1.71 (d, $J = 1.2$ Hz, 3H), 2.52 (q, $J = 7.4$ Hz, 2H), 3.85 (s, 3H), 7.23 (q, $J = 1.2$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.4, 9.0, 30.5, 61.3, 117.0, 159.3, 200.9.



(1*E*,3*Z*)-1-Methoxy-2-methyl-3-[(trimethylsilyl)oxy]-penta-1,3-diene (1a). To a solution of (*E*)-1-methoxy-2-methyl-1-penten-3-one (6.4 g, 49.9 mmol) and triethylamine (17 mL, 122 mmol) in Et_2O (30 mL) was added trimethylsilyl trifluoromethanesulfonate (9.69 mL, 49.9 mmol) at 0 °C. After stirring for 3 h, the organic layer was poured into saturated $NaHCO_3$ solution and extracted with Et_2O. The combined organic layer was washed with brine and dried over Na_2SO_4. The solution was filtered and distilled under reduced pressure (65 °C/6 mmHg) to give (1*E*,3*Z*)-1-methoxy-2-methyl-3-[(trimethylsilyl)oxy]-penta-1,3-diene in 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.20 (s. 9H), 1.64 (d, $J = 6.9$ Hz, 3H), 1.66 (d, $J = 1.3$ Hz, 3H), 3.63 (s, 3H), 4.73 (q, $J = 6.9$ Hz, 1H), 6.32 (q, $J = 1.3$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.5, 10.2, 11.5, 60.0, 101.8, 112.9, 145.6, 150.0.

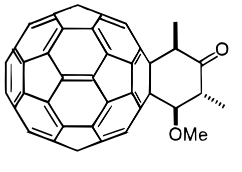


Procedure for the Fullerene Diels−Alder Reactions with Dimethyl Danishefsky's Diene To a solution of C_{60} (10 mg, 0.0139 mmol) in deaerated benzene (10 mL) was added (1*E*,3*Z*)-1-methoxy-2-methyl-3-[(trimethylsilyl)oxy]-penta-1,3-diene (**1a**, 13.7 mg, 0.0683 mmol), and the reaction mixture was either irradiated with a high-pressure mercury lamp or stirred in the dark. The reaction mixture was poured into a suspension of silica gel (∼3 g) in hexane (20 mL) and ethyl acetate (5 mL) with triethylamine (2 mL). After stirring for 30−50 min, the reaction mixture was concentrated under reduced pressure. The residue was separated by flash silica gel chromatography (hexane, then hexane/ethyl acetate = 40:1−5:1 and triethylamine as an additive) to give the desilylated Diels−Alder adducts.



***trans*-Adduct (3):** ^{1}H NMR (300 MHz, C_6D_6) δ 1.57 (d, $J = 7.2$ Hz, 3H), 1.89 (d, $J = 6.6$ Hz, 3H), 3.43 (s, 3H), 3.68 (dq, $J = 2.7$, 7.2

Hz, 1H), 4.62 (d, $J = 2.7$ Hz, 1H), 5.12 (q, $J = 6.6$ Hz, 1H). ^{13}C NMR (75 MHz, C_6D_6) δ 209.41 (C═O), 155.73, 155.23, 155.13, 154.78, 147.97, 147.92, 147.74, 147.11, 146.92, 146.84, 146.66, 146.61, 146.53, 145.85, 145.80 (br), 147.72 (br), 145.69, 145.30, 144.96, 144.90, 143.63, 143.05, 143.00, 142.58, 142.42, 142.26 (br), 142.21, 142.03, 141.95, 141.92, 141.81, 141.72, 141.69 (br), 140.75, 140.61, 139.35, 139.27, 138.30, 136.79, 136.48, 135.33, 134.74, 92.40 (C_{60}−*C*−OMe), 70.26, 67.10, 62.94 (OMe), 50.18 (C_{60}−*C*(Me)−C═O), 47.71 (O═C−*C*(Me)−C(OMe)), 13.80, 13.48. UV−vis (λ_{max}, $CHCl_3$) 701, 433, 370 nm. FAB-MS m/z = 849 ([M + H]$^+$), 848 ([M]$^+$), 720 ([M − $C_7H_{12}O_2$]$^+$). HRMS for $C_{67}H_{12}O_2$ calcd 848.0837, found 848.0855.



***cis*-Adduct (4):** ^{1}H NMR (300 MHz, C_6D_6/CS_2) δ 1.61 (d, $J = 6.9$ Hz, 3H), 1.74 (d, $J = 6.9$ Hz, 3H), 3.41 (dq, $J = 11.4$, 6.9 Hz, 1H), 3.66 (s, 3H), 4.20 (q, $J = 6.9$ Hz, 1H), 4.92 (d, $J = 11.4$ Hz, 1H). (in C6D6) δ 1.55 (d, $J = 6.9$ Hz, 3H), 1.77 (d, $J = 6.9$ Hz, 3H), 3.36 (s, 3H), 3.50 (dq, $J = 11.4$, 6.9 Hz, 1H), 3.73 (q, $J = 6.9$ Hz, 1H), 4.54 (d, $J = 11.4$ Hz, 1H). ^{13}C NMR (75 MHz, C_6D_6/CS_2) δ 207.49 (C═O), 154.58, 153.83, 152.46, 152.02, 148.90, 147.91, 147.77, 147.56, 146.86, 146.83, 146.80, 146.75, 146.70, 146.57 (br), 146.51, 146.47, 146.43, 146.13, 146.10, 145.79 (thresh high), 145.75 (br), 145.68, 145.62, 145.57, 145.03, 144.87, 144.84, 144.71, 143.37, 143.09, 143.04, 142.98, 142.67, 142.56 (br), 142.48, 142.03, 141.96, 141.80, 141.75 (br), 141.16, 140.10, 139.52, 139.31, 136.11, 136.06, 134.94, 134.70, 86.91 (C_{60}-*C*-OMe), 70.25, 67.16, 63.08 (OMe), 50.89 (C_{60}−*C*(Me)−C═O), 49.03 (O═C−*C*(Me)−C(OMe)), 14.94, 13.84. UV−vis (λ_{max}, $CHCl_3$) 696, 431, 381 nm. FAB-MS m/z = 849 ([M + H]$^+$), 848 ([M]$^+$), 720 ([M − $C_7H_{12}O_2$]$^+$). HRMS for $C_{67}H_{12}O_2$ calcd 848.0837, found 848.0817.

Procedure for the Fullerene Diels−Alder Reactions with Parent Danishefsky's Diene To a solution of C_{60} (10 mg, 0.0139 mmol) in deaerated benzene (10 mL) was added (*E*)-1-methoxy-3-[(trimethylsilyl)oxy]-buta-1,3-diene (**1b**, 11.8 mg, 0.0683 mmol), and irradiated with high-pressure mercury lamp or stirred in the dark. The reaction mixture was treated by the same workup procedure in the reaction with dimethyl Danishefsky's diene to give the Diels−Alder product.[4c]

Laser Flash Photolysis. A deaerated benzonitrile solution of C_{60} (1.0×10^{-4} M) and **1a** (2.0×10^{-2} M) was excited by a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 532 nm with the power of 32 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 mm × 10 mm) and a monochromator. The output from the Ge-APD module was recorded with a digitizing oscilloscope (Hewlett-Packard 54510B, 300 MHz). Since the purple solution of C_{60} in benzonitrile disappeared by each laser shot (532 nm, 32 mJ) in the presence of **1a**, 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 **1a**, the irradiation laser wavelength of C_{60} was 532 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 benzonitrile solutions containing C_{60} (1.0×10^{-4} M) and **1a** 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 **1a**. The pseudo-first-order relation was obtained for the triplet decay rate constants (k_d) in the absence and presence of **1a**, and the concentrations of **1a**. The quenching rate constants k_q were determined from the slope of a linear plot of k_d vs [**1a**].

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[30] was used for the quantum yield determination of the photoinduced Diels−Alder reaction of C_{60} with **1**. Square quartz cuvettes (10 mm i.d.) which contained a deaerated benzonitrile solution (3.0 cm^3) of C_{60} (1.3×10^{-4} M) with **1** at various concentrations ($8.6 \times 10^{-4} - 1.7 \times 10^{-2}$ M) were irradiated with monochromatized light of $\lambda = 546$ nm from a Shimadzu RF-5000 fluorescence spectrophotometer. The light intensity of monochromatized light of $\lambda = 546$ nm was determined as 4.99×10^{-9} einstein s^{-1} with the slit width of 5.0 nm. The photochemical reaction was monitored by means of a Hewlett-Packard 8453 diode-array spectrophotometer. Since the thermal cycloaddition reactions of C_{60} (1.3×10^{-4} M) with **1a** as well as **1b** proceed slowly at 298 K, the quantum yields for certain concentrations of **1a** or **1b** were determined from the increase in absorbance due to photochemically produced C_{60} adducts at 434 nm ($\epsilon_{max} = 3.7 \times 10^3$ M^{-1} cm^{-1} in benzonitrile) by subtracting the small change in the absorbance due to the thermal reaction from the total absorbance change. To avoid the contribution of light absorption of the products, only the initial rates were determined for determination of the quantum yields.

Kinetic Measurements. The kinetic measurements were performed using Hewlett-Packard 8452A or 8453 diode array spectrophotometers which were thermostated at 298 K. Rates of Diels−Alder reactions of Danishefsky's dienes with C_{60} in deaerated benzonitrile at 298 K were monitored by following an increase in absorbance due to the adducts at 434 nm ($\epsilon_{max} = 3.7 \times 10^3$ M^{-1} cm^{-1} in benzonitrile) under pseudo-first-order conditions where the diene concentrations were maintained at more than 10-fold excess of the C_{60} concentration (1.3×10^{-4} M). The pseudo-first-order plots were linear for three or more half-lives with a correlation coefficient greater than 0.999.

Theoretical Calculations. Theoretical calculations were performed by means of the MOPAC program (version 6) which is incorporated in the MOLMOLIS program by Daikin Industries, Ltd. The PM3 Hamiltonian was used for the semi-empirical MO calculations.[18] Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The heats of formation (ΔH_f) were calculated with the restricted Hartree−Fock (RHF) formalism using a key word "PRECISE". The density-functional theory (DFT) calculations were performed at the Becke3LYP/6-31G* level[34,35] with GAUSSIAN 94.[37]

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Supporting Information Available: The optimized structures and heat of formation of **3** and **4** calculated by the PM3 method (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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