Photoinduced Electron-Transfer Cope Rearrangements of 3,6-Diaryl-2,6-octadienes and 2,5-Diaryl-3,4-dimethyl-1,5-hexadienes: Stereospecificity and an Unexpected Formation of the Bicyclo[2.2.0]hexane Derivatives

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Under the 9,10-dicyanoanthracene-sensitized photoinduced electron-transfer conditions, *(Z,Z)-, (E,E)-, (E,Z)*-3,6-diaryl-2,6-octadiene and *(d,l),(meso)*-2,5-diaryl-3,4-dimethyl-1,5-hexadiene stereospecifically undergo the Cope rearrangement to give a Cope photostationary mixture. Remarkably, the photoinduced electron-transfer Cope rearrangements of the 4-methylphenyl derivatives are concurrent with the formation of *trans-* or *endo,cis*-1,4-bis(4-methylphenyl)-2,3-dimethylbicyclo[2.2.0]hexane in a Cope photostationary mixture. Observed stereospecificity of the Cope rearrangement and the formation of the bicyclo[2.2.0]hexane derivatives demonstrate the intermediacies of both the chair and boat 1,4-diaryl-1,2-dimethylcyclohexane-1,4-diyl and cation radical intermediates in a Cope rearrangement cycle. Photoreactions of *trans-* and *exo,cis*-1,4-diaryl-5,6-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-enes further support the interventions of the diyl intermediates in the Cope rearrangement cycle. By photoacoustic analysis, a cation radical cyclization−diradical cleavage mechanism is proposed for the photoinduced electron-transfer Cope rearrangement of the title dienes.

We previously reported that the 9,10-dicyanoanthracene (DCA)-sensitized electron-transfer degenerate Cope rearrangement of 2,5-diaryl-3,3,4,4-tetradeuterio-1,5-hexadienes (d_4-**1**) occurs in a cation radical cyclization (CRCY)−diradical cleavage (DRCL) mechanism as shown in Scheme 1.[1] The important key process of this mechanism is the highly exothermic back electron transfer (BET) from DCA$^{•−}$ to 1,4-diarylcyclohexane-1,4-diyl cation radical (d_4-**2**$^{•+}$) to form 1,4-diarylcyclohexane-1,4-diyl (d_4-**2**). Since the direct cleavage of d_4-**2**$^{•+}$ to d_4-**1**$^{•+}$ and d_4-**1′**$^{•+}$ is highly endothermic, a competitive BET preferentially occurs to give diyl d_4-**2**, which, in turn, undergoes cleavage to give a Cope photostationary mixture of d_4-**1** and d_4-**1′**. If stereochemistry of d_4-**2**$^{•+}$ is conserved in d_4-**2**, the most important step to determine the stereochemical course of the Cope rearrangement is the initial CRCY step. Since the theoretical argument of Bauld on cyclization of the parent 1,5-hexadiene cation radical to cyclohexane-1,4-diyl cation radical suggested that the energy difference between the chair and boat conformations will be quite small,[2] it is of particular interest to know experimentally which conformation is favorable in the CRCY step in the photoinduced electron-transfer Cope rearrangement.

Scheme 1
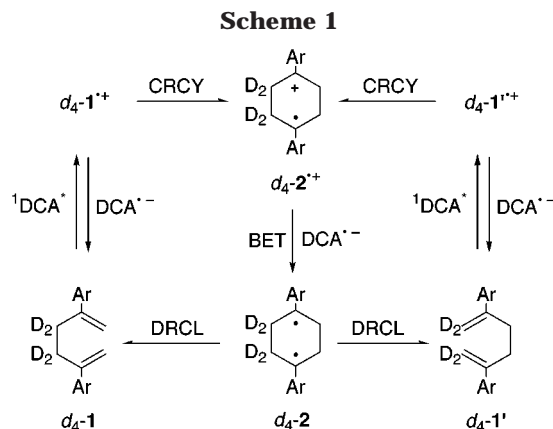
For this purpose, the DCA-sensitized electron-transfer photoreactions of 3,6-diaryl-2,6-octadienes (*ZZ*-**3a**−**c**, *EE*-**3a**−**c**, and *EZ*-**3a**−**c**) and 3,4-dimethyl-2,5-diaryl-1,5-hexadienes (*dl*-**4a**−**c** and *meso*-**4a**−**c**) (Chart 1) were investigated under nitrogen and oxygen atmosphere.[1b,4] The role of the boat 1,4-diaryl-2,3-dimethylcyclohexane-1,4-diyl cation radical intermediates in the Cope rearrangement sequence was investigated by electron-transfer photoreactions of 1,4-diaryl-2,3-dimethylbicyclo[2.2.0]hexanes (*trans*-**5a**−**c**, *n,cis*-**5a**−**c**, and *x,cis*-**5a**−**c**) and 1,4-diaryl-5,6-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-enes (*trans*-**6b**−**c** and *x,cis*-**6b**−**c**) (Chart 1).

While the thermal Cope rearrangements of *dl*-**4a** and *meso*-**4a** are irreversible, the DCA-sensitized photoin-

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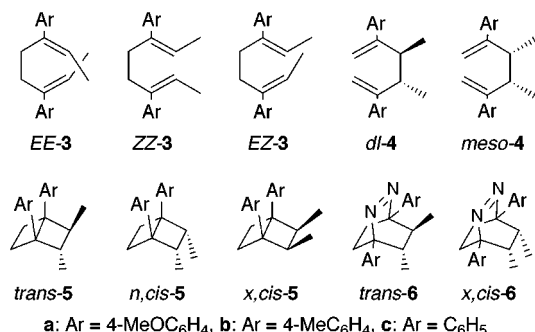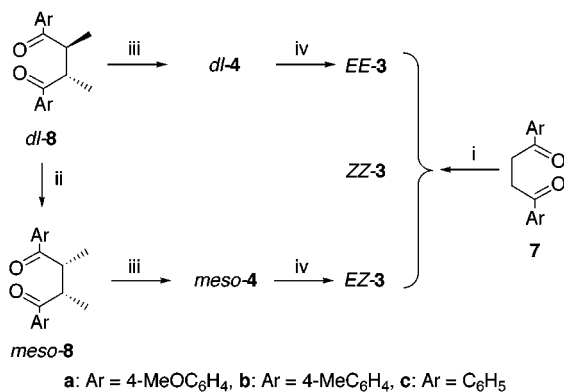† Tohoku University.
‡ University of Rochester.
(1) (a) Ikeda, H.; Minegishi, T.; Abe, H.; Konno, A.; Goodman, J. L.; Miyashi, T. *J. Am. Chem. Soc.* **1998**, *120*, 87−95. (b) Miyashi, T.; Konno, A.; Takahashi, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3676−3677. (c) Ikeda, H.; Minegishi, T.; Miyashi, T. *J. Chem. Soc., Chem. Commun.* **1994**, 297−298. (d) Ikeda, H.; Minegishi, T.; Takahashi, Y.; Miyashi, T. *Tetrahedron Lett.* **1996**, *37*, 4377−4380.
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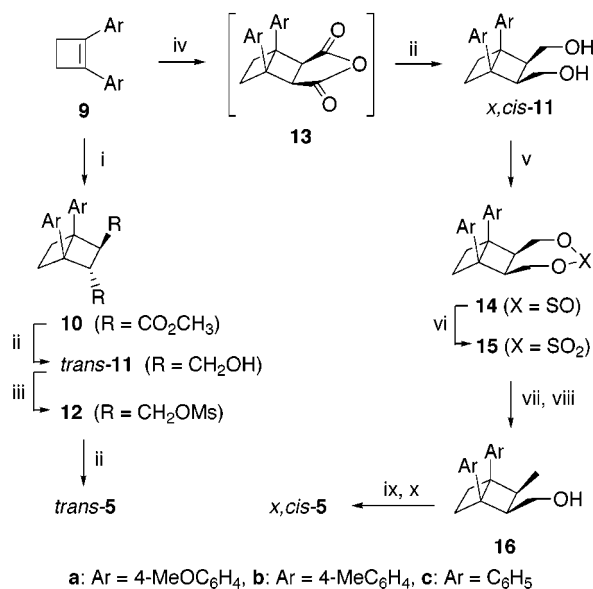
Chart 1

EE-3   *ZZ-3*   *EZ-3*   *dl-4*   *meso-4*

trans-5   *n,cis-5*   *x,cis-5*   *trans-6*   *x,cis-6*

a: Ar = 4-MeOC$_6$H$_4$, **b**: Ar = 4-MeC$_6$H$_4$, **c**: Ar = C$_6$H$_5$

Scheme 2^a

a: Ar = 4-MeOC$_6$H$_4$, **b**: Ar = 4-MeC$_6$H$_4$, **c**: Ar = C$_6$H$_5$

^{a} Key: (i) Ph$_3$P$^+$C$_2$H$_5$·I$^-$, *n*-BuLi/THF; (ii) MeONa/THF; (iii) Ph$_3$P$^+$CH$_3$·I$^-$, *t*-BuOK/THF; (iv) reflux in toluene.

Scheme 3^a

a: Ar = 4-MeOC$_6$H$_4$, **b**: Ar = 4-MeC$_6$H$_4$, **c**: Ar = C$_6$H$_5$

^{a} Key: (i) *hv*/dimethyl fumarate/C$_6$H$_6$; (ii) LiAlH$_4$/Et$_2$O; (iii) MsCl/Py; (iv) *hv*/maleic anhydride/C$_6$H$_6$; (v) SOCl$_2$/Et$_3$N/CH$_2$Cl$_2$; (vi) NaIO$_4$/RuCl$_3$/CCl$_4$–CH$_3$CN–H$_2$O; (vii) NaBH$_4$/DMSO; (viii) dil H$_2$SO$_4$/Et$_2$O; (ix) *n*-BuLi/(CF$_3$SO$_2$)$_2$O/C$_6$H$_6$; (x) LiEt$_3$BH/THF.

duced electron-transfer Cope rearrangements of **3a** and **4a** are reversible and form a photostationary mixture.[4] Remarkably, the Cope rearrangements of the 4-methylphenyl derivatives **3b** and **4b** proceed in concurrence with the formation of the bicyclo[2.2.0]hexane derivative (**5b**). Herein, we report characteristics of the photoinduced Cope rearrangement of **3** and **4** in detail.

Results and Discussion

Syntheses and DCA-Fluorescence Quenching Rate Constants of 3–6. The 4-methoxyphenyl, 4-methylphenyl, and phenyl derivatives of 3,6-diaryl-2,6-octadienes (*ZZ*-**3a**–**c**, *EE*-**3a**–**c**, and *EZ*-**3a**–**c**) and 2,5-diaryl-3,4-dimethyl-1,5-hexadienes (*dl*-**4a**–**c** and *meso*-**4a**–**c**) were prepared as illustrated in Scheme 2. The Wittig reaction of **7** with ethyltriphenylphosphonium iodide gave *ZZ*-**3** as a major product together with *EE*-**3** and *EZ*-**3**. Because yields of *EE*-**3** and *EZ*-**3** were low in this procedure, these dienes as well as *dl*-**4** and *meso*-**4** were prepared by different procedures. The key precursor, (d,l)-1,4-diaryl-2,3-dimethyl-1,4-butadione (*dl*-**8**), was selectively prepared by the base-catalyzed condensation[7] of the substituted propiophenone and α-bromopropiophenone. The subsequent Wittig reaction of *dl*-**8** gives *dl*-**4**. Upon heating at 110 °C in toluene, *dl*-**4** quantitatively rear-

ranged to *EE*-**3**. Diketone *dl*-**8** was selectively converted to the *meso* isomer (*meso*-**8**) by a continuous isomerization–crystallization technique.[8] The Wittig reaction of *meso*-**8** gave *meso*-**4**, which was quantitatively converted to *EZ*-**3** upon heating at 110 °C in toluene. The *dl* and *meso* forms of **8** were confirmed by ^{1}H NMR analyses using a chiral shift reagent, tris[3-(2,2,2-trifluoro-1-hydroxyethylidene)-*d*-camphorato] europium [Eu(*tfc*)$_3$]. Liquid chromatographic analyses using an optically active column further confirmed the configuration of **4** and **8**. Stereochemistries of **3** were determined by comparison of their ^{1}H NMR with those of 4-substituted α,β-dimethylstyrene and NOE analyses between C-2-H on the benzene ring and methyl or olefinic proton.

1,4-Diaryl-2,3-dimethylbicyclo[2.2.0]hexanes (*trans*-**5** and *x,cis*-**5**) were synthesized as shown in Scheme 3. Irradiation of 1,2-diarylcyclobutene (**9**) and dimethyl fumarate gave *trans*-1,4-diaryl-2,3-dicarbomethoxybicyclo[2.2.0]hexane (**10**), which was converted to *trans*-**5** through *trans*-**11** and **12**. Three derivatives, *trans*-**5a**–**c**, were prepared by this procedure. The *exo* adduct **13**, an exclusive product of the photoreaction of **9** and maleic anhydride, was used as the starting material for *x,cis*-**5**. Diol *x,cis*-**11** was converted to **15** through **14**. Reduction of **15** followed by hydrolysis gave alcohol **16**. Reaction of **16** with *n*-BuLi/(CF$_3$SO$_2$)$_2$O followed by reduction with LiEt$_3$BH gave *x,cis*-**5**. Three derivatives, *x,cis*-**5a**–**c**, were prepared by this procedure. Because the *endo* isomers of **13a**–**c** were not formed in this photoreaction, *n,cis*-**5** was isolated from a photostationary mixture obtained in the DCA-sensitized photoreaction of *EZ*-**3** or *meso*-**4** as noted

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Scheme 4[a]
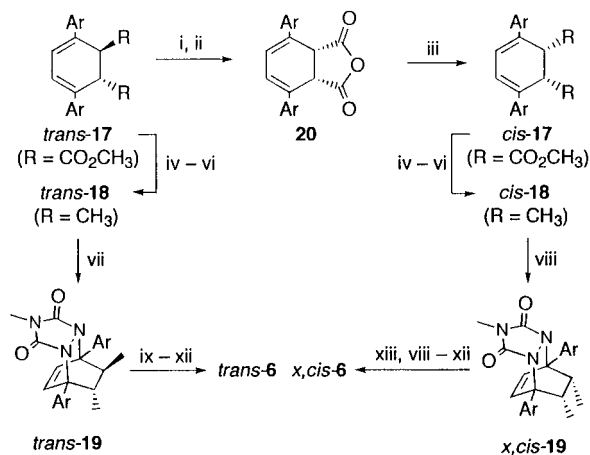
a Key: (i) KOH/EtOH; (ii) Ac$_2$O; (iii) MeOH/HCl; (iv) LiAlH$_4$/THF; (v) MsCl/Py; (vi) LiEt$_3$BH/THF; (vii) 4-methyl-1,2,4-triazoline-3,5-dione/AcOEt; (viii) 4-methyl-1,2,4-triazoline-3,5-dione/CH$_2$Cl$_2$; (ix) H$_2$/Pt–CaCO$_3$/AcOEt; (x) KOH/*i*-PrOH; (vii) CuCl$_2$/*i*-PrOH; (viii) NH$_4$OH; (xiii) H$_2$/PtO$_2$/AcOEt.

Table 1. Photostationary Ratios of the DCA-Sensitized Cope Rearrangement of 3a and 4a in CD$_2$Cl$_2$ at 20 °C[a]

		photostationary ratios[b]					
sub	time (h)	*ZZ*-**3a**	*EE*-**3a**	*dl*-**4a**	*EZ*-**3a**	*meso*-**4a**	yields (%)[b]
ZZ-**3a**	20	51	19	30	0	0	57
EE-**3a**	10	2	42	55	0	0	92
dl-**4a**	4	2	40	57	0	0	87
EZ-**3a**	8	0	0	0	80	20	77
meso-**4a**	10	0	0	0	80	20	83

a A 0.5 mL solution was irradiated with a 2 kW Xe lamp through a cutoff filter (λ > 360 nm) at 20 °C. [sub] = 0.1 M, [DCA] = 5.3 × 10^{-4} M. *b* Determined by ^{1}H NMR analyses.

rangement (Scheme 1) the initial CRCY forms a chair cation radical intermediate.[3] The DCA-sensitized electron-transfer photoreactions of **3a** and **4a** will provide the direct information for the stereochemical course of the Cope rearrangement.

Upon irradiation of DCA with *EE*-**3a** in dichloromethane-d_2 at 20 °C, *EE*-**3a** gradually diminishes, forming *dl*-**4a** and a small amount of *ZZ*-**3a**. After 10 h irradiation, a photostationary mixture of *ZZ*-**3a**, *EE*-**3a**, and *dl*-**4a** in the ratio of 2:42:55 is formed in 92% yield. Similar photoreaction of *dl*-**4a** gives nearly the same photostationary mixture in 87% yield after 4 h irradiation as shown in Table 1. By contrast, the rearrangement of *ZZ*-**3a** is apparently slow so that the reaction does not reach a photostationary state even upon prolonged irradiation, but a mixture of *ZZ*-**3a**, *EE*-**3a**, and *dl*-**4a** is obtained in the ratio of 51:19:30 in 57% yield after 20 h irradiation. Like *EE*-**3a** and *dl*-**4a**, *EZ*-**3a** and *meso*-**4a** give nearly the same photostationary mixture under similar DCA-sensitized photoconditions (Table 1). The *E*–*Z* isomerization of *ZZ*-**3a**, *EE*-**3a**, or *EZ*-**3a** is not observed under the DCA-sensitized electron-transfer conditions. The *dl*-family dienes (*ZZ*-**3a**, *EE*-**3a** and *dl*-**4a**) and the *meso*-family dienes (*EZ*-**3a** and *meso*-**4a**) interconvert within their own family through the Cope rearrangement (Scheme 5). The observed stereochemical results clearly demonstrate that both the CRCY and DRCL processes take place stereospecifically in the chair conformation[14] as described by a CRCY–DRCL mechanism in Schemes 6 and 7.

On the cation radical energy surface, *EE*-**3a**$^{•+}$ and *ZZ*-**3a**$^{•+}$ initially form *aaC*-**21a**$^{•+}$ and *eeC*-**21a**$^{•+}$, respectively. However, *aaC*-**21a**$^{•+}$ is more stable than *eeC*-**21a**$^{•+}$ because of steric hindrance between the methyl and aryl groups in *eeC*-**21a**$^{•+}$. Hence *dl*-**4a**$^{•+}$ preferentially cyclizes to *aaC*-**21a**$^{•+}$, though *dl*-**4a**$^{•+}$ may cyclize to both *aaC*-**21a**$^{•+}$ and *eeC*-**21a**$^{•+}$. The facts that *ZZ*-**3a** is a minor component in photostationary mixtures formed from *EE*-**3a** and *dl*-**4a** and that the rearrangement of *ZZ*-**3a** is slow suggest that *aaC*-**21a**$^{•+}$ formed from *EE*-**3a**$^{•+}$ and *dl*-**4a**$^{•+}$ is slow to interconvert to *eeC*-**21a**$^{•+}$, and that *eeC*-**21a**$^{•+}$ formed from *ZZ*-**3a**$^{•+}$ suffers BET from DCA$^{•-}$ in

in the Supporting Information. The structures of *trans*-**5c**, *x,cis*-**5c** and *n,cis*-**5c** were directly confirmed by X-ray analyses.

Diazenes *trans*-**6b,c**, and *x,cis*-**6b,c** were prepared as shown in Scheme 4. *trans*-3,6-Diaryl-1,2-dicarbomethoxy-1,4-cyclohexadiene prepared from dimethyl acetylenedicarboxylate and 1,4-diaryl-1,3-butadiene was converted to *trans*-**17**.[9] The isomeric *cis*-**17** was obtained through **20**.[9] Both *trans*-**18** and *cis*-**18** were derived, respectively, from *trans*-**17** and *cis*-**17** by reduction and mesylation followed by reduction according to the known procedure.[9,10] The Diels–Alder reactions of *trans*-**18** and *cis*-**18** with 4-methyl-1,2,4-triazoline-3,5-dione gave *trans*-**19** and *x,cis*-**19**, respectively. By usual procedures, *trans*-**6b,c** and *x,cis*-**6b,c** were prepared in good yields.

Dienes (**3a**–**c** and **4a**–**c**), bicyclo[2.2.0]hexanes (**5a**–**c**), and diazenes (**6b**–**c**) are relatively good electron donors, and their oxidation potentials ($E^{ox}_{1/2}$) are low enough to quench the excited singlet of DCA exothermically. Free energy changes (ΔG) associated with the forward electron transfers are all negative as calculated according to the Rehm–Weller equation.[11] In accord with calculated thermodynamics, the DCA fluorescence was efficiently quenched by **3**–**6** in acetonitrile with large rate constants (k_q) close to the diffusion-control rate. In less polar dichloromethane and nonpolar benzene, the DCA fluorescence was also quenched, albeit less efficiently. Values for $E^{ox}_{1/2}$, ΔG, and k_q for each substrate are shown in the Supporting Information.

The DCA-Sensitized Electron-Transfer Photoreactions of 3a, 4a, and 5a. The thermal Cope rearrangement generally occurs through the chair six-membered cyclic transition state[12] which is energetically more stable than a boat counterpart.[13] Thus, it is assumable that in the photoinduced electron-transfer degenerate Cope rear-

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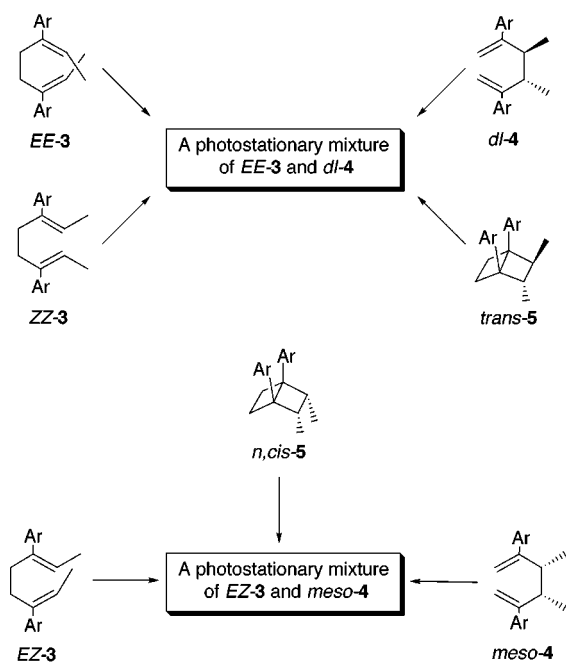
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(14) The observed result does not always exclude a possibility that the CRCY or DRCL step occurs in the twist-boat conformation. In this paper, however, only chair and boat intermediates are discussed for clarity and comparison with results of the theoretical calculation.[2]

Scheme 5

a: Ar = 4-MeOC$_6$H$_4$, b: Ar = 4-MeC$_6$H$_4$, c: Ar = C$_6$H$_5$

Scheme 6

Scheme 7

Table 2. Absorption Maxima (λ_{max}) and Rate Constants for Decay (k_0) and for MeOH Addition (k_{MeOH}) of a Transient Intermediate Generated from the *dl*-Family Compounds (3–6) under NMQ$^+$BF$_4^-$–BP-Cosensitized Conditions in CH$_2$Cl$_2^a$

	a: 4-MeOC$_6$H$_4$			b: 4-MeC$_6$H$_4$			c: C$_6$H$_5$		
sub	λ_{max}, nm	k_0,^{c} 10^5 s^{-1}	k_{MeOH},^{c} 10^5 M^{-1}s^{-1}	λ_{max}, nm	k_0,^{b} 10^5 s^{-1}	k_{MeOH},^{b} 10^7 M^{-1}s^{-1}	λ_{max}, nm	k_0,^{c} 10^5 s^{-1}	k_{MeOH},^{c} 10^7 M^{-1}s^{-1}
ZZ-3	523	1.1	8.3	499	3.4	2.6	481	5.6	d
EE-3	523	1.1	7.9	499	3.9	2.0	483	4.1	8.8
dl-4	523	1.1	8.1	499	3.8	2.6	482	4.2	d
trans-5	523	1.0	8.5	499	4.1	2.4	483	4.5	5.6
trans-6				499	4.3	2.0	484	7.1	5.8

^{a} At 20 °C. ^{b} An average of experimental error was about 10%. ^{c} An average of experimental error was about 20%. ^{d} No attempt.

Cope rearrangement sequence is that the DCA-sensitized photoreaction of *trans*-**5a** gives a 39:61 photostationary mixture of *EE*-**3a** and *dl*-**4a**, and no *ZZ*-**3a**. The boat cation radical *tB*-**21a**$^{\bullet+}$ formed from *trans*-**5a**$^{\bullet+}$ and boat diyl *tB*-**21a** formed from *trans*-**5a**$^{\bullet+}$ flip preferentially to *aaC*-**21a**$^{\bullet+}$ and *aaC*-**21a**, respectively, as shown in Scheme 6. Accordingly, *trans*-**5a** enters into a *dl-EE* Cope manifold through *tB*-**21a**$^{\bullet+}$ and gives nearly the same photostationary mixture as those from *EE*-**3a** and *dl*-**4a**.

For the spectroscopic confirmation of the initial cyclizations of *EE*-**3a**$^{\bullet+}$ and *dl*-**4a**$^{\bullet+}$ as well as the preferential ring flip of *tB*-**21a**$^{\bullet+}$ to *aaC*-**21a**$^{\bullet+}$, *EE*-**3a**, *dl*-**4a**, and *trans*-**5a** were subjected to nanosecond laser flash photolysis (LFP) under the *N*-methylquinolinium tetrafluoroborate (NMQ$^+$BF$_4^-$)–biphenyl (BP)-cosensitized conditions in aerated dichloromethane, minimizing BET to form diyl intermediates.[1a,15] As shown in Table 2, *EE*-**3a**, *dl*-**4a**, and *trans*-**5a** yield the intense transient

preference to the ring flip to *aaC*-**21a**$^{\bullet+}$. Thus, the concentration of *eeC*-**21a**$^{\bullet+}$ becomes low relative to that of *aaC*-**21a**$^{\bullet+}$ in a Cope rearrangement cycle. In addition, the ring cleavage of *eeC*-**21a** presumably gives *ZZ*-**3a** as a major product. The BET from DCA$^{\bullet-}$ to *aaC*-**21a**$^{\bullet+}$ similarly occurs to form *aaC*-**21a** which, in turn, undergoes DRCL to form *EE*-**3a** and *dl*-**4a**. In a *dl-EE* Cope manifold, *EE*-**3a** and *dl*-**4a** then repeat the Cope rearrangement to make a photostationary mixture, while *ZZ*-**3a** fades gradually into a minor component of a Cope photostationary mixture. Strong evidence to support the
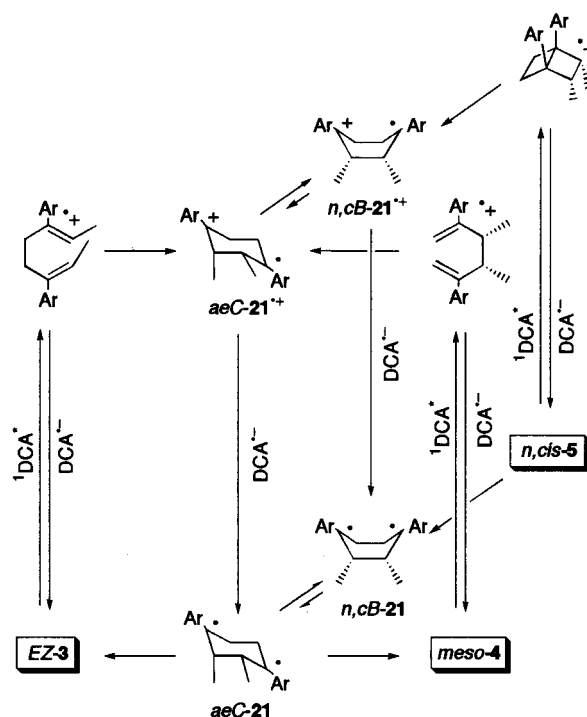
(15) Ikeda, H.; Nakamura, T.; Miyashi, T.; Goodman, J. L.; Akiyama, K.; Tero-Kubota, S.; Houmam, A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1998**, *120*, 5832–5833.

absorption with λ_{max} at 523 nm. They appear to be the same transient species on the basis of the same observed rate constants for decay (k_0) and for methanol addition (k_{MeOH}). The observed transient species is assigned to *aaC*-**21a**•+ by comparison with λ_{max} of 2,5-bis(4-methoxyphenyl)hexane-2,5-diyl cation radical (λ_{max} = 520 nm in 1,2-dichloroethane)[16] and 1,4-bis(4-methoxyphenyl)cyclohexane-1,4-diyl cation radical (λ_{max} = 508 nm in acetonitrile).[1a] If correct, results of LFP are consistent with experimental conclusions that *aaC*-**21a**•+ is formed directly from *EE*-**3a**•+, selectively from *dl*-**4a**•+, and stepwise from *trans*-**5a**•+. The transient species due to *aaC*-**21b**•+ (λ_{max} = 499 nm) and *aaC*-**21c**•+ (λ_{max} = 483 nm) are similarly observed from *EE*-**3b,c**, *dl*-**4b,c**, *trans*-**5b,c**, and *trans*-**6b,c** as shown in Table 2.[17]

The stereochemical results observed in the electron-transfer photoreactions of *EZ*-**3a** and *meso*-**4a** can be similarly explained by a CRCY−DRCL mechanism through common intermediates *aeC*-**21a**•+ and *aeC*-**21a**, as shown in Scheme 7. The masked intermediacy of *n,cB*-**21a**•+ is suggested by the DCA-sensitized photoreaction of *n,cis*-**5a** which gives a 82:18 photostationary mixture of *EZ*-**3a** and *meso*-**4a** in 98% yield in dichloromethane-d_2. Interestingly, the result of similar electron-transfer photoreaction of *x,cis*-**5a** is entirely different[18] from that of *n,cis*-**5a**, revealing that the isomeric exo intermediate, *x,cB*-**21a**•+ shown in Scheme 8, does not participate in a Cope rearrangement cycle of the *meso*-family dienes.

In conclusion, both chair and boat intermediates appear on the cation radical and diradical energy surfaces, but boat intermediates never participate either in the CRCY or in the DRCL step. However, as discussed later, boat intermediates are immediate precursors of the bicyclo[2.2.0]hexane derivatives in a Cope photostationary mixture, supporting the Cope rearrangement sequences shown in Schemes 6 and 7.

The DCA-Sensitized Photooxygenations of 3−5. In a CRCY−DRCL mechanism, the initial CRCY occurs in the chair conformation. Hence, when a cage-escaped cation radical intermediate in a Cope rearrangement cycle is captured by molecular oxygen, stereochemistry gained at the initial cyclization step should be conserved throughout oxygenation, no matter which conformational isomer is captured by oxygen. For instance, as shown in Scheme 8, *trans*-1,4-diaryl-5,6-dimethyl-2,3-dioxabicyclo[2.2.2]octane (*trans*-**22**) should be formed stereoselectively

(16) Tojo, S.; Toki, S.; Takamuku, S. *J. Org. Chem.* **1991**, *56*, 6240−6243.

(17) Interestingly, similar transients with λ_{max} = 523, 499, and 481 nm were observed from *ZZ*-**3a**, *ZZ*-**3b**, and *ZZ*-**3c**, respectively, under similar photoconditions (Table 2), suggesting an occurrence of the ring-flip of *eeC*-**21**•+ to *aaC*-**21**•+. This is attributed to suppression of BET in *eeC*-**21a**•+ under the NMQ+BF4−−BP-cosensitized conditions. Thus, free *eeC*-**21a**•+ formed under the cosensitized conditions readily flips to *aaC*-**21a**•+ whereas in an ion radical pair *eeC*-**21a**•+ suffers rapid BET as mentioned above. An alternative interpretation for this observation may be accidental coincidence in λ_{max}, k_0, and k_{MeOH} between *eeC*-**21a**•+ and *aaC*-**21a**•+. However, this is not likely because *eeC*-**21a**•+ formed by γ-ray irradiation of *ZZ*-**3a** in BuCl matrixes at 77 K exhibits an absorption band with λ_{max} at 525 nm while *aaC*-**21a**•+ from *EE*-**3a** or *trans*-**5a** has an absorption with λ_{max} at 515 nm under similar conditions.[4] A possibility of the observation of *tB*-**21**•+ can be also ruled out since a preliminary calculation using PM3 showed that energy of *tB*-**21b**•+ is higher than that of *aaC*-**21b**•+. The detail of calculation study will be given separately elsewhere.

(18) Under similar photoinduced electron-transfer conditions *x,cis*-**5a**, a potential precursor of *x,cB*-**21**•+, gave not only the *meso*-family but also the *dl*-family PS mixtures. The detail of the photoinduced electron-transfer reaction of *x,cis*-**5a**−**c** will be given separately elsewhere.

Scheme 8

Scheme 9
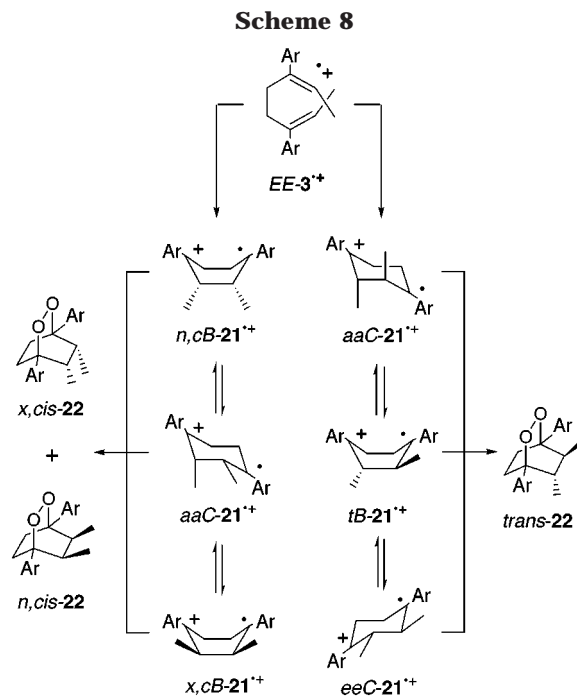
a: Ar = 4-MeOC6H4, **b**: Ar = 4-MeC6H4, **c**: Ar = C6H5

through *aaC*-**21**•+, *tB*-**21**•+, or *eeC*-**21**•+ if *EE*-**3**•+ cyclizes in the chair conformation, while cyclization in the boat conformation should afford a mixture of the cyclic peroxides, *x,cis*-**22** and *n,cis*-**22**. For the direct chemical capture of the initially formed intermediate, the DCA-sensitized photoreactions of **3**−**5** were investigated under oxygen atmosphere.

The DCA-sensitized photoreaction of *ZZ*-**3a** in oxygen-saturated acetonitrile results in a quantitative formation of *trans*-**22a** (Scheme 9). Under similar conditions, *EE*-**3a** and *dl*-**4a** give *trans*-**22a** in excellent yields as shown in Table 3. On the other hand, both *EZ*-**3a** and *meso*-**4a**

Table 3. The DCA-Sensitized Photoreaction of 3 and 4 under Oxygen[a]

				yields (%)[b]			
sub	solvent	time (min)	convn (%)[b]	trans-**22**	x,cis-**22**	n,cis-**22**	**3, 4**, and **5**
ZZ-**3a**	CH₃CN	1	100	100	0	0	0
ZZ-**3b**	CH₃CN	1	21	21	0	0	0
EE-**3a**	CH₃CN	1	100	94	0	0	0
	CH₂Cl₂	5	67	67	0	0	0
	C₆H₆	10	57	0	0	0	15 (dl-**4a**)
EE-**3b**	CH₃CN	5	98	78	0	0	2 (dl-**4b**)
	CH₂Cl₂	5	90	27	0	0	21 (dl-**4b**), 3 (trans-**5b**)
	C₆H₆	10	85	0	0	0	35 (dl-**4b**), 1 (trans-**5b**)
EE-**3c**	CH₃CN	1	64	13	0	0	11 (dl-**4c**), 5 (trans-**5c**)
EZ-**3a**	CH₃CN	1	20	0	15	4	0
		5	100	0	77	19	0
EZ-**3b**	CH₃CN	5	67	0	18	tr[c]	5 (dl-**4b**)
dl-**4a**	CH₃CN	1	100	90	0	0	0
dl-**4b**	CH₃CN	5	51	44	0	0	2 (EE-**3b**)
meso-**4a**	CH₃CN	1	21	0	12	3	0
		5	100	0	72	17	0
meso-**4b**	CH₃CN	1	26	0	13	tr[c]	3 (n,cis-**5b**)

[a] A 5 mL solution was irradiated with 2 kW Xe lamp through a cutoff filter (λ > 360 nm) at 20 °C. [sub] = 0.01 M. [b] Determined by ¹H NMR analyses. [c] Less than 2%.

Table 4. Photostationary Ratios of the DCA-Sensitized Photoreaction of ZZ-3b, EE-3a−c, and dl-4b in CD₃CN, CD₂Cl₂, and C₆D₆ at 20 °C[a]

	CD₃CN					CD₂Cl₂					C₆D₆				
	photostationary ratios[b]					photostationary ratios[b]					photostationary ratios[b]				
sub	ZZ-**3**	EE-**3**	dl-**4**	trans-**5**	yields (%)[b]	ZZ-**3**	EE-**3**	dl-**4**	trans-**5**	yields (%)[b]	ZZ-**3**	EE-**3**	dl-**4**	trans-**5**	yields (%)[b]
ZZ-**3b**						0	8	39	52	72					
EE-**3a**	0	48	52	0	58	2	42	55	1	92	0	44	50	6	100
EE-**3b**	0	41	33	26	61[c]	0	9	40	50	91[d]	0	9	76	15	97[d]
EE-**3c**	0	18	67	15	73[c]	0	5	68	27	98[d]	0	1	98	tr[e]	100
dl-**4b**	0	29	58	13	64[c]	0	8	39	52	89[d]	0	8	77	15	95

[a] A 0.5 mL solution was irradiated with a 2 kW Xe lamp through a cutoff filter (λ > 360 nm) at 20 °C. [sub] = 0.1 M, [DCA] = 5.3 × 10⁻⁴ M. [b] Determined by ¹H NMR analyses. [c] Not photostationary mixture. [d] A small amount of the meso-family compounds was formed. [e] Less than 2%.

give a 4:1 mixture of x,cis-**22a** and n,cis-**22a**. The structure of x,cis-**22a** was determined by X-ray analysis[1b] and those of trans-**22a** and n,cis-**22a** were determined by comparisons of their NMR and NOE difference spectra with those of x,cis-**22a**.

Solvent and substituent effects on oxygenation were tested for EE-**3a**−**c**. As shown in Table 3, yields of trans-**22a** from EE-**3a** and EE-**3b** significantly decrease in dichloromethane. In nonpolar benzene, oxygenations of EE-**3a** and EE-**3b** are suppressed. Interestingly, EE-**3b** gives a small amount of trans-**5b** in dichloromethane and benzene. The oxygenation efficiency in acetonitrile decreases in the order of a decrease in the electron-donating ability of EE-**3**. The rearrangement of EE-**3c** to dl-**4c** and the formation of trans-**5c** are observed for the less electron-donating EE-**3c**.

The observed stereochemical results of oxygenation are consistent with those of the Cope rearrangement, supporting the initial CRCY in the chair conformation.[14] Cation radicals ZZ-**3**•⁺ and EE-**3**•⁺ cyclize to eeC-**21**•⁺ and aaC-**21**•⁺, respectively, and dl-**4**•⁺ preferentially cyclizes to aaC-**21**•⁺. Molecular oxygen then captures either eeC-**21**•⁺, aaC-**21**•⁺, or tB-**21**•⁺, giving rise to trans-**22** via trans-**23**•⁺. Both EZ-**3**•⁺ and meso-**4**•⁺ cyclize to aeC-**21**•⁺, and the sterically more favorable x,cis-**22** is consequently afforded as a major product together with n,cis-**22** via x,cis-**23**•⁺ and n,cis-**23**•⁺, respectively. Similar DCA-sensitized photooxygenation of trans-**5a** gives trans-**22a** quantitatively in acetonitrile, supporting the Cope rearrangement sequences shown in Scheme 6.

The Photoinduced Electron-Transfer Cope Rearrangement Accompanied by the Formation of the Bicyclo[2.2.0]hexane Derivative. The Cope rearrange-

ment sequences shown in Schemes 6 and 7 suggest that trans-**5** and n,cis-**5** should be in an equilibrium with the dl- and meso-family dienes, respectively, if trans-**5** and n,cis-**5** are stable enough to survive under the DCA-sensitized electron-transfer conditions. In fact, in photooxygenation reactions in dichloromethane and benzene, EE-**3b** and EE-**3c** unexpectedly gave trans-**5b** and trans-**5c**, respectively, in low yields together with trans-**22b,c** (Table 3). Because the Cope rearrangement accompanied by the formation of the bicyclo[2.2.0]hexane derivative is unprecedented, it was of particular interest to know how **5** is formed. In addition, if the formation of **5** is concomitant stereoselectively with the Cope rearrangement, these results will provide direct evidence for the masked intermediacy of boat intermediates in the Cope rearrangement cycle. To confirm the mechanistic connection between the Cope rearrangement and the formation of the bicyclo[2.2.0]hexane derivative, the DCA-sensitized photoreactions of **3** and **4** were further investigated in terms of solvent and substituent effects.

As mentioned before, while EE-**3a** gives a photostationary mixture of EE-**3a** and dl-**4a** in acetonitrile and dichloromethane, EE-**3a** gives trans-**5a** in 6% yield together with EE-**3a** and dl-**4a** in nonpolar benzene (Table 4). Remarkably, a photostationary mixture from the less electron-donating EE-**3b** includes a large amount of trans-**5b**. The DCA-sensitized photoreaction of EE-**3b** gives a photostationary mixture of EE-**3b**, dl-**4b** and trans-**5b** in the ratio of 9:40:50 in dichloromethane (Scheme 10). Similar electron-transfer photoreactions of ZZ-**3b** and dl-**4b** in dichloromethane afford nearly the same photostationary mixture. Similarly, EE-**3c** affords a photostationary mixture of EE-**3c**, dl-**4c**, and trans-**5c**

**Table 5. Photostationary Ratios of the DCA-sensitized Photoreaction of *EZ*-3a−c and *meso*-4a−c in CD$_3$CN, CD$_2$Cl$_2$, and C$_6$D$_6$ at 20 °C[a]**

	CD$_3$CN				CD$_2$Cl$_2$				C$_6$D$_6$			
	photostationary ratios[b]				photostationary ratios[b]				photostationary ratios[b]			
sub	*EZ*-3	*meso*-4	*n,cis*-5	yields (%)[b]	*EZ*-3	*meso*-4	*n,cis*-5	yields (%)[b]	*EZ*-3	*meso*-4	*n,cis*-5	yields (%)[b]
EZ-**3a**					80	20	0	77				
EZ-**3b**	90	5	5	64[c]	53	14	33	78[c]	27	35	38	96[c]
EZ-**3c**												
meso-**4a**					80	20	0	83	75	7	18	97[d]
meso-**4b**	4	89	7	84[c]	67	18	15	94				
meso-**4c**	5	81	14	100	19	34	45	92	10	87	3	82[c]

[a] A 0.5 mL solution was irradiated with a 2 kW Xe lamp through a cutoff filter ($\lambda > 360$ nm) at 20 °C. [sub] = 0.1 M, [DCA] = 5.3 × 10^{-4} M. [b] Determined by ^{1}H NMR analyses. [c] Not photostationary mixture. [d] A small amount of the *dl*-family compounds was formed.

Table 6. Photostationary Ratios of the DCA-Sensitized Photoreaction of *trans*-5a−c at 20 °C[a]

			yields (%)[b]					
sub	solvent	time (h)	*ZZ*-3	*EE*-3	*dl*-4	*trans*-5	*meso*-family compounds	note
trans-**5a**	CD$_2$Cl$_2$	20	0	30	48	0	0	c
trans-**5b**	CD$_2$Cl$_2$	8	0	6	24	51	6 (*EZ*-**3b**), 8 (*n,cis*-**5b**)	d
trans-**5c**	CD$_2$Cl$_2$	14	0	5	46	18	2 (*meso*-**4c**), 7 (*n,cis*-**5c**)	d
trans-**5c**	CD$_3$CN	10	0	2	4	87	0	d

[a] A 0.5 mL solution was irradiated with a 2 kW Xe lamp through a cutoff filter ($\lambda > 360$ nm) at 20 °C. [sub] = 0.1 M, [DCA] = 5.3 × 10^{-4} M. [b] Determined by ^{1}H NMR analyses. [c] Photostationary mixture. [d] Not photostationary mixture.

Scheme 10

a: Ar = 4-MeOC$_6$H$_4$, **b**: Ar = 4-MeC$_6$H$_4$, **c**: Ar = C$_6$H$_5$
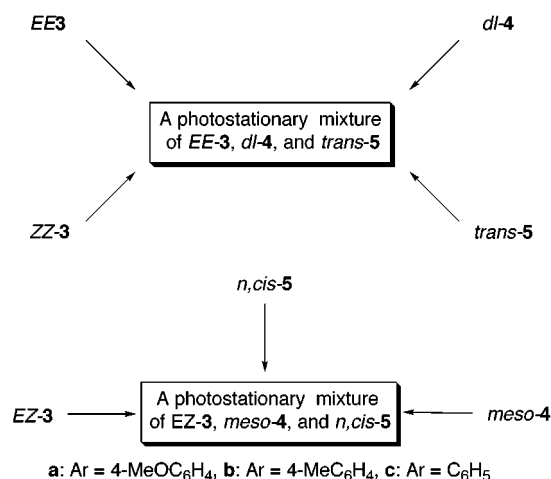
in the ratio of 5:68:27 in dichloromethane, while in acetonitrile *EE*-**3c** does not afford a clear photostationary mixture.

A photostationary mixture from *EZ*-**3a** or *meso*-**4a** does not include either *n,cis*-**5a** or *x,cis*-**5a** in dichloromethane, but in nonpolar benzene *meso*-**4a** gives *n,cis*-**5a** (Scheme 10). As shown in Table 5, in dichloromethane *EZ*-**3b** gives a 67:18:15 photostationary mixture of *EZ*-**3b**, *meso*-**4b**, and *n,cis*-**5b**. The fact that the exo isomers, *x,cis*-**5a**−**c**, are not formed from *EZ*-**3a**−**c** and *meso*-**4a**−**c** is consistent with the assumption that the exo intermediate, *x,cB*-**21**·$^+$ shown in Scheme 8, does not participate in the Cope rearrangements of *EZ*-**3** and *meso*-**4** as mentioned previously.[18]

Since bicyclo[2.2.0]hexanes are thermally labile, the formation of bicyclo[2.2.0]hexanes has never been observed in thermal reactions of 1,5-hexadienes. Consequently, the formation of bicyclo[2.2.0]hexanes is the most unique characteristic of the photoinduced electron-transfer Cope rearrangement. The formation of bicyclo[2.2.0]hexanes can be explained either by the cation radical closure of *tB*-**21**·$^+$ and *n,cB*-**21**·$^+$ or by the diradical closure of *tB*-**21** and *n,cB*-**21** as shown in Schemes 6 and 7. The diradical closure mechanism is favorable, and in fact direct irradiation of *trans*-**6** and *x,cis*-**6** give *trans*-**5**

and *n,cis*-**5**, respectively (vide supra). As shown in Tables 4 and 5, the solvent polarity and the electron-donating ability of **3**−**5** are important for the formation of *trans*-**5** and *n,cis*-**5**. In a Cope rearrangement cycle, these bicyclo-[2.2.0]hexanes are formed and collapsed in the diradical and cation radical energy surfaces, respectively, and thereby the solvent polarity and the electron-donating ability of substrates affect more significantly cleavage of **5**·$^+$ to **21**·$^+$ than closure of **21** to **5**, because the ring cleavage of nondistonic **5**·$^+$ to distonic **21**·$^+$ involves localization of the unpaired electron and positive charge. Hence, the ring cleavage of **5**·$^+$ to **21**·$^+$ is facilitated much more than closure of **21** to **5** with an increase in the solvent polarity and the electron-donating ability of substrates. Remarkable substituent effects on the bond cleavage of bicumyl cation radical to the cumyl cation and cumyl radical[19] is a suitable example in favor of this assumption. Thus, under the DCA-sensitized electron-transfer conditions in acetonitrile, the highly electron-donating *trans*-**5a** ($E^{ox}_{1/2}$ = +1.00 V vs SCE in acetonitrile) and *n,cis*-**5a** (+0.87 V) cannot survive in a Cope rearrangement cycle. In contrast, the ring cleavages of *trans*-**5b,c**·$^+$ and *n,cis*-**5b,c**·$^+$ become relatively slow, and thus **3b,c** and **4b,c** form less electron-donating *trans*-**5b,c** (+1.38 V and +1.54 V) and *n,cis*-**5b,c**, (+1.19 V and +1.31 V), respectively, even in acetonitrile. In fact, the DCA-sensitized photoreaction of *trans*-**5a** gives a photostationary mixture of *EE*-**3a** and *dl*-**4a**, but those of *trans*-**5b,c** give photostationary mixtures of *EE*-**3b,c**, *dl*-**4b,c**, and *trans*-**5b,c** (Table 6). Similar results are observed for the DCA-sensitized photoreactions of *n,cis*-**5a**−**c** as shown in Table 7.

The DCA-Sensitized Electron-Transfer Photoreactions of *trans*-6b and *x,cis*-6b. To gain further insight into the formation of *trans*-**5b** and *n,cis*-**5b** in the Cope photostationary mixture, the reactivities of the boat intermediates *tB*-**21b**·$^+$ and *n,cB*-**21b**·$^+$ were investigated by the independent generation from *trans*-**6b** and *x,cis*-**6b** under the DCA-sensitized electron-transfer conditions.

As shown in Table 8, the DCA-sensitized electron-transfer photoreaction of *trans*-**6b** gives *trans*-**5b**, *EE*-

(19) Maslak, P.; Asel, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 8260−8261.

Table 7. Photostationary Ratios of the DCA-Sensitized Photoreaction of *n,cis*-5a in CD$_2$Cl$_2$ at 20 °C[a]

|		yields (%)[b]				
sub	time (h)	*EZ*-**3**	*meso*-**4**	*n,cis*-**5**	*dl*-family compounds	note
n,cis-**5a**	10	81	19	0	0	c
n,cis-**5b**	3	59	16	21	0	d
n,cis-**5c**	8	21	32	38	7 (*dl*-**4c**), 3 (*ZZ*-**3c**)	d

[a] A 0.5 mL solution was irradiated with a 2 kW Xe lamp through a cutoff filter (λ > 360 nm) at 20 °C. [sub] = 0.1 M, [DCA] = 5.3 × 10^{-4} M. [b] Determined by ^{1}H NMR analyses. [c] Photostationary mixture. [d] Not photostationary mixture.

Table 8. Deazetation of *trans*-6b (1) and *x,cis*-6b (2) under Photoinduced Electron-Transfer and Direct Irradiation Conditions at 20 °C[a]

(1)					
			relative yields (%)[b]		
sub	conditions	convn (%)[b]	*EE*-**3**	*dl*-**4**	*trans*-**5**
trans-**6b**	$h\nu_{sens}$/DCA[c]	9	37	25	38
	$h\nu_{CT}$/TCNB[c]	21	42	26	32
	$h\nu$ (direct)[d]	21	42	30	28

(2)					
			relative yields (%)[b]		
sub	conditions	convn (%)[b]	*EZ*-**3**	*meso*-**4**	*n,cis*-**5**
x,cis-**6b**	$h\nu_{sens}$/DCA[c]	24	0	0	100
	$h\nu_{CT}$/TCNB[c]	17	0	0	100
	$h\nu$ (direct)[d]	18	0	0	100

[a] A 0.5 mL of CD$_2$Cl$_2$ solution was irradiated with a 2 kW Xe lamp through a cutoff filter. [**6b**] = 0.01 M. [b] Determined by ^{1}H NMR analyses. [c] λ > 410 nm. [d] λ > 360 nm.

3b, and *dl*-**4b** in the ratio of 38:37:25 at 9% conversion in dichloromethane-d_2 as well as photoexcitation of the charge-transfer complex of *x,cis*-**6b** and 1,2,4,5-tetracyanobenzene (TCNB). Upon prolonged irradiation, a photostationary mixture of these three compounds is formed in nearly the same ratio as those from *EE*-**3b**, *dl*-**4b**, and *trans*-**5b** (Table 4). Interestingly, direct irradiation of *trans*-**6b** in dichloromethane-d_2 gives *trans*-**5b** together with *EE*-**3b** and *dl*-**4b** in the ratio of 28:42:30 at 21% conversion (Table 8). Thus, under the photosensitized electron-transfer conditions, both *trans*-**5b** and dienes (*EE*-**3b**, *dl*-**4b**) are probably formed from *tB*-**21b** formed by BET from DCA$^{•-}$ to *tB*-**21b**$^{•+}$. A ring-closure of *tB*-**21b** affords the former whereas the latter is given by ring flip of *tB*-**21b** followed by cleavage of *aaC*-**21b**. Alternatively, dienes (*EE*-**3b**, *dl*-**4b**) may be formed by ring flip of *tB*-**21b**$^{•+}$ followed by BET and cleavage as shown in Scheme 11. However, results of the reactions under the photosensitized and directly irradiated conditions and calcu-

Scheme 11
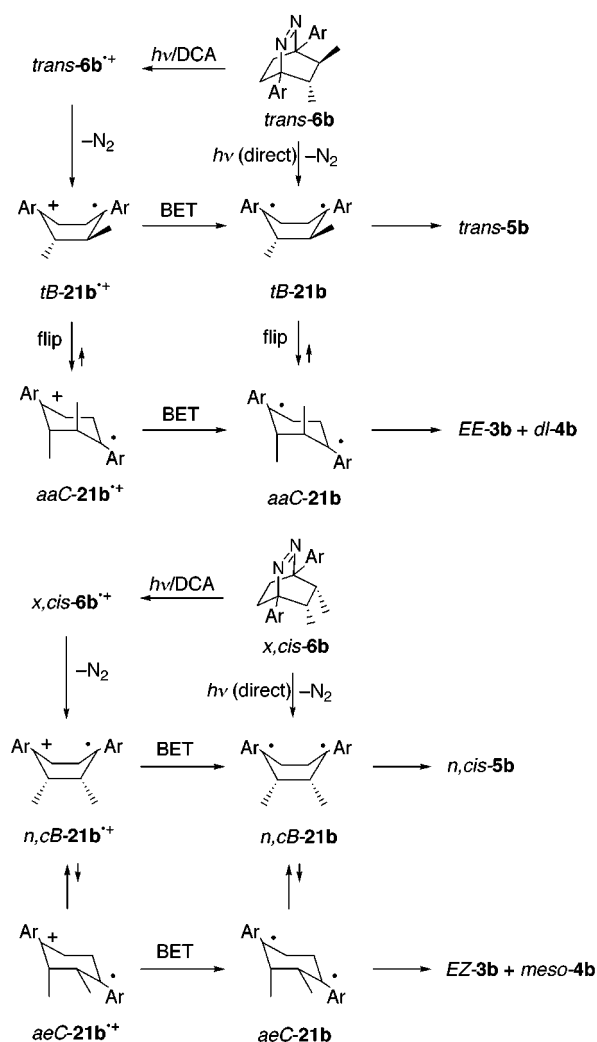
lated rate constant, $k_{bet} = 2 \times 10^{10}$ s^{-1}, in dichloromethane,[20,23] suggest that the rapid BET takes place in [*tB*-**21b**$^{•+}$/DCA$^{•-}$] to afford *tB*-**21b** in preference to the ring flip.

In contrast to photoreaction of *trans*-**6b**, *n,cis*-**5b** is exclusively formed in similar DCA-sensitized photoreaction of *x,cis*-**6b** and photoexcitation of the charge-transfer complex of *x,cis*-**6b** and TCNB as shown in Table 8. Thus, under the photoinduced electron-transfer conditions the BET from DCA$^{•-}$ to *n,cB*-**21b**$^{•+}$ followed by closure of *n,cB*-**21b** to *x,cis*-**5b** occur much faster than flip of *n,cB*-**21b**$^{•+}$ to *aeC*-**21b**$^{•+}$. The observed result is consistent with the Cope rearrangement sequence shown in Scheme 7.

(20) Rate constant, k_{bet}, of the BET in [**21**$^{•+}$/DCA$^{•-}$] at 20 °C in dichloromethane was estimated by using the following eqs. (1, 2,[21] and 3) and parameters reported by Kikuchi.[22]

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

$$S = \lambda_v/h\nu \quad (2)$$

$$\Delta G_{bet} \text{ (eV)} = -[E^{ox}_{1/2}(\mathbf{21}) - E^{red}_{1/2}(\text{DCA}) - e^2/\epsilon r] \quad (3)$$

where parameters $|V|^2$, λ_s, λ_v, ν, and ΔG_{bet} are respectively an electronic matrix element squared, solvent reorganization energy, vibrational reorganization energy, single average frequency, and free energy change for BET process.[23] $E^{red}_{1/2}$(DCA) is -0.89 and -0.95 V vs SCE in dichloromethane and acetonitrile, respectively. The Coulombic term ($e^2/\epsilon r$) is 0.23 eV in dichloromethane while this term is ignored in acetonitrile.[11c]

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(23) These calculations have been done on the assumption that $E^{ox}_{1/2}$ of *tB*-**21b** and *aaC*-**21a** are comparable with $E^{ox}_{1/2}$ of the 4-methylcumyl radical[24] (+0.03 V vs SCE in acetonitrile) and 4-methoxycumyl radical[25] (-0.14 V), respectively, and that $E^{ox}_{1/2}$ in dichloromethane are generally more positive by ca. 0.1 V than those in acetonitrile. These estimations give higher limits of ΔG_{bet} because $E^{ox}_{1/2}$ of **21** may be more positive. This was suggested from a significant electronic coupling between the substituted cumyl cation and cumyl radical parts in a cyclohexane-1,4-diyl cation radical.[1a,d] Unfortunately, however, it is difficult to evaluate this electronic coupling effects upon redox potentials.

Table 9. Deconvolution Fitting Parameters[a] of PAC Analyses for Determination of Energy of the Ion Radical Pair, $\Delta H_{\text{irp}}([aaC\text{-}21a^{\bullet+}/DCA^{\bullet-}])$

sub	α_1	α_2	τ_2 (ns)	$\Delta H_{\text{irp}}([aaC\text{-}21a^{\bullet+}/DCA^{\bullet-}])$ (kcal/mol)[b]
ZZ-**3a**	0.25 ± 0.02	0.24 ± 0.02	205 ± 25	44.9 ± 2.1
EE-**3a**	0.26 ± 0.03	0.22 ± 0.02	160 ± 53	46.3 ± 1.5
dl-**4a**	0.25 ± 0.01	0.26 ± 0.00	191 ± 16	43.0 ± 0.4
trans-**5a**	0.28 ± 0.00	0.40 ± 0.01	219 ± 11	29.3 ± 1.5

[a] The errors are 1σ. [b] Face values relative to each substrate and DCA.

Upon prolonged irradiation *n,cis*-**5b** enters into a Cope rearrangement cycle to give a Cope photostationary mixture as shown in Table 7. The fact that direct irradiation of *x,cis*-**6b** forms *n,cis*-**5b** exclusively supplements a diradical closure mechanism shown in Scheme 7.

Photoacoustic Calorimetric Analysis and Energetics of the Photoinduced Electron-Transfer Cope Rearrangements of *EE*-3a and *dl*-4a. Nanosecond time-resolved photoacoustic calorimetry (PAC)[26] allows for the simultaneous determination of dynamics and energetics of various photoinduced electron-transfer reactions.[1a,15,27] In fact, our recent PAC experiments demonstrated that a CRCY−DRCL mechanism (Scheme 1) is energetically most favorable for the photoinduced electron-transfer degenerate Cope rearrangement of d_4-**1**.[1a] For further confirmation of this mechanism, we have used PAC to investigate the Cope rearrangement of *EE*-**3a** and *dl*-**4a**.

Experiments were done under DCA−BP-cosensitized conditions in acetonitrile.[1a,15,27e] The enthalpy of formation of $[aaC\text{-}21a^{\bullet+}/DCA^{\bullet-}]$ can be expressed by $\Delta H_{\text{irp}}([aaC\text{-}21a^{\bullet+}/DCA^{\bullet-}]) = h\nu(1 - \alpha_1 - \alpha_2)/\phi$ and $\phi = h\nu(1 - \alpha_1)/E([BP^{\bullet+}/DCA^{\bullet-}])$, where $h\nu$, α, ϕ, and $E([BP^{\bullet+}/DCA^{\bullet-}])$ are the photon energy (415 nm, 68.9 kcal/mol), the deconvolution parameters, the quantum yield to form $[BP^{\bullet+}/DCA^{\bullet-}]$, and the energy (66.2 kcal/mol) of $[BP^{\bullet+}/DCA^{\bullet-}]$ determined from redox potentials of BP and DCA, respectively. ΔH_{irp} was determined from several experiments for *EE*-**3a** and *dl*-**4a**, and shown in Table 9 together with another deconvolution parameter, τ_2. The energy of ion radical pair, $\Delta H_{\text{irp}}([aaC\text{-}21a^{\bullet+}/DCA^{\bullet-}])$, relative to *dl*-**4a** and DCA is determined to be 43.0 ± 0.4 kcal/mol. By adding this value to the difference in heat of formation between *dl*-**4a** and *EE*-**3a**, 6.0 ± 1.5 kcal/mol, determined by differential scanning calorimetry, $\Delta H_{\text{irp}}([aaC\text{-}21a^{\bullet+}/DCA^{\bullet-}])$ relative to *EE*-**3a** and DCA is estimated to be 49.2 ± 1.9 kcal/mol which corresponds to the experimental value, 46.3 ± 1.5 kcal/mol, obtained from *EE*-**3a** within experimental errors. In Figure 1, the
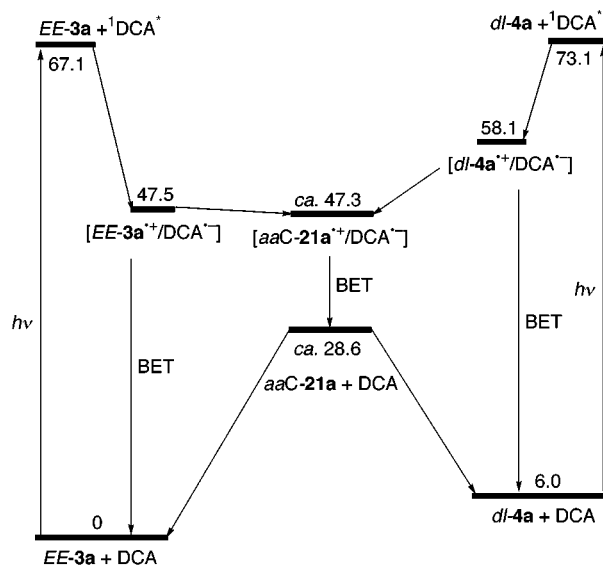
(24) $E^{\text{ox}}_{1/2}$ of the 4-methylcumyl radical is estimated by interpolation from the correlation between the known $E^{\text{ox}}_{1/2}$ of 4-substituted cumyl radicals[25] and the substituent constants σ^+.

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Figure 1. Potential energy diagram for the DCA-sensitized PET Cope rearrangement of *EE*-**3a** and *dl*-**4a**. Relative energy was represented in kcal/mol.

statistic value, 47.3 kcal/mol is used for $\Delta H_{\text{irp}}([aaC\text{-}21a^{\bullet+}/DCA^{\bullet-}])$.

By using redox potentials of *EE*-**3a**, *dl*-**4a**, and DCA, the energies of ion pair $[EE\text{-}3a^{\bullet+}/DCA^{\bullet-}]$ and $[dl\text{-}4a^{\bullet+}/DCA^{\bullet-}]$ are calculated to be 58.1 and 47.5 kcal/mol, respectively. The CRCY of *dl*-**4a**$^{\bullet+}$ to *aaC*-**21a**$^{\bullet+}$ is thus about 11 kcal/mol exothermic. In contrast, the energy of $[EE\text{-}3a^{\bullet+}/DCA^{\bullet-}]$ is close to that of $[aaC\text{-}21a^{\bullet+}/DCA^{\bullet-}]$, and hence the direct cleavage of *aaC*-**21a**$^{\bullet+}$ to *EE*-**3a**$^{\bullet+}$ seems to be energetically feasible but perhaps slower. However, BET to form diyl *aaC*-**21a** is assumed to occur faster than cleavage to *EE*-**3a**$^{\bullet+}$. To judge experimentally whether cleavage of *aaC*-**21a**$^{\bullet+}$ to *EE*-**3a**$^{\bullet+}$ is operative, *aaC*-**21a**$^{\bullet+}$ was independently generated from *trans*-**5a**, and temperature effects on product ratios from *aaC*-**21a**$^{\bullet+}$ were examined at low conversion in the temperature range between 60 and −80 °C. The product ratios, *dl*-**4a**:*EE*-**3a**, at low conversion does not depend on temperature, and the average ratio is near 32:68.[4] This observation suggests that cleavage of *aaC*-**21a**$^{\bullet+}$ to *EE*-**3a**$^{\bullet+}$ is not thermally accelerated and thus unlikely to occur in a Cope rearrangement sequence. Thus, *aaC*-**21a**$^{\bullet+}$ generated from *EE*-**3a**$^{\bullet+}$ and *dl*-**4a**$^{\bullet+}$ preferentially suffers BET to give *aaC*-**21a**, through which *EE*-**3a** and *dl*-**4a** are formed. Using ΔG_{bet} for the BET from DCA$^{\bullet-}$ to *aaC*-**21a**$^{\bullet+}$ to be about 19 kcal/mol,[20,23] *aaC*-**21a** is about 29 kcal/mol higher in energy than *EE*-**3a**.

Conclusion. Observed stereospecificity and energetics based on PAC support a CRCY−DRCL mechanism of the Cope rearrangement for the title dienes. The initial cyclization of the diene cation radicals occurs in the chair conformation to give the chair 1,4-diaryl-2,3-dimethylcyclohexane-1,4-diyl cation radical intermediates. Subsequent cleavage of the chair 1,4-diaryl-2,3-dimethylcyclohexane-1,4-diyl intermediates regenerates the neutral dienes. These two processes are connected by the highly exothermic BET from DCA$^{\bullet-}$ to the 1,4-diaryl-2,3-dimethylcyclohexane-1,4-diyl cation radicals. A CRCY−DRCL mechanism is thus a general rearrangement sequence for the photoinduced electron-transfer Cope rearrangement of the 2,5-diaryl-1,5-hexadiene system. The chair intermediates interconvert with the boat

intermediates on the cation radical and diradical energy surfaces in a Cope rearrangement cycle, but the boat diyl intermediates formed by BET never participate in the cleavage step, perhaps because of poor orbital overlap. The boat intermediates, however, play an important role in an unusual Cope rearrangement yielding the bicyclo-[2.2.0]hexane derivative in the photostationary mixture. The concurrent formation of bicyclo[2.2.0]hexane derivatives with the Cope rearrangement is thus the most remarkable characteristic of the photoinduced electron-transfer Cope rearrangement of the title dienes.

Experimental Section

General Method. See the Supporting Information.

Syntheses of Substrates Shown in Chart 1. See the Supporting Information.

X-ray Structural Analyses. All of data collections of *trans-***5c**, *n,cis-***5c**, and *x,cis-***5c** were performed on an AFC-5R automated four-circle diffractometer (45 kV, 200 mA) equipped with a rotating anode (Mo Kα radiation, $\lambda = 0.71049$ Å or Cu Kα radiation, $\lambda = 1.5418$ Å) at the Instrumental Analyses Center for Chemistry, Graduate School of Science, Tohoku University. These structure were solved by direct method using the RANTAN81[28] program with some modification. Atomic parameters were refined by the block-diagonal least-squares methods by applying anisotropic temperature factors for non-hydrogen atoms. At the final stage, hydrogen atoms were included in the refinement with isotropic temperature factors. All the calculations were carried out on a ACOS 2020 and ACOS 3900 computers at Tohoku University by using the applied library program of the UNICS III system.[29] Details of X-ray structural analyses, ORTEP diagrams, final atomic coordinates and thermal parameters, bond length and angles, structure factors, and thermal ellipsoids with atom numbering systems are given in the Supporting Information.

Analyses of Time-Dependent Change of Product Ratios for the DCA-Sensitized Photoreactions of 3–6. A typical procedure: A 0.1 M solution (0.5 mL) containing 0.05 mmol of substrate (**3–6**) and 2–3 mg of DCA in CD$_3$CN, CD$_2$-Cl$_2$, or C$_6$D$_6$ was irradiated with a 2 kW Xe lamp through a Toshiba cutoff filter L-39 ($\lambda > 360$ nm) for **3–5** or Y-44 ($\lambda >$ 410 nm) for **6** under N$_2$ at 20 ± 1 °C. Time-dependent changes of product ratios were determined by 200 MHz ^{1}H NMR analyses.

DCA-Sensitized Photoreactions of 3–5 under O$_2$ in Various Solvents. A general procedure: A 5 mL solution containing 0.05 mmol of substrate (**3–5**) (0.01 M) and 2–3 mg of DCA in CH$_3$CN, CH$_2$Cl$_2$, or C$_6$H$_6$ was irradiated with a 2 kW Xe lamp through a Toshiba cutoff filter L-39 ($\lambda > 360$ nm) under O$_2$ at 20 ± 1 °C. Removal of solvent and PTLC followed by recrystallization afforded cyclic peroxide **22**. Physical data of **22** are shown in Supporting Information.

Photoexcitation of the Charge-Transfer Complex of 6b and TCNB. A 0.5 mL CH$_2$Cl$_2$ solution containing 15.9 mg (0.05 mmol) of **6b** and ca. 1 mg (ca. 0.005 mmol) of TCNB was irradiated with a 2 kW Xe lamp through a Toshiba cutoff filter Y-44 ($\lambda > 410$ nm) under N$_2$ at 20 ± 1 °C. The product ratios at low conversion were determined by 200 MHz ^{1}H NMR analyses.

Direct Irradiation of 6b. A 0.5 mL CD$_2$Cl$_2$ solution containing 15.9 mg (0.05 mmol) of **6b** in CD$_2$Cl$_2$ was irradiated with a 2 kW Xe lamp through a Toshiba cutoff filter L-39 ($\lambda > 360$ nm) under N$_2$ at 20 ± 1 °C. The product ratios at low conversion were determined by 200 MHz ^{1}H NMR analyses.

Energy Determination by Time-Resolved PAC. The detail of PAC experiment has been described previously.[1a,26] A chart of the PAC waveforms for *EE-***3a**-DCA-BP system and lists of deconvolution fitting parameters for experimental waveforms in each PAC experiment are shown in the Supporting Information. Values were obtained by at least two separate runs and errors are with in 1σ.

Supporting Information Available: Syntheses of substrates shown in Chart 1, details of X-ray structural analyses of *trans-***5c**, *n,cis-***5c**, and *x,cis-***5c**, a table of $E^{ox}_{1/2}$, ΔG, and k_q for **3–6**, physical data of *trans-***22a,b**, *x,cis-***22a,b**, and *n,cis-***22a**, a chart of the PAC waveforms (*EE-***3a**–DCA-BP system in CH$_3$CN), tables of deconvolution fitting parameters for experimental waveforms in each PAC experiment, and a table of differential scanning calorimetric analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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