Photosensitized Electron-Transfer Reactions of 1-Isopropylidene-2-methylene-3,3-diphenylcyclobutane − [4 + 4] Cycloaddition and Cyclodimerization Initiated by a Buta-1,3-diene Radical Cation Functionality

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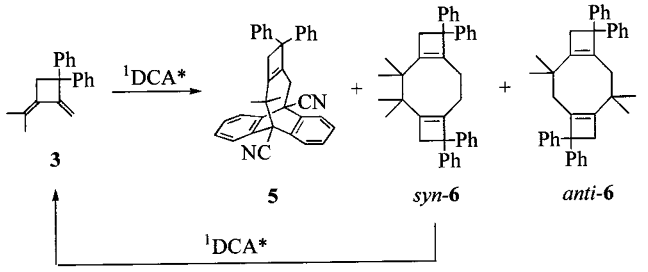
Keywords: Cycloadditions / Electron transfer / Photochemistry / Radical ions / Reaction mechanisms

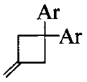
The 9,10-dicyanoanthracene-photosensitized (DCA-photosensitized) electron-transfer reaction of 1-isopropylidene-2-methylene-3,3-diphenylcyclobutane (**3**) gives a mixture of the [4 + 4] DCA adduct (**5**) and two [4 + 4] cyclodimers (*syn*-**6** and *anti*-**6**), demonstrating that **3**$^{\cdot+}$ functions as a buta-1,3-diene radical cation with its SOMO in a mainly localized state.

Introduction

We have investigated electron-transfer photoreactions of diaryl-substituted methylenecyclobutanes in terms of the structure and reactivity of methylenecyclobutane radical cations and observed that substitution effects are important for the reactivity of methylenecyclobutane radical cations. 3,3-Diaryl-1-methylenecyclobutane radical cation (**1**$^{\cdot+}$), for instance, undergoes a degenerate rearrangement involving an allylic-stabilized 1,4-radical cation intermediate (**2**$^{\cdot+}$),[1,2] whereas 2,2-diaryl-1-methylenecyclobutane[3] and 1-(diarylmethylene)cyclobutane[3] exhibit dissimilar reactivities under these photosensitized conditions. In an extension of our studies, we investigated the 9,10-dicyanoanthracene (DCA) sensitized electron-transfer photoreactions of 1-isopropylidene-2-methylene-3,3-diphenylcyclobutane (**3**), expecting that **3**$^{\cdot+}$ would behave like **1**$^{\cdot+}$ and form the tetramethyleneethane radical cation derivative (**4**$^{\cdot+}$). Contrary to our expectations, radical cation **3**$^{\cdot+}$ did not behave like **1**$^{\cdot+}$, but acted as a buta-1,3-diene radical cation. Here we report the [4 + 4] cycloaddition of **3** with DCA in detail, together with its [4 + 4] cyclodimerization under photosensitized electron-transfer (PET) conditions (Scheme 1).



Scheme 1



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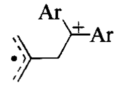
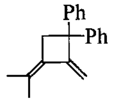


2$^{\cdot+}$



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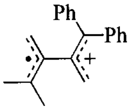
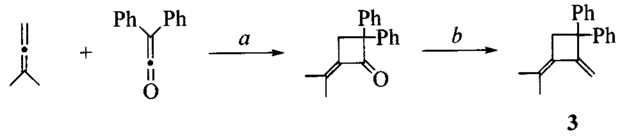


4$^{\cdot+}$

Results and Discussion

Synthesis and Electron-Donating Properties of 3

1-Isopropylidene-2-methylene-3,3-diphenylcyclobutane (**3**) was prepared in good yield by methylenation of 2-isopropylidene-4,4-diphenylcyclobutan-1-one,[4] obtained from 3-methylbuta-1,2-diene[5] and diphenylketene,[6] using µ-chloro-µ-methylene[bis(cyclopentadienyl)titanium]dimethylaluminum (Tebbe reagent) as shown in Scheme 2. The half-wave oxidation potential ($E_{1/2}^{\mathrm{ox}}$) of **3** is low enough to quench the excited state of DCA (^{1}DCA*) exergonically, as suggested by the calculated free energy changes (ΔG_{et}) for electron transfer shown in Table 1. In agreement with the calculation, **3** quenches the DCA fluorescence efficiently in aerated acetonitrile, dichloromethane, and benzene. The values of $E_{1/2}^{\mathrm{ox}}$, ΔG_{et}, and rate constants (k_{q}) for DCA fluorescence quenching by **3** are shown in Table 1.



Scheme 2. *a)* Room temperature, neat. − *b)* µ-chloro-µ-methylene-[bis(cyclopentadienyl)titanium]dimethylaluminum, THF

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Table 1. Oxidation potentials ($E^{\mathrm{ox}}_{1/2}$), free energy changes (ΔG_{et}), and quenching rate constants (k_q) associated with electron-transfer reactions of **3**, **5**, *syn*-**6**, and *anti*-**6**, with ^{1}DCA* in various solvents

Substrate	Solvent	$E^{\mathrm{ox}}_{1/2}$ [a] [V vs. SCE]	ΔG_{et}[b] [eV]	k_q [10^{10} M^{-1}s^{-1}]
3	CH_3CN	+1.51	−0.45	1.1
	CH_2Cl_2	+1.65	−0.56	1.0
	C_6H_6	–	–	0.23
5	CH_2Cl_2	>2.00	–	[c]
syn-**6**	CH_2Cl_2	+1.85	−0.36	ca. 0.1
anti-**6**	CH_2Cl_2	+1.96	−0.02	[c]

[a] In CH_3CN containing 0.1 M $Et_4N^+\ ClO_4^-$ or in CH_2Cl_2 containing 0.1 M $n\mathrm{Bu}_4N^+\ BF_4^-$. – [b] $\Delta G_{\mathrm{et}} = E^{\mathrm{ox}}_{1/2}(\mathrm{substrate}) - E^{\mathrm{red}}_{1/2}(\mathrm{DCA}) - E_{0-0} - e^2/\varepsilon r$, where $E^{\mathrm{red}}_{1/2}$(DCA) are −0.95 and −0.89 V vs. SCE in CH_3CN and CH_2Cl_2, respectively, and E_{0-0} are 2.91 and 2.87 eV in CH_3CN and CH_2Cl_2, respectively. The Coulombic term ($e^2/\varepsilon r$) is disregarded in CH_3CN and is 0.23 eV in CH_2Cl_2. – [c] No attempt.

DCA-Sensitized Photoreactions of 3 in Degassed Solvents

Upon irradiation ($\lambda > 360$ nm) of a degassed benzene, dichloromethane, or acetonitrile solution containing **3** and DCA, the [4 + 4] DCA adduct (**5**, Scheme 1) and two isomeric [4 + 4] cyclodimers (*syn*-**6** and *anti*-**6**) were formed in the yields shown in Table 2. The structures of **5**, *syn*-**6**, and *anti*-**6** were determined by X-ray crystallographic analyses, as shown in Figure 1. Interestingly, the yields of **5**, *syn*-**6**, and *anti*-**6** depended significantly both upon solvent polarity and on concentration of **3**. At low concentrations of **3** (0.01 M), as shown in Table 2, the DCA adduct **5** is formed exclusively in the nonpolar benzene, whereas in moderately polar dichloromethane and polar acetonitrile, the relative yields of *syn*-**6** and *anti*-**6** increase, although the total yield of cycloadducts is poor. At high concentrations of **3** (0.1 M), on the other hand, the yield of *syn*-**6** as a major cyclodimer is significantly higher in dichloromethane or acetonitrile, while in benzene **5** is slowly formed, still as the sole product. The fact that no formation of *syn*-**6** and *anti*-**6** is observed in electron-transfer photoreactions of **3** in benzene thus clearly indicates that the formation of **5** is the sole process in nonpolar benzene. The observed results strongly suggest that the DCA adduct **5** is formed through a radical ion-pair [$\mathbf{3}^{\cdot+}$/DCA$^{\cdot-}$] or an exciplex [$\mathbf{3}^{\delta+}$/DCA$^{\delta-}$], especially in nonpolar benzene, whereas the cage-escaped free radical cation $\mathbf{3}^{\cdot+}$ is a key intermediate for the formation of the [4 + 4] cyclodimers *syn*-**6** and *anti*-**6** in dichloromethane and acetonitrile. The fact that a weak and broad, but new, emission band with $\lambda_{\max}$ at 526 nm was observed in the DCA fluorescence quenching by **3** (0.15 M) in benzene (Figure 2) supports the intermediacy of the exciplex.

Table 2. DCA-Sensitized photoreactions of **3** in degassed solvents

[**3**] and [DCA] [M]	Solvent	Time [min]	Con. [%][a]	Yield [%] **5**	*syn*-**6**	*anti*-**6**
0.01[b]	C_6H_6	30	43	43	0	0
		120	96	90	0	0
	CH_2Cl_2	30	55	5	36	3
		120	69	17	9	4
	CH_3CN	15	55	0	16	2
		30	69	4	2	2
		120	89	5	1	2
0.1[b]	C_6H_6	30	5	5	0	0
		120	7	7	0	0
	CH_2Cl_2	30	63	3	56	3
		120	67	15	27	6
	CH_3CN[c]	30	37	<1	32	1
		60	51	<1	45	1
		120	73	4	53	1

[a] Conversion of **3**. – [b] See ref.[7] – [c] *syn*-**6** was precipitated as a colorless solid during photoreaction.

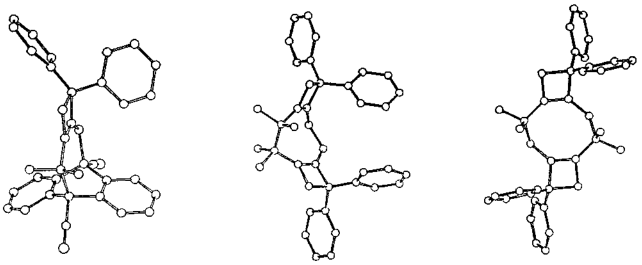


Figure 1. The ORTEP drawing of **5** (left), *syn*-**6** (center), and *anti*-**6** (right). Hydrogen atoms are omitted for clarity

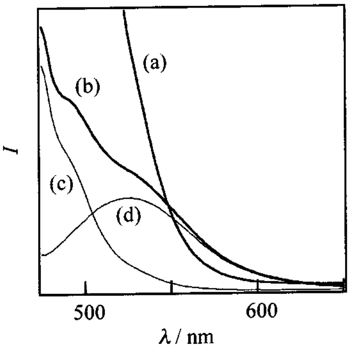


Figure 2. Fluorescence spectra of DCA in benzene in the absence (a) and presence (b) of **3** ([DCA] = $1.3 \cdot 10^{-5}$ M, [**3**] = 0.15 M). The fine solid lines (c) and (d), obtained by waveform solution analyses of spectrum (b), show emission spectra of DCA and a new, persistent component, respectively

It is also noteworthy that, upon prolonged irradiation in dichloromethane, the yield of **5** increases as that of *syn*-**6** decreases, indicating the secondary transformation of *syn*-**6** into **5**. The most likely explanation for the secondary transformation of *syn*-**6** into **5** is a [4 + 4] cycloreversion of *syn*-**6** to **3** followed by a [4 + 4] cycloaddition of **3** to DCA (Scheme 1). This was confirmed by study of independent DCA-sensitized electron-transfer photoreactions of *syn*-**6**. Electron transfer from *syn*-**6** to ^{1}DCA* is exergonic in dichloromethane, as the free energy change $-\Delta G_{\mathrm{et}}$ – shown in Table 1 suggests. As expected, irradiation of DCA and *syn*-**6** (0.005 M) in dichloromethane gives **3**, together with **5** and *anti*-**6**, in the yields shown in Table 3. In benzene, **5** is formed preferentially, but the reaction is very slow, probably owing to the quenching of ^{1}DCA* by *syn*-**6** being less efficient than that by **3**. This is also responsible for the accumulation of *syn*-**6** and its slow conversion in the photoreaction of **3** with DCA in dichloromethane and acetonitrile. In contrast to *syn*-**6**, the DCA adduct **5** does not undergo the [4 + 4] cycloreversion either under the DCA-sensitized conditions or under similar PET conditions using stronger acceptors such as 1,2,9,10-tetracyanoanthracene (TECA, $E_{1/2}^{red} = -0.30$ V vs. SCE and $E_{0-0} = 2.67$ eV in dichloromethane)[8] or 2,4,6-triphenylpyrilium tetrafluoroborate (TPP$^+$BF$_4^-$, $E_{1/2}^{red} = -0.20$ V and $E_{0-0} = 2.82$ eV[9] in dichloromethane). This is attributable to the less efficient quenching of the excited states of TECA ($k_q\tau$ = ca. 4 $\text{M}^{-1}\text{s}^{-1}$) or TPP$^+BF_4^-$ by **5**, with very slight electron-donating properties ($E_{1/2}^{ox} > +2.00$ V).

Table 3. DCA-Sensitized photoreactions of *syn*-**6** in degassed solvents

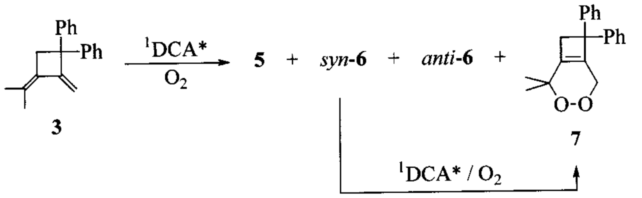
[*syn*-**6**] [M]	[DCA] [M]	Solvent[a]	Time [h]	Con. [%][b]	Yield [%] **3**	**5**	*anti*-**6**
0.005	0.01[c]	C_6H_6	10	29	2	27	0
		CH_2Cl_2	0.5	39	31	3	1
			2	81	33	15	3

[a] Not attempted in CH_3CN because of the low solubility of *syn*-**6**. – [b] Conversion of *syn*-**6**. – [c] See ref.[7]

DCA-Sensitized Photoreactions of 3 and *syn*-6 under Oxygen

The results observed in electron-transfer photoreactions of **3** and *syn*-**6** in degassed solvents clearly indicate that radical cation $\mathbf{3}^{\cdot+}$ must function as a buta-1,3-diene radical cation in order to undergo the [4 + 4] cyclodimerization and cycloaddition with DCA. In order to gain further insight into the mechanistic sequences of the [4 + 4] cyclodimerization and cycloreversion, the DCA-sensitized electron-transfer photoreactions of **3** and *syn*-**6** under oxygen were investigated.

Irradiation of DCA with **3** (0.01 M) in dichloromethane under oxygen gave 2,2-dimethyl-7,7-diphenyl-3,4-dioxabicyclo[4.2.0]oct-1(6)-ene (**7**) in good yield, as shown in Scheme 3 and Table 4. One intriguing observation was that the bicyclic endoperoxide **7** was formed much more efficiently in nonpolar benzene than in dichloromethane and in acetonitrile. This fact suggests that **7** is formed by addition of $^1O_2$, generated through an energy-transfer mechanism, to **3** rather than by addition of $\mathbf{3}^{\cdot+}$, generated through an electron-transfer mechanism, to $^3O_2$.[10] Compound **7** is in fact formed in 79% yield in the tetraphenylporphyrine-sensitized photoreaction of **3** in carbon tetrachloride under oxygen. Under the DCA-sensitized conditions, $^1O_2$ can be formed by exergonic energy transfer from ^{1}DCA* to $^3O_2$.[14,15] Apparently, the energy-transfer quenching of ^{1}DCA* by $^3O_2$ in nonpolar benzene occurs much more efficiently than electron-transfer quenching of ^{1}DCA* by **3**, and so photoirradiation of **3** in benzene under oxygen produces **7** in preference to **5** and *syn*-**6**. In moderately polar dichloromethane, the electron-transfer process to form *syn*-**6** probably competes with the energy-transfer process to form **7**. However, the sequential [4 + 4] cycloreversion of *syn*-**6** to **3**, followed by addition of $^1O_2$, ultimately converts *syn*-**6** into **7**. This sequence is supported by the independent photoconversion of *syn*-**6** into **7** under similar conditions, as shown in Scheme 3 and Table 5. In contrast to the results obtained at low concentrations of **3** (0.01 M), an electron-transfer mechanism to form *syn*-**6** operates preferentially at high concentrations of **3** (0.1 M) in dichloromethane and acetonitrile, as shown in Table 4. The cage-escaped $\mathbf{3}^{\cdot+}$ is probably trapped much more efficiently by **3** (to give *syn*-$\mathbf{9}^{\cdot+}$, a precursor of *syn*-**6**) under high concentration conditions than it is at low concentrations..



Scheme 3

Table 4. DCA-Sensitized photoreactions of **3** in O_2-saturated solvents

[**3**] and [DCA] [M]	Solvent	Time [min]	Con. [%][a]	Yield [%] **5**	*syn*-**6**	*anti*-**6**	**7**
0.01[b]	C_6H_6	5	63	5	0	0	58
		10	85	7	0	0	60
	CH_2Cl_2	5	61	1	14	1	30
		10	100	0	3	<1	72
	CH_3CN	5	60	0	3	1	32
		10	100	0	0	0	70
0.1[b]	C_6H_6	5	9	2	0	0	7
		30	12	3	0	0	9
	CH_2Cl_2	5	38	<1	33	2	3
		30	68	4	49	3	11
		120	85	11	13	5	11
	CH_3CN[c]	30	40	0	34	1	<1
		120	64	0	40	1	2

[a] Conversion of **3**. – [b] See ref.[7] – [c] *syn*-**6** was precipitated as a colorless solid during photoreaction.

Table 5. DCA-Sensitized photoreactions of *syn*-**6** in O_2-saturated solvents

[*syn*-**6**] [M]	[DCA] [M]	Solvent[a]	Time [h]	Con.[b] [%]	Yield of **7** [%]
0.005	0.01[c]	C_6H_6	0.5	1	1
			10	18	16
		CH_2Cl_2	0.17	33	17
			0.5	72	41

[a] Not attempted in CH_3CN because of the low solubility of *syn*-**6**. – [b] Conversion of *syn*-**6**. – [c] See ref.[7]

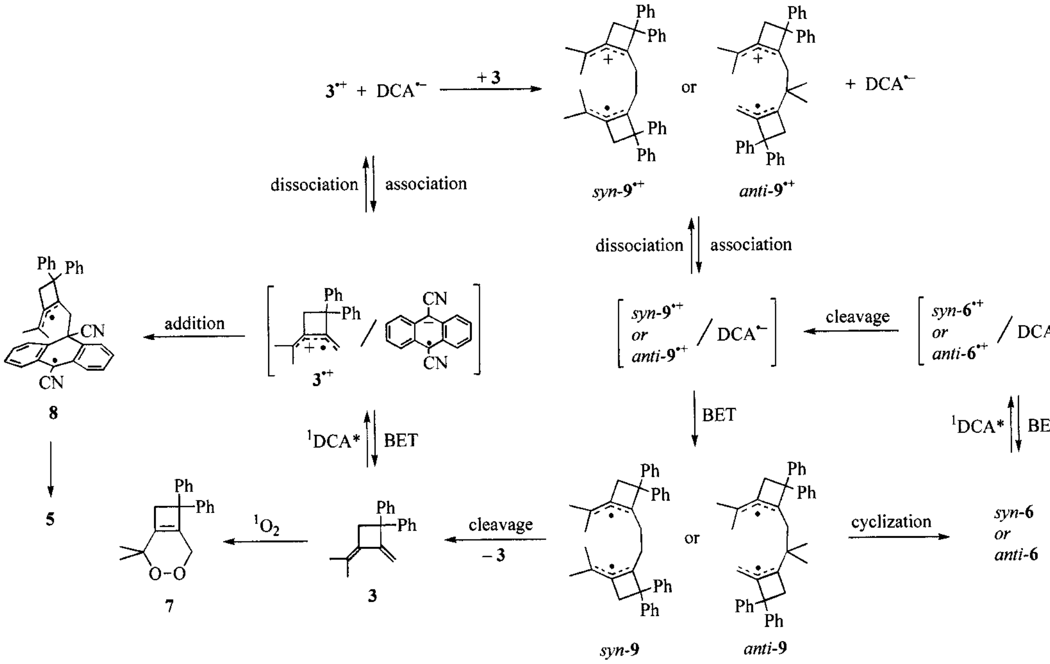
Mechanism

The nature of the observed reactivity of **3**$^{\cdot+}$ is suggestive of a typical buta-1,3-diene radical cation. This can be interpreted in terms of the electronic nature of **3**$^{\cdot+}$. According to PM3 calculations,[16] the HOMO of **3** is mainly localized, as a buta-1,3-diene moiety, and the next HOMO (two phenyl groups) of **3** lies ca. 0.4 eV lower in energy than HOMO, suggesting the predominant localization of the SOMO of **3**$^{\cdot+}$ in a buta-1,3-diene moiety. Species **3**$^{\cdot+}$ thus behaves as a buta-1,3-diene radical cation, and not as a methylenecyclobutane radical cation like **1**$^{\cdot+}$. Radical cation **3**$^{\cdot+}$, however, does not undergo [4 + 2]-type cyclodimerization.[17] This is most probably due to steric hindrance in a hypothetical transition state for a [4 + 2]-type cyclodimerization of **3**$^{\cdot+}$ and **3**.

A plausible electron-transfer mechanism, taking all observed results into account, is shown in Scheme 4. The initially generated **3**$^{\cdot+}$ undergoes ionic addition with DCA$^{\cdot-}$, either in the radical ion pair [**3**$^{\cdot+}$/DCA$^{\cdot-}$] or in an exciplex [**3**$^{\delta+}$/DCA$^{\delta-}$], to give a biradical intermediate **8**, which in nonpolar benzene yields the [4 + 4] DCA adduct **5** exclusively. In polar acetonitrile, a free radical cation **3**$^{\cdot+}$ dissociates from [**3**$^{\cdot+}$/DCA$^{\cdot-}$] to react with **3**, affording two types of allyl cation−allyl radical intermediates: *syn*-**9**$^{\cdot+}$ and *anti*-**9**$^{\cdot+}$. Differences in steric hindrance between the two transition states producing *syn*-**9**$^{\cdot+}$ and *anti*-**9**$^{\cdot+}$ are probably responsible for the formation of the thermodynamically less stable *syn*-**6** in preference to the more stable *anti*-**6**.[21] Successive association with DCA$^{\cdot-}$, followed by back-electron transfer (BET)[22] in [*syn*-**9**$^{\cdot+}$/DCA$^{\cdot+}$] or [*anti*-**9**$^{\cdot+}$/DCA$^{\cdot-}$], forms bisallyl biradical intermediates *syn*-**9** and *anti*-**9**, which then cyclize to give *syn*-**6** and *anti*-**6**, respectively. In dichloromethane, the [4 + 4] cyclodimerization to form *syn*-**6** and *anti*-**6** occurs concurrently with the [4 + 4] cycloaddition to form **5**.

The [4 + 4] cycloreversion of *syn*-**6** proceeds similarly, in an electron-transfer mechanism, involving the same intermediates as in the [4 + 4] cyclodimerization. Ring-cleavage of *syn*-**6**$^{\cdot+}$ to form *syn*-**9**$^{\cdot+}$, followed by BET from DCA$^{\cdot-}$, forms *syn*-**9**, which in turn disintegrates to afford two molecules of **3**. Alternatively, **3** might be formed by ring-cleavage of *syn*-**9**$^{\cdot+}$ to **3**$^{\cdot+}$, followed by BET from DCA$^{\cdot-}$. This process is not feasible, however, because in this case the DCA adduct **5** should be formed at least concurrently with **7** under oxygen. The fact that the DCA-sensitized photoreaction of *syn*-**6** under oxygen in dichloromethane solely forms **7**, and not **5** at all, supports the proposed mechanism.

The processes proposed in Scheme 4 are also energetically feasible, as shown in Figure 3. The initial electron-transfer quenchings of ^{1}DCA* by **3** and *syn*-**6** occur exergonically as shown in Table 1. According to PM3 calculation,[28] the free energy change, ΔG, for addition of **3** to **3**$^{\cdot+}$ to give *syn*-**9**$^{\cdot+}$ is ca. −1.02 eV.[21] Similarly, cleavage of *syn*-**6**$^{\cdot+}$ to *syn*-**9**$^{\cdot+}$ is expected to be exergonic by ca. 0.51 eV.[21] BET from DCA$^{\cdot-}$ to *syn*-**9**$^{\cdot+}$ in the radical ion pair [*syn*-**9**$^{\cdot+}$/DCA$^{\cdot-}$] is a key step both for the [4 + 4] cyclodimerization and for the cycloreversion. The free energy change, ΔG_{bet}, for this BET process could be calculated by using $E_{1/2}^{\text{red}}$ of DCA and $E_{1/2}^{\text{ox}}$ of *syn*-**9** if the $E_{1/2}^{\text{ox}}$ of *syn*-**9** as a transient intermediate were experimentally available. We thus assume that the $E_{1/2}^{\text{ox}}$ of *syn*-**9** is comparable to that of *tert*-butyl radical (*t*Bu$^{\cdot}$), at +0.09 V vs. SCE.[29] By using this value, ΔG_{bet} and the rate constant (k_{bet})[30] for BET at 20 °C in acetonitrile are calculated as −1.04 eV and $3 \cdot 10^{10}$ s^{-1}, respectively. If our assumption is correct, BET from DCA$^{\cdot-}$ to *syn*-**9**$^{\cdot+}$ will take place rapidly to form *syn*-**9**, and so com-



Scheme 4. Reaction mechanism for the DCA-sensitized electron-transfer reactions of **3**, *syn*-**6**, and *anti*-**6**

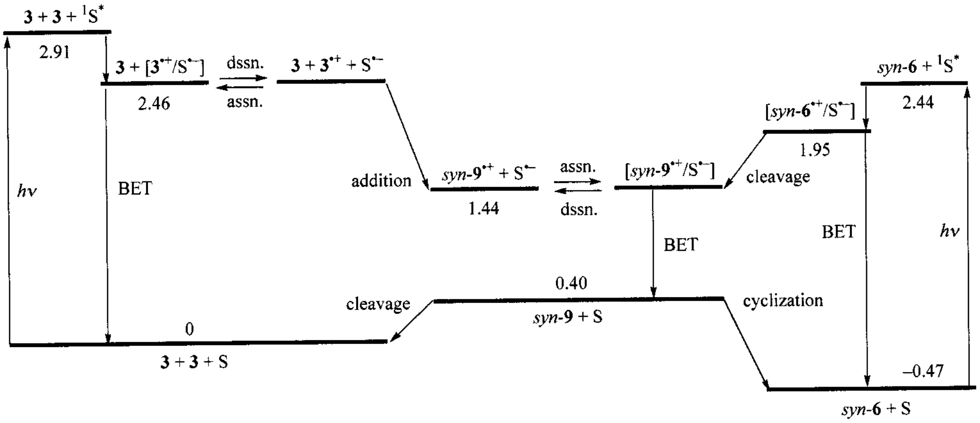


Figure 3. Energy diagram for the reversible [4 + 4] cyclodimerization of **3** in CH_3CN under the DCA (S)-sensitized electron-transfer conditions (assn: association, dssn: dissociation). The values are relative energies in eV

petitive final processes, cyclization and cleavage of *syn*-**9**, will also take place exergonically.

Conclusion

Both the positive charge and the unpaired electron of radical cation $\mathbf{3}^{\cdot+}$ are predominantly localized on a buta-1,3-diene moiety rigidly constrained in a *cisoid* form. These electronic and structural features result in the unprecedented [4 + 4] cycloaddition and cyclodimerization of **3** under DCA-photosensitized electron-transfer (PET) conditions. Most intriguing is the electron-transfer-induced reversible [4 + 4] electrocyclic reaction between **3** and *syn*-**6**, in which both allyl cation−allyl radical (*syn*-$\mathbf{9}^{\cdot+}$) and bisallyl biradical intermediates (*syn*-**9**) participate. The latter biradical intermediate is most probably formed by BET from $DCA^{\cdot-}$ to the former radical cation intermediate. The [4 + 4] cyclodimerization of **3** thus provides another example that demonstrates the importance of BET in producing a biradical intermediate in the PET reaction.[23−27] The [4 + 4] cyclodimerization of **3** also provides a new photochemical methodology for synthesizing tricyclic compounds containing cyclooctadiene moieties. Further studies along these lines are now in progress.

Experimental Section

General Remarks: All melting points are uncorrected. − Elemental analyses were performed by the Instrumental Analyses Center for Chemistry, Graduate School of Science, Tohoku University. − ^1H NMR spectra were recorded at 200 MHz on a Varian XL-200 spectrometer. Chemical shifts are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br., broad; *J*, coupling constants (Hz). Product analyses by ^1H NMR were performed in $CDCl_3$, using 1,1,2,2- or 1,1,1,2-tetrachloroethane as an internal standard for integration. ^{13}C NMR spectra were obtained at 50 MHz on a Varian XL-200 spectrometer. − Mass spectrometry (MS) was performed on a Hitachi M-2500 mass spectrometer under electron ionization conditions. − Redox potentials ($E^{ox}_{1/2}$ and $E^{red}_{1/2}$ in V vs. SCE) were measured by cyclic voltammetry with a Toho polarization unit PS-07 in acetonitrile and dichloromethane containing $Et_4N^+ClO_4^-$ (0.1 M) and $nBu_4N^+BF_4^-$ (0.1 M), respectively, as supporting electrolytes (Pt electrode, scan rate 100 mV/s). Because all of the substrates gave irreversible waves, their $E^{ox}_{1/2}$ values were estimated as E_{ap} (anodic peak potential) − 0.03 V, assuming a one-electron oxidation process. − Fluorescence spectra were recorded on a Hitachi F-4010 fluorescence spectrophotometer. Irradiation was performed at 20±1 °C with a Ushio 2-kW Xe short-arc lamp through a Toshiba cutoff filter L-39 ($\lambda > 360$ nm) for DCA, TECA, and $TPP^+BF_4^-$, or Y-50 ($\lambda > 470$ nm) for tetraphenylporphyrine. − THF was dried and distilled from $LiAlH_4$. Acetonitrile was dried and distilled from P_2O_5 and then CaH_2. Benzene, dichloromethane, and carbon tetrachloride were dried and distilled from CaH_2. Wako gel C-200 EB (75−150 μm) or Merck silica gel 60 (0.040−0.063 mm) was used for column chromatography. − Preparative thick layer chromatography was performed on 0.5 mm × 20 cm × 20 cm plates (Merck 60 PF_{254} silica gel). − Data collection for all X-ray crystallographic studies was performed on a Rigaku/MSC CCD (46 kV, 36 mA) diffractometer with a rotating anode (Mo-K_α radiation, $\lambda = 0.71069$ Å) at the Instrumental Analyses Center for Chemistry, Graduate School of Science, Tohoku University.

2-Isopropylidene-4,4-diphenylcyclobutan-1-one: 2-Isopropylidene-4,4-diphenylcyclobutan-1-one was prepared by [2 + 2] cycloaddition between 3-methylbuta-1,2-diene[5] and diphenylketene[6] according to known procedures,[4] as colorless plates (EtOH); m.p. 150−150.5 °C (ref.[4] 147 °C). − IR (KBr): $\tilde{\nu} = 1724, 1662\ cm^{-1}$ (ref.[4] 1720 cm^{-1}). − ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 1.80$ (s, 3 H), 2.15 (s, 3 H), 3.32 (br. s, 2 H), 7.15−7.45 (m, 10 H). − ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 21.46$, 21.59, 37.06, 70.20, 126.67 (2 C), 126.98 (4 C), 128.54 (4 C), 138.19, 142.79 (2 C), 145.83, 199.00. − MS (EI, 70 eV): *m*/*z* (%) = 262 (80) [M^+], 247 (10), 219 (8), 180 (100, $Ph_2{=}C{=}CH_2$). − $C_{19}H_{18}O$ (262.4): calcd. C 86.99, H 6.92; obsd. C 86.80, H 7.14.

1-Isopropylidene-2-methylene-3,3-diphenylcyclobutane (3): A solution of μ-chloro-μ-methylene[bis(cyclopentadienyl)titanium]dimethylaluminum (Tebbe reagent) in toluene (0.5 M, 25 mL, 12.5 mmol) was added dropwise, over 20 min at ambient temperature under nitrogen, to a solution of 2-isopropylidene-4,4-diphenylcyclobutan-1-one (2.62 g, 10 mmol) in dry THF (7 mL). After stirring for 18 h, the reaction was quenched with 10% aq. NaOH. The resulting brown solution was filtered through Celite, extracted with ether, washed with water, and dried with anhydrous Na_2SO_4. Column chromatography after evaporation of the solvent in vacuo gave

1.62 g (62% yield) of crude **3**, together with recovered starting ketone (0.71 g, 2.72 mmol, 27%). Recrystallization from *n*-hexane gave 1.31 g (5.01 mmol, 50%) of pure **3** as colorless prisms; m.p. 53.5−54 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.66 (s, 3 H), 1.87 (s, 3 H), 3.26 (br. s, 2 H), 4.94 (s, 1 H), 5.31 (s, 1 H), 7.20−7.40 (m, 10 H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 20.31, 20.72, 43.08, 55.78, 106.56, 125.95 (2 C), 127.69 (4 C), 128.10 (4 C), 129.79, 130.02, 147.06 (2 C), 155.95. − MS (EI, 70 eV): *m*/*z* (%) = 260 (100) [M^+], 245 (61), 230 (16), 217 (60), 192 (20), 165 (28). − $C_{20}H_{20}$ (260.4): calcd. C 92.26, H 7.74; obsd. C 92.33, H 7.91.

DCA Fluorescence Quenching: The DCA fluorescence quenching experiments were carried out under air, monitoring the changes in the intensity (*I*) of fluorescence at λ_{max} = ca. 436 and ca. 460 nm as a function of concentration of the substrate. The slope of I_0/I vs. [substrate] in the Stern−Volmer plot, which equals $k_q\tau$, was determined by the least-squares method. Quenching rate constants (k_q) were calculated by using the reported lifetime (τ) in each aerated solvent.

General Procedure for the DCA-Sensitized Photoreactions in Degassed Solution: A 5-mL solution containing substrate (0.05 mmol for **3**, 0.025 mmol for *syn*-**6**) and DCA (0.05 mmol) in a Pyrex test tube (diameter 1.5 cm) or a 0.6 mL solution containing substrate (0.06 mmol for **3**, 0.03 mmol for *syn*-**6**) and DCA (0.06 mmol) in a Pyrex NMR tube was degassed by five repeated freeze(−196 °C)−pump(10^{-2} Torr)−thaw(0 °C) cycles and then sealed at 10^{-2} Torr. After precipitation of DCA by standing for 5 min, the sample solution, containing a slight suspension of DCA, was irradiated through a cutoff filter ($\lambda > 360$ nm) with a 2-kW Xe lamp at 20±1 °C. The yields of products were determined by ^{1}H NMR analyses after evaporation in vacuo.

9,10,11,12-Dibenzo-2,2-dimethyl-5,5-diphenyltricyclo[6.2.2.0^{3,6}]-dodeca-3(6),9,11-triene-1,8-dicarbonitrile (5): A benzene solution (10 mL) containing **3** (260 mg, 1 mmol) and DCA (240 mg, 0.90 mmol) in a Pyrex test tube (diameter 2.5 cm) was degassed by five repeated freeze(−196 °C)−pump(10^{-2} Torr)−thaw(0 °C) cycles and then sealed at 10^{-2} Torr. After precipitation of DCA by standing for 5 min, the sample solution, containing a suspension of DCA, was irradiated through a cutoff filter ($\lambda > 360$ nm) with a 2-kW Xe lamp at 20±1 °C for 18 h. Column chromatography after evaporation of benzene in vacuo gave 368 mg (75% yield) of crude **5** as a pale yellow powder. Recrystallization from ethyl acetate gave 208 mg (0.43 mmol, 43% yield) of pure **5** as colorless plates; decomp. 243−245 °C. − IR (KBr): $\tilde{\nu}$ = 2243 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.35 (s, 6 H), 2.55 (t, *J* = 2.6 Hz, 2 H), 3.19 (t, *J* = 2.6 Hz, 2 H), 6.70 (m, 4 H), 7.10−7.20 (m, 6 H), 7.50−7.60 (m, 4 H), 7.80−7.95 (m, 4 H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 24.98 (2 C), 42.27, 46.12, 49.01, 51.05, 52.52, 55.38, 121.33, 122.44, 126.41 (2 C), 127.13 (4 C + 2 C), 128.18 (2 C), 128.34 (4 C), 129.36 (2 C), 129.67 (2 C), 131.28 (2 C), 133.17 (2 C), 134.82, 141.76, 143.93 (2 C). − MS (EI, 70 eV): *m*/*z* (%) = 488 (6) [M^+], 260 (100, $M^+ - C_{16}H_8N_2$), 245 (60), 217 (32). − $C_{36}H_{28}N_2$ (488.6): calcd. C 88.49, H 5.78, N 5.73; obsd. C 88.70, H 5.59, N 5.72.

2,2,3,3-Tetramethyl-6,6,11,11-tetraphenyl- and 2,2,8,8-Tetramethyl-5,5,11,11-tetraphenyltricyclo[8.2.0.0^{4,7}]dodeca-1(10),4(7)-diene (*syn*-6 and *anti*-6): A dry dichloromethane solution (18 mL) containing **3** (556 mg, 2.1 mmol) and DCA (23 mg, 0.038 mmol) in a Pyrex test tube (diameter 2.5 cm) was degassed by five repeated freeze(−196 °C)−pump(10^{-2} Torr)−thaw(0 °C) cycles and then sealed at 10^{-2} Torr. After precipitation of DCA by standing for 5 min, the sample solution, containing a suspension of DCA, was irradiated through a cutoff filter ($\lambda > 360$ nm) with a 2-kW Xe lamp at 20±1 °C for 12 h. Replacement of the solvent with ethyl acetate after filtration gave 220 mg (40% yield) of crude *syn*-**6** as a pale yellow precipitate, together with yellow filtrate. The precipitate was recrystallized from ethyl acetate to give pure *syn*-**6** (201 mg, 0.39 mmol, 36% yield) as colorless prisms. Removal of the solvent from the yellow filtrate gave a mixture of *syn*-**6** and *anti*-**6** (365 mg) as a pale yellow powder. Purification of this material by column and preparative thick layer chromatography followed by recrystallization from *n*-hexane gave pure *anti*-**6** (11.8 mg, 0.023 mmol, 2% yield) as a colorless powder.

syn-**6:** M.p. 184−186 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.14 (s, 12 H), 2.14 (s, 4 H), 2.95 (s, 4 H), 7.10−7.30 (m, 20 H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 26.76 (4 C), 41.80 (2 C), 45.20 (2 C + 2 C), 53.59 (2 C), 125.73 (4 C), 127.64 (8 C), 128.05 (8 C), 143.86 (2 C), 146.21 (4 C), 148.09 (2 C). − MS (EI, 70 eV): *m*/*z* (%) = 520 (27) [M^+], 477 (4), 260 (100, $M^+ - C_{20}H_{20}$), 245 (43), 217 (38), 167 (35). − $C_{40}H_{40}$ (520.8): calcd. C 92.26, H 7.74; obsd. C 92.25, H 8.03.

anti-**6:** M.p. 211−211.5 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.52 (s, 12 H), 2.48 (s, 4 H), 2.80 (s, 4 H), 7.10−7.30 (20 H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 26.52 (4 C), 36.60 (2 C), 38.03 (2 C), 40.27 (2 C), 55.90 (2 C), 125.76 (4 C), 127.96 (16 C), 140.19 (2 C), 146.79 (4 C), 149.27 (2 C). − MS (EI, 70 eV): *m*/*z* (%) = 520 (89) [M^+], 505 (8), 477 (10), 260 (80), 245 (43), 217 (56), 167 (100, phenyltropylium ion). − $C_{40}H_{40}$ (520.8): calcd. C 92.26, H 7.74; obsd. C 92.11, H 7.98.

General Procedure for the DCA-Sensitized Photoreactions under Oxygen: A solution (5 mL) containing substrate (0.05 mmol for **3**, 0.025 mmol for *syn*-**6**) and DCA (0.05 mmol) in a Pyrex test tube (diameter 1.5 cm) or a solution (0.6 mL) containing **3** (0.06 mmol) and DCA (0.06 mmol) in a Pyrex NMR tube was saturated with oxygen by bubbling for 10 min. After precipitation of DCA by standing for 5 min, the sample solution, containing a slight suspension of DCA, was irradiated at 20±1 °C, under oxygen and through a cutoff filter ($\lambda > 360$ nm), with a 2-kW Xe lamp. The yields of products were determined by ^{1}H NMR analyses after evaporation in vacuo.

2,2-Dimethyl-7,7-diphenyl-3,4-dioxabicyclo[4.2.0]oct-1(6)-ene (7): A dry benzene solution (5 mL) containing **3** (122 mg, 0.47 mmol) and DCA (13.1 mg, 0.057 mmol) in a Pyrex test tube (diameter 1.5 cm) was saturated with oxygen by bubbling. After precipitation of DCA by standing for 5 min, the sample solution, containing a slight suspension of DCA, was irradiated at 20±1 °C, under oxygen and through a cutoff filter ($\lambda > 360$ nm), with a 2-kW Xe lamp for 12 h. Removal of the solvent followed by column chromatography gave crude **7** (88 mg) as a colorless powder. Recrystallization from *n*-hexane gave pure **7** (55 mg, 0.19 mmol, 41% yield) as colorless prisms; m.p. 97−98 °C. − IR (KBr): $\tilde{\nu}$ = 2920, 1493, 1445, 1192, 756, 700 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.38 (s, 6 H), 3.21 (br. s, 2 H), 4.71 (br. s, 2 H), 7.10−7.35 (m, 10 H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 23.00 (2 C), 45.92, 59.23, 69.15, 80.12, 126.42 (2 C), 127.17 (4 C), 128.42 (4 C), 141.38, 144.40 (2 C), 145.55. − MS (EI, 70 eV): *m*/*z* (%) = 292 (20) [M^+], 260 (4), 245 (13), 234 (86), 205 (100, $C_{16}H_{13}$), 167 (35). − $C_{20}H_{20}O_2$ (292.4): calcd. C 82.16, H 6.89; obsd. C 82.31, H 7.20.

Tetraphenylporphyrin-Sensitized Photoreaction of 3 under Oxygen: A dry carbon tetrachloride solution (5 mL) containing **3** (45 mg, 0.17 mmol) and tetraphenylporphyrin (1.9 mg, 3.1 mmol) in a Pyrex test tube (diameter 1.5 cm) was saturated with oxygen by bubbling and irradiated at 20±1 °C, under oxygen and through a cutoff

Table 6. Crystallographic data for **5**, *syn*-**6**, and *anti*-**6**

Compound	5	*syn*-**6**	*anti*-**6**
Empirical formula	$C_{36}H_{28}N_2$	$C_{40}H_{40}$	$C_{40}H_{40}$
Molecular mass	488.6	520.8	520.8
Color	colorless prism	colorless prism	colorless prism
Crystal size [mm]	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3
Space group	$P2_1/n$	$P2_1$	$C2/c$
a [Å]	17.4545(6)	11.4353(7)	28.211(6)
b [Å]	10.148(1)	20.045(1)	10.993(3)
c [Å]	17.8345(6)	12.994(1)	10.2280(3)
β [°]	123.4602(9)	96.7492(8)	107.3003(6)
V [A^3]	2635.4(4)	2957.9(3)	3028.5(9)
Z	4	4	4
$D_{\mathrm{calcd.}}$ [g cm^{-3}]	1.231	1.169	1.142
μ(Mo-K_α [cm^{-1}]	0.71	0.65	0.64
F(000)	1032.00	1120.0	1120.0
$2\theta_{\max}$ [°]	54.9	55.0	55.0
No. of reflections: measured, unique	18843, 6069	20165, 6582	10541, 3350
R_{int}	0.041	0.032	0.021
No. of reflections to calcd. $R1$, R_w	3283 with $I > 4\ \sigma\|I\|$	5751 with $I > 3\ \sigma\|I\|$	2057 with $I > 5\ \sigma\|I\|$
$R1$, R_w	0.055, 0.060	0.062, 0.063	0.041, 0.043

filter ($\lambda > 470$ nm), with a 2-kW Xe lamp for 6 h. ^{1}H NMR analyses indicated that **7** was formed in 79% yield at 100% conversion. Purification by column chromatography gave **7** (33 mg, 0.11 mmol, 74% yield) as a colorless powder, the physical data of which were consistent with those of the product obtained by DCA-sensitized photoreaction of **3** under oxygen (vide supra).

Attempted PET Reaction of 5: A dry [D$_2$]dichloromethane solution (0.6 mL) containing **5** (27.8 mg, 0.06 mmol) and TECA (2 mg, 0.007 mmol) in a Pyrex NMR tube (diameter 0.5 cm) was degassed by five repeated freeze(−196 °C)−pump(10^{-2} Torr)−thaw(0 °C) cycles and then sealed at 10^{-2} Torr. The sample solution was irradiated at 20±1 °C, through a cutoff filter ($\lambda > 360$ nm), with a 2-kW Xe lamp for 14 h. ^{1}H NMR analyses showed that **5** was recovered in 100% yield. A similar attempted photoreaction using TPP$^+$ BF$_4^-$ instead of TECA for 12 h resulted in recovery of **5** in 94% yield.

X-ray Crystallographic Study: Independent crystallization of **5**, *syn*-**6**, and *anti*-**6** from acetonitrile gave single crystals suitable for X-ray analysis. All data collection was performed at 22.0 °C. These structures were solved by using direct methods (SIR92[38] or SHELXS-97[39]), the teXsan[40] program with some modification, and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. A summary of the crystal data, data collection, and refinement parameters for the three crystal structures reported in this paper are given in Table 6. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151413 (**5**), -151414 (*syn*-**6**), and -151415 (*anti*-**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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$$k_{\mathrm{bet}} = \left(\frac{4\pi^{3}}{h^{2}\lambda_{\mathrm{s}} k_{\mathrm{b}} T}\right)^{1/2} |V|^{2} \sum_{w=0}^{\infty} \left(\frac{e^{-S} S^{\omega}}{\omega!}\right) \exp\left\{-\frac{(\lambda_{\mathrm{s}} + \Delta G_{\mathrm{bet}} + \omega h\nu)^{2}}{4\lambda_{\mathrm{s}} k_{\mathrm{b}} T}\right\} \quad (1)$$

$$S = \lambda_{\mathrm{v}} / h\nu \quad (2)$$

$$\Delta G_{\mathrm{bet}}(\mathrm{eV}) = -[E_{1/2}^{\mathrm{ox}}\ (t\mathrm{Bu}^{\bullet}) - E_{1/2}^{\mathrm{red}}\ (\mathrm{DCA}) - e^{2}/\varepsilon r] \quad (3)$$

in which parameters $|V|^2$, λ_s, λ_v, ν, and ΔG_{bet} are, respectively, an electronic coupling matrix element squared, solvent reorganization energy, vibrational reorganization energy, single average frequency, and the free energy change for the BET process. The Coulombic term ($e^2/\varepsilon r$) is disregarded.[37]

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