Photoinduced Electron-Transfer Degenerate Cope Rearrangement of 2,5-Diaryl-1,5-hexadienes: A Cation-Radical Cyclization−Diradical Cleavage Mechanism

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Abstract: Under the 9,10-dicyanoanthracene (DCA)-sensitized photoinduced electron-transfer (PET) conditions, 2,5-diaryl-3,3,4,4-tetradeuterio-1,5-hexadiene (d_4-**1**) undergoes a degenerate Cope rearrangement to give a photostationary mixture of d_4-**1** and its 1,1,6,6-tetradeuterio analogue d_4-**1′** in 52:48. This reaction involves 1,4-diaryl-2,2,3,3-tetradeuteriocyclohexane-1,4-diyl cation radical (d_4-**2**$^{\bullet+}$), which can be captured by molecular oxygen as 1,4-diaryl-2,3-dioxabicyclo[2.2.2]octane (**3**). In contrast, nonphotoinduced electron-transfer (non-PET) reaction of d_4-**1** with cerium(IV) ammonium nitrate similarly forms d_4-**2**$^{\bullet+}$, but the degenerate Cope does not take place. This observed striking contrast between PET and non-PET was ascribed to the formation of 1,4-diaryl-2,2,3,3-tetradeuteriocyclohexane-1,4-diyl (d_4-**2**) in the PET process by back-electron transfer from DCA$^{\bullet-}$ to d_4-**2**$^{\bullet+}$. The results of similar PET and non-PET reactions of 1,4-diphenyl-2,3-diazabicyclo[2.2.2]-oct-2-ene (**4c**) and its 5,5,6,6-tetradeuterio analogue (d_4-**4c**) support this conclusion. Photoacoustic calorimetry of the PET reaction of 2,5-diphenyl-1,5-hexadiene (**1c**) suggests that 1,4-diphenylcyclohexane-1,4-diyl (**2c**) lies *ca.* 18.8 kcal/mol higher in energy than **1c** and *ca.* 25.6 kcal/mol below the ion-radical pair [**2c**$^{\bullet+}$/DCA$^{\bullet-}$]. Deazetation of d_4-**4c** demonstrates that d_4-**2c** undergoes cleavage to d_4-**1c** and d_4-**1c′** with bond-breaking kinetic isotope effects, $k(d_4\text{-}\mathbf{2c})^{H}4 / k(d_4\text{-}\mathbf{2c})^{D}4 = 1.11$, completing a cation-radical cyclization−diradical cleavage mechanism.

Introduction

Upon heating, acyclic 1,5-hexadienes undergo the Cope rearrangement, which is an extremely useful thermal rearrangement in organic synthesis, and the rearrangement occurs stereospecifically through a chair six-membered cyclic transition state. The reaction is characterized by large negative entropy of activation and is relatively insensitive to substituent and solvent effects.[1] In fact, most Cope rearrangements display these characteristics and have been accounted for consistently by a concerted mechanism. However, a stepwise cyclization−cleavage (CY−CL) mechanism through a chair cyclohexane-1,4-diyl intermediate has been argued as one possible nonconcerted mechanism.[2,3] Dewar previously proposed that this mechanism would operate in the Cope rearrangement of the labeled 2,5-diphenyl-1,5-hexadiene (d_4-**1c′**) through a 1,4-diphenylcyclohexane-1,4-diyl intermediate (d_4-**2c**) (Scheme 1a).[3f] Although no direct experimental evidence for the intermediacy of d_4-**2c** is reported yet, Doering's recent theoretical calculation for the enthalpy of formation of diyl **2c** and the "frustrated" Cope rearrangement of 2,6-diphenyl-1,6-heptadiene[2b] are intriguing results to assert a possible operation of a CY−CL mechanism in the thermal Cope rearrangement of d_4-**1c**.

On the other hand, Bauld and co-workers have theoretically argued a cation radical (CR) variant[4] of a thermal CY−CL process. Their calculation suggests that the parent 1,5-hexadiene CR would cyclize either to a chair or to a boat cyclohexane-1,4-diyl CR intermediate with a low energy barrier, but the second cleavage step would require a relatively high activation, suggesting that the CR cleavage is a crucial key step in a cation-radical cyclization−cation-radical cleavage (CRCY−CRCL) mechanism (Scheme 1b). Independent of this theory, we investigated the 9,10-dicyanoanthracene (DCA)-sensitized photoinduced electron-transfer (PET) reaction of d_4-**1** to examine if the PET degenerate Cope rearrangement proceeds through a cyclohexane-1,4-diyl CR intermediate.[5] Under DCA-sensitized conditions, the degenerate Cope of d_4-**1** occurs efficiently, giving

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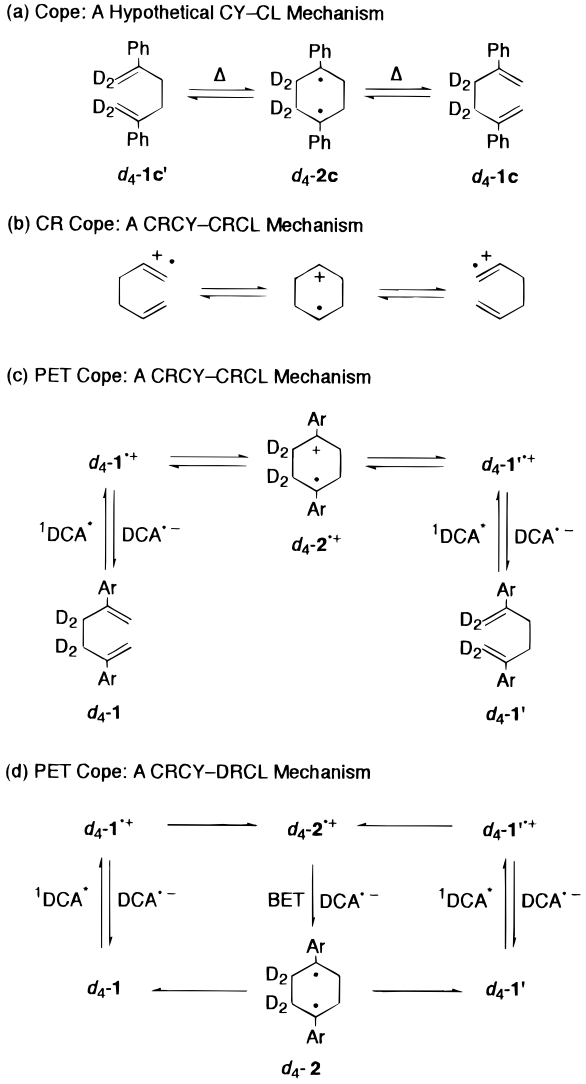
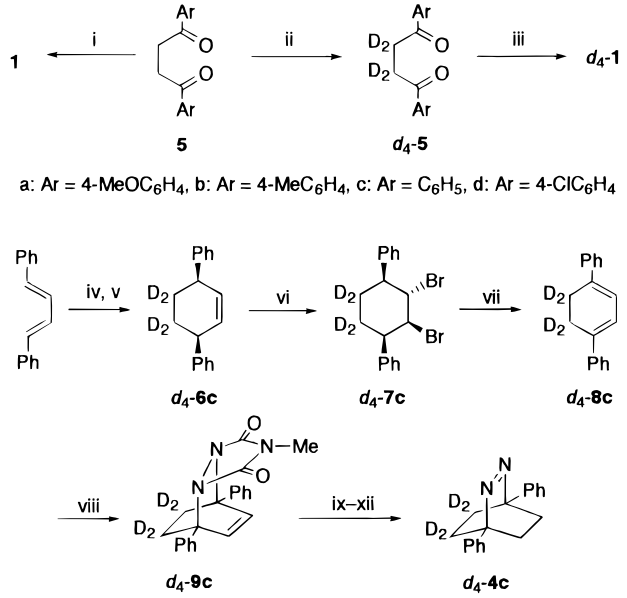
Scheme 1



rise to a photostationary (PS) mixture of d_4-**1** and the 1,1,6,6-tetradeuterio analogue (d_4-**1′**). The degenerate Cope rearrangement of d_4-**1**, however, did not take place in non-PET reactions such as a single-electron transfer with cerium(IV) ammonium nitrate (CAN). In order to gain insight into the mechanism of the PET degenerate Cope, 1,4-diphenyl-2,3-diazabicyclo[2.2.2]-oct-2-ene (**4c**) and its 5,5,6,6-tetradeuterio analogue (d_4-**4c**) were also subjected to similar PET and non-PET reactions. Diene **1c** was formed from **4c** under PET conditions but not under non-PET conditions. On the basis of those results, the cation-radical cyclization−diradical cleavage (CRCY−DRCL) mechanism (Scheme 1d) was proposed for the PET degenerate Cope. In addition, an energetic argument also favors a CRCY−DRCL mechanism rather than a CRCY−CRCL mechanism. Herein, we report characteristics and energetics of the PET degenerate Cope rearrangement of d_4-**1** in detail.

Scheme 2[a]



[a] Key: (i) $Ph_3P^+CH_3 \cdot I^-$, *t*-BuOK/THF; (ii) D_2O, Et_3N/dioxane; (iii) $Ph_3P^+CH_3 \cdot I^-$, *n*-BuLi/THF; (iv) Mg*/THF; (v) 1,2-dichlorotetradeuterioethane; (vi) pyridinium bromide perbromide/AcOH; (vii) DBU/C_6H_6; (viii) 4-methyl-1,2,4-triazoline-3,5-dione/AcOEt; (ix) H_2/Pt−$CaCO_3$/AcOEt; (x) KOH/*i*-PrOH; (xi) $CuCl_2$/*i*-PrOH; (xii) NH_4OH.

Results and Discussion

Syntheses and Electron-Donating Properties of 1a−d, d_4-1a−d, 4c, and d_4-4c. The labeled and unlabeled 4-methoxyphenyl, 4-methylphenyl, phenyl, and 4-chlorophenyl derivatives of 2,5-diaryl-1,5-hexadienes (d_4-**1a**−**d** and **1a**−**d**) were prepared from d_4-**5a**−**d** and **5a**−**d**,[8−11] respectively (Scheme 2). 1,4-Diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (**4c**)[12] and the labeled d_4-**4c** were derived from 1,4-diphenylcyclohexa-1,3-diene (**8c**) and the labeled d_4-**8c**, respectively, as shown in Scheme 2. The labeled d_4-**6c** prepared by the reaction[13a] of (*E*,*E*)-1,4-diphenyl-1,3-butadiene and 1,2-dichlorotetradeuterioethane using active Mg was converted to d_4-**8c** and d_4-**9c**. The deuterium incorporations in d_4-**1a**−**d** and d_4-**4c** were shown to be 98−99% (3.92−3.96 atom D per molecule at C-2 and C-3) and 97% (3.88 atom D per molecule at C-5 and C-6), respectively, by ^{1}H NMR (CW, FT) and MS analyses.

2,5-Diaryl-1,5-hexadienes (**1a**−**d**) and diazene **4c** are good electron donors, and their oxidation potentials, $E^{ox}_{1/2}$, are low enough to quench the excited singlet state of DCA (^{1}DCA*) exothermically. Free energy changes,[14] ΔG, associated with the forward electron transfer are calculated according to the Rehm−Weller equation[15ab] and are listed in Table 1 together with $E^{ox}_{1/2}$ and the DCA-fluorescence quenching rate constants,

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(14) ΔG (kcal/mol) = 23.06 [$E^{ox}_{1/2}$(substrate) − $E^{red}_{1/2}$(DCA) − E_{0-0}] − $e^2/\epsilon r$ where $E^{red}_{1/2}$(DCA) is −0.95 V, E_{0-0} is 2.91 eV in CH_3CN, and the coulombic term ($e^2/\epsilon r$) was ignored after Farid's example.[15c]

Table 1. Oxidation Potentials ($E^{ox}_{1/2}$) and Free Energy Changes (ΔG) Associated with Electron Transfer with ^{1}DCA* and DCA-Fluorescence Quenching Rate Constants (k_q) for **1** and **4c**

			$10^{10}k_q$ (M^{-1} s^{-1})		
sub	$E^{ox}_{1/2}$[a] (V)	ΔG[c] (kcal/mol)	CH_3CN	CH_2Cl_2	C_6H_6
1a	+1.27	−15.9	2.0	1.5	1.1
1b	+1.54	−9.7	1.5	1.0	0.50
1c	+1.68	−6.5	1.2	0.36	0.06
1d	+1.71	−5.8	1.1	0.28	0.03
4c	+1.16, +1.39[b]	−18.4	1.6	1.2	1.1

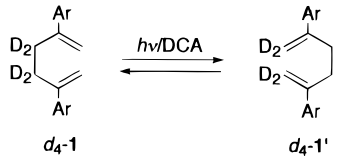
[a] Vs SCE in CH_3CN, scan rate 100 mV s^{-1}. [b] In CH_2Cl_2. [c] In CH_3CN.

k_q. In accord with the calculated thermodynamics, **1a**−**d** quench the DCA-fluorescence with nearly the same rate constants, k_q, close to the diffusion control rate constant, but in the less polar solvent dichloromethane and the nonpolar solvent benzene, rate constants decrease with an increase in oxidation potential of **1**. Rate constants, k_q, of highly electron-donating **1a** in the three solvents were nearly the same regardless of solvent polarity, but those of the less electron-donating **1b**−**d** decrease with a decrease in solvent polarity.

The DCA-Sensitized PET Degenerate Cope Rearrangement of d_4-1 and Chemical Capture of $2^{\bullet+}$. According to theoretical arguments, the Cope rearrangement of the parent 1,5-hexadiene CR can be explained either by a concerted or by a stepwise mechanism. In the former process, a suprafacial−suprafacial pathway was suggested to be favored based on orbital-symmetry correlations,[16] while in the latter process, the rearrangement would occur through the "long-bonded" boat-like or chair cyclohexane-1,4-diyl CR intermediate (Scheme 1b).[4] If a stepwise process similar to the latter operates in the PET degenerate Cope rearrangement of d_4-**1** (Scheme 1c), we thought that a cyclohexane-1,4-diyl CR intermediate (d_4-$\mathbf{2}^{\bullet+}$) may be intercepted by molecular oxygen, as various other intriguing CR intermediates have been.[17]

First, we investigated the degenerate Cope rearrangement of d_4-**1** and oxygenation of **1** under various DCA-sensitized conditions. Irradiation (λ > 360 nm) of DCA with d_4-**1** at 20 °C gives a PS mixture of d_4-**1** and d_4-**1′** in acetonitrile, dichloromethane, and benzene as shown in Table 2. In dichloromethane, the Cope rearrangement of d_4-**1b**−**d** occurs efficiently even at −80 °C. The PS ratios are nearly the same regardless of solvent polarity and the electron-donating nature of substrates. The average PS ratio observed for four aryl derivatives in three different solvents is approximately 52:48 at 20 °C. However, the quantum efficiency for the degenerate Cope rearrangement was strongly dependent upon solvent polarity and the electron-donating nature of the substrates. Quantum efficiencies, Φ_{cor}, corrected by quenching efficiencies, Q_e, are shown in Table 2. The Φ_{cor} tends to increase as solvent polarity and the electron-donating nature of substrates decrease, except for the least electron-donating substrates d_4-**1d**.

Table 2. Photostationary Ratio (d_4-**1**:d_4-**1′**)[a] and Corrected Quantum Yield (Φ_{cor}) for the PET Degenerate Cope Rearrangement of d_4-**1** at 20 °C

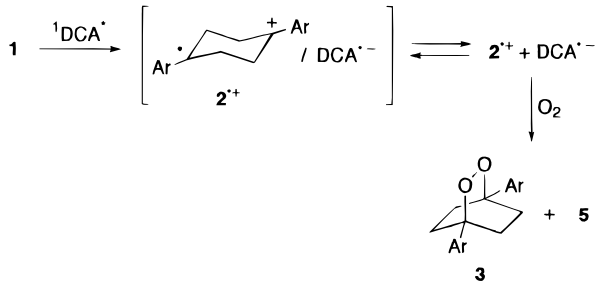


d_4-**1** d_4-**1′**

	d_4-**1**:d_4-**1′**			Φ_{cor}[e]		
sub	CD_3CN	CD_2Cl_2	C_6D_6	CD_3CN	CD_2Cl_2	C_6D_6
d_4-**1a**	52:48[b]	51:49[c]	51:49[d]	n.a.[f]	0.14	0.38
d_4-**1b**	53:47[c]	52:48	54:46	0.21	0.32	0.48
d_4-**1c**	53:47	52:48	53:47	0.34	0.42	0.50
d_4-**1d**	52:48	53:47	53:47	0.33	0.36	0.35

[a] [d_4-**1**] = 100 mM. [b] [d_4-**1**] = 1.25 mM. [c] [d_4-**1**] = 50 mM. [d] [d_4-**1**] = 25 mM. [e] $\Phi_{cor} = \Phi/Q_e$, where $Q_e = k_q\tau[\mathbf{1}]/(1 + k_q\tau[\mathbf{1}])$ and [**1**] = 10 mM. [f] No attempt.

Scheme 3



a: Ar = 4-$MeOC_6H_4$, b: Ar = 4-MeC_6H_4, c: Ar = C_6H_5, d: Ar = 4-ClC_6H_4

Table 3. Solvent and Substituent Effects on the DCA-Sensitized Photooxygenation of **1**[a]

				yields (%)	
sub	solvent	time (min)	conversion (%)	**3**	**5**
1a	C_6H_6	60	0	0	0
	CH_2Cl_2	5	37	37	0
	CH_2Cl_2	20	100	93	0
1b	CH_3CN[b]	5	100	93	0
	CH_3CN	5	62	59	1
1c	CH_3CN	5	6	4	1
	CH_3CN	20	42	10	3
1d	CH_3CN	20	30	14	3

[a] λ > 360 nm irradiation, [**1**] = 10 mM. [b] [**1**] = 2 mM.

In contrast, irradiation of DCA with **1a** in oxygen-saturated acetonitrile results in the formation of the oxygenation products 1,4-bis(4-methoxyphenyl)-2,3-dioxabicyclo[2.2.2]octane (**3a**) in 93% yield after 5-min irradiation (Scheme 3). As solvent polarity decreases, yields of oxygenation decrease significantly. In less polar dichloromethane, **3a** is formed in 93% yield after 20-min irradiation, but **1a** is quantitatively recovered even after 60-min irradiation in benzene, in which the degenerate Cope rearrangement efficiently occurs. The electron-donating nature of **1** also affects the efficiency of the oxygenation reaction. As shown in Table 3, the yield of **3** significantly increase with an increase in the electron-donating nature of **1a**−**d**. Since the CAN- and cerium(IV) tetra-*n*-butylammonium nitrate [Ce(*n*-$Bu_4N)_2(NO_3)_6$, CBN][18]-catalyzed reaction of **1a** also afforded **3a** together with 4,4″-dimethoxy-*p*-terphenyl (**10a**) under oxygen (Table 4), it is reasonable to conclude that oxygen intercepted CR $\mathbf{2a}^{\bullet+}$ in a PET process. By combination of those

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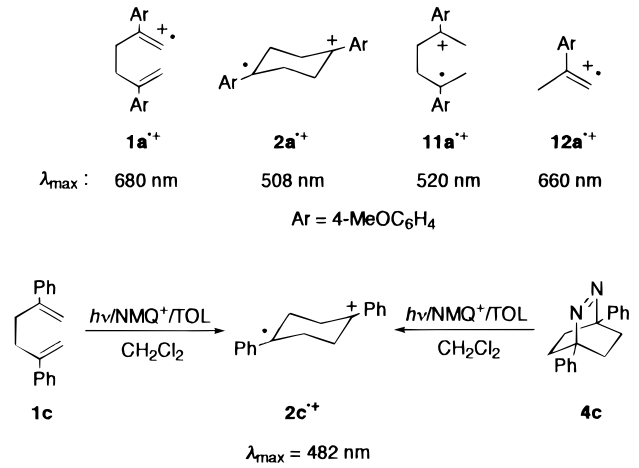
Table 4. CAN- or CBN-Catalyzed Oxygenations of **1a** under O_2 and d_4-**1a** under N_2 in CH_3CN[a]

			yields (%)			
sub	oxidant	convsn (%)	**3a**	**10a**	d_2-**10a**	d_4-**1**:d_4-**1′**
1a	CAN	80	63	9		
1a	CBN	80	58	10		
d_4-**1a**	CAN	28			4	>99:<1
d_4-**1a**	CBN	40			5	>99:<1

[a] [**1**] = [d_4-**1**] = 1 mM.

Scheme 4



experimental results it can be concluded that the PET degenerate Cope rearrangement of d_4-**1** occurs in a stepwise mechanism involving the chair[5,7c] 1,4-diarylcyclohexane-1,4-diyl CR (d_4-**2**$^{\bullet+}$). The inverse solvent effects observed in the PET degenerate Cope rearrangement and oxygenation suggest that the degenerate Cope rearrangement preferentially occurs as an in-cage process, while oxygenation occurs as an out-of-cage process.[19]

Spectroscopic Identification of 2$^{\bullet+}$**.** In order to observe **2**$^{\bullet+}$ spectroscopically, nanosecond laser flash photolysis was carried out for **1a** and **1c** under the DCA- or *N*-methylquinolinium tetrafluoroborate ($NMQ^+BF_4^-$)-sensitized conditions. Upon irradiation (355 nm) of an acetonitrile solution of **1a** (1 mM), DCA (0.35 mM), and biphenyl (BP) (0.2 M) under nitrogen atmosphere, an intense transient absorption with λ_{max} at 508 nm appears after 200 ns. This absorption is assigned to **2a**$^{\bullet+}$ by comparison with the absorption maximum of 2,5-bis(4-methoxyphenyl)hexane-2,5-diyl CR (**11a**$^{\bullet+}$, λ_{max} = 520 nm in 1,2-dichloroethane) reported by Takamuku and co-workers (Scheme 4).[20] CR **2a**$^{\bullet+}$ was relatively stable and persisted for several μs under nitrogen at room temperature, but under aerated conditions **2a**$^{\bullet+}$ quickly disappeared. A transient absorption due to **1a**$^{\bullet+}$, however, could not be observed before **2a**$^{\bullet+}$ appeared and after **2a**$^{\bullet+}$ disappeared under those conditions. Since our preliminary experiments[21] of γ-ray irradiation for **1a** in butyl chloride matrix at 77 K exhibited transient absorptions of both **1a**$^{\bullet+}$ (λ_{max} = 680 nm)[22] and **2a**$^{\bullet+}$ (λ_{max} = 520 nm), the CR

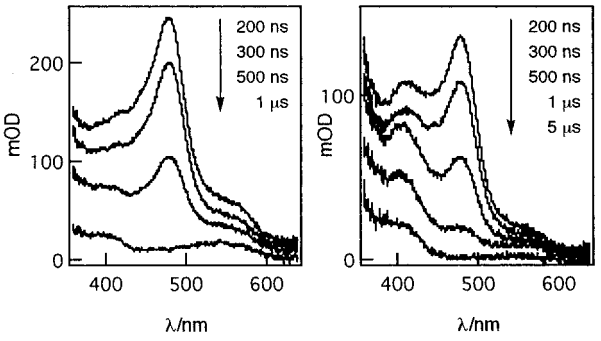


Figure 1. Nanosecond absorption spectra of an aerated dichloromethane solution of **1c** (1 mM, left) and **4c** (1 mM, right) under the $NMQ^+BF_4^-$ (1 mM)−TOL (2 M) cosensitized conditions.

cyclization of **1a**$^{\bullet+}$ to **2a**$^{\bullet+}$ in acetonitrile presumably is fast at room temperature.

The laser flash photolysis of **1c** under the $NMQ^+BF_4^-$-sensitized conditions using toluene (TOL) as a cosensitizer in an aerated dichloromethane showed a transient absorption with λ_{max} at 482 nm together with that of NMQ$^{\bullet}$ with λ_{max} at *ca.* 400 and 550 nm[24] (Figure 1). This absorption is assigned to **2c**$^{\bullet+}$ by comparison with a transient absorption observed in the laser flash photolysis of **4c** under similar conditions (Scheme 4).[25] In favor of this assignment is that the decay rate constant with methanol, k_{MeOH}, of the transient intermediate from **1c** (6×10^8 M^{-1} s^{-1}) is comparable to that from **4c** (8×10^8 M^{-1} s^{-1}). It is of interest to note that the λ_{max} of **2c**$^{\bullet+}$ is significantly red-shifted as compared with those of the cumyl cation (λ_{max} = 326, 390 nm in FSO_3H-SbF_5 at −60 °C)[26] and cumyl radical (λ_{max} = 315 nm in cyclohexane),[27] suggesting a possible through-bond interaction[7f] between the cumyl cation and cumyl radical parts of **2c**$^{\bullet+}$ in the chair form.

Single-Electron-Transfer Reactions of 4c and d_4-4c under Photoinduced and One-Electron Oxidation Conditions. One possible mechanism for the observed degenerate Cope rearrangement of d_4-**1** is a CRCY−CRCL mechanism in which CR d_4-**2**$^{\bullet+}$ directly undergoes cleavage to form a mixture of d_4-**1** and d_4-**1′** as shown in Scheme 1c. This mechanism, however, does not account for the failure in cleavage of cyclohexane-1,4-diyl CRs generated by the CAN-catalyzed reaction of **4c**[28] and γ-ray irradiations of 1,5-hexadiene,[29a] bicyclo[2.2.0]-hexane,[29b] and 2,3-diazabicyclo[2.2.2]oct-2-ene[29c,d] in Freon matrices. In fact, we also found that the CAN-catalyzed reaction of **1a** in an oxygen-saturated acetonitrile gave **3a** in 63% yield, but the degenerate Cope of d_4-**1a** does not occur (Table 4). This result further suggests that d_4-**1**$^{\bullet+}$ cyclizes to d_4-**2**$^{\bullet+}$ under both PET and non-PET conditions employed, but d_4-**2**$^{\bullet+}$ does not

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(22) The absorption maximum at 680 nm was assigned to **1a**$^{\bullet+}$ by the comparison with that of α-methyl-4-methoxystyrene CR (**12a**$^{\bullet+}$, λ_{max} = 660 nm in 4:1 water:acetonitrile).[23]

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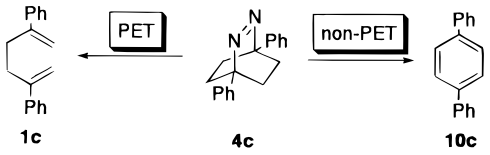
Table 5. Deazetation of **4c** under Various PET[a] and Non-PET Conditions



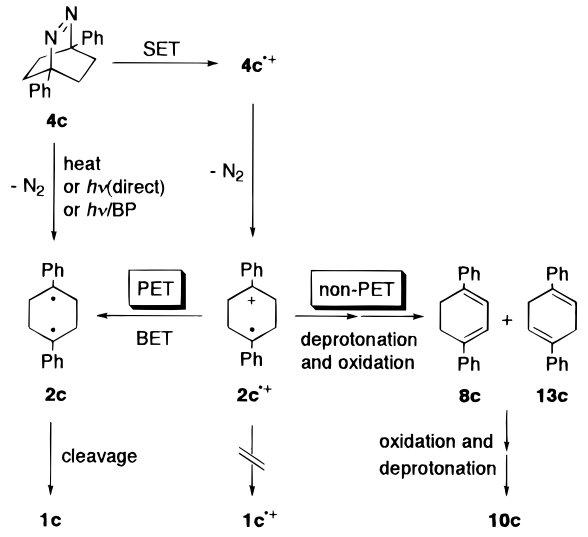
conditions	solvent	conversion (%)	yields (%) 1c	10c
PET				
hν/DCA (4 h)	CH_3CN	12	12	0
hν/DCA (6 h)	CH_2Cl_2	100	100	0
hν/DCA (2 h)	C_6H_6	100	100	0
$h\nu_{CT}$/TCNB (5 h)	CH_2Cl_2	100	100	0
$h\nu_{CT}$/TCNE (2 h)	CH_2Cl_2	92	40	0
non-PET				
CAN, *n*-Bu_4NHSO_4[b]	$CHCl_3$	100	0	46
CBN (1 equiv)	CH_2Cl_2	55	0	18[c]
$(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$ (2 equiv)	CH_2Cl_2	40	0	29
electrolysis (+1.25 V)	CH_2Cl_2	39	0	11

[a] [**4c**] = 0.33 mM (CH_3CN), 10 mM (CH_2Cl_2), or 5 mM (C_6H_6). [DCA] = 1 mM (CH_2Cl_2 and C_6H_6), 0.37 mM (CH_3CN). [TCNB] = [TCNE] =10 mM. [b] Ref 28. [c] Including the yield for **8c** (11%) and **13c** (3%).

undergo cleavage directly to d_4-**1**$^{\bullet+}$ and d_4-**1′**$^{\bullet+}$. In contrast, cyclohexane-1,4-diyls undergo facile ring cleavage to give 1,5-hexadienes in pyrolyses[12] and direct photolyses[30] of 2,3-diazabicyclo[2.2.2]oct-2-enes. Thus, if a diyl intermediate (d_4-**2**) is formed by BET from DCA$^{\bullet-}$ to d_4-**2**$^{\bullet+}$ under PET conditions, but not under non-PET conditions, then d_4-**1** would be expected to undergo the degenerate Cope under PET conditions but not under non-PET conditions. The alternative mechanism including this BET process is a CRCY−DRCL mechanism shown in Scheme 1d, which includes three successive processes; the CR cyclization of d_4-**1**$^{\bullet+}$ to d_4-**2**$^{\bullet+}$, the BET from DCA$^{\bullet-}$ to d_4-**2**$^{\bullet+}$ to form diyl d_4-**2**, followed by the DR cleavage of d_4-**2**. The CRCY−DRCL mechanism explains the failure of cyclohexane-1,4-diyl CRs to cleave under non-PET conditions. Apparently, the key step of this mechanism is the BET from DCA$^{\bullet-}$ to d_4-**2**$^{\bullet+}$. Thus, it was of particular interest to know whether or not a similar BET process is operative in PET deazetation of **4c**. Deazetations of **4c** were investigated under various PET conditions, and results were compared with those under non-PET conditions.[31]

Irradiation of **4c** with λ > 410-nm light in dichloromethane results in the quantitative recovery of **4c**. However, the DCA-sensitized photoreaction of **4c** with light of similar wavelength quantitatively affords **1c** as shown in Table 5. A solution of **4c** and 1,2,4,5-tetracyanobenzene (TCNB) in dichloromethane exhibits weak and broad charge-transfer (CT) absorption in the visible region over 410 nm. Irradiation of this solution with λ > 410-nm light gives rise to **1c** quantitatively. Similar irradiation of the CT complex of **4c** and tetracyanoethylene (TCNE) (λ_{max}^{CT} = 478 nm in dichloromethane) affords **1c** in 40% yield.[32] In contrast, like the CAN-catalyzed reaction of **4c**, the CBN-, tris(4-bromophenyl)aminium hexachloroantimonate[33] [$(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$]-, and anode-catalyzed reactions afforded *p*-terphenyl (**10c**) in low yields, but no **1c**.

Scheme 5



Using the oxidation potential of **4c** shown in Table 1, **4c**$^{\bullet+}$ presumably is formed in the DCA-sensitized PET reaction of **4c** as well as non-PET reactions. It is thus reasonable that both PET and non-PET deazetations of **4c** form **2c**$^{\bullet+}$, and hence, the striking contrast between PET and non-PET reactions of **4c** can be ascribed to differences in the processes following deazetation as shown in Scheme 5.

In non-PET reactions, **2c**$^{\bullet+}$ suffers rapid deprotonation−oxidation processes to form a mixture of 1,4-diphenylcyclohexane-1,3-diene (**8c**) and 1,4-diphenylcyclohexane-1,4-diene (**13c**) and successive one-electron oxidation followed by deprotonation to form **10c**. This was confirmed by the CBN-catalyzed reaction of **4c** which gave a mixture of cyclohexadienes (**8c** and **13c**) along with **10c**, and the $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$-catalyzed oxidation of **8c** afforded **10c** in 70% yield.[34] In PET processes, the BET from DCA$^{\bullet-}$, TCNB$^{\bullet-}$, or TCNE$^{\bullet-}$ to **2c**$^{\bullet+}$ occurs efficiently to form **2c**, which, in turn, undergoes cleavage to **1c**. Deazetations of **4c** under PET conditions thus provided the same products as those under pyrolytic,[12] direct irradiation[30] and benzophenone-sensitized[35] reactions in which diyl **2c** is known to serve as a common key intermediate. In fact, BET processes under those PET conditions are energetically favorable. On the basis of reported redox potentials of the cumyl radical ($E^{ox}_{1/2}$ = +0.16 V vs SCE in acetonitrile)[36] and the electron acceptors ($E^{red}_{1/2}$ = −0.95 V for DCA, −0.70 V for TCNB, and +0.22 V for TCNE), free energy changes, ΔG_{bet}, for BET in the ion radical pair [**2c**$^{\bullet+}$/acceptor$^{\bullet-}$] to form **2c** and acceptors are calculated to be −25.5, −20.7, and +1.4 kcal/mol, respectively, for DCA, TCNB, and TCNE.[37]

In non-PET reactions, however, such BET process from Ce^{III} or $(4\text{-}BrC_6H_4)_3N$ to **2c**$^{\bullet+}$ are unlikely as calculated free energy changes [ΔG_{bet} = *ca.* +16.7 for Ce^{III} and +20.5 kcal/mol for

(30) Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 7108−7114.

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(32) By control experiments, the low yield of **1c** in the reaction of **4c** and TCNE can be ascribed to the secondary reaction of **1c** with TCNE followed by decomposition.

(33) Reaction of azoalkanes with CR salts: Engel, P. S.; Robertson, D. M.; Scholz, J. N.; Shine, H. J. *J. Org. Chem.* **1992**, *57*, 6178−6187 and references cited therein.

(34) The parent cyclohexane-1,4-diyl CR was reported to undergo a formal 1,3-H shift to give cyclohexene CR.[29,7f] 1,4-Diphenylcyclohexene, however, was not detected in non-PET reactions of **1c** and **4c**. Since 1,4-diphenylcyclohexene was recovered quantitatively without the formation of **8c** and **13c** in the $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$-catalyzed oxidation, a possible 1,3-H shift pathway can be excluded under the conditions employed.

(35) Adam, W.; Grabowski, S.; H. Platsch; Hannemann, K.; Wirz, J.; Wilson, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 751−753.

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$(4\text{-}BrC_6H_4)_3N$] indicate. Under PET conditions, a rapid BET[38] from $DCA^{\bullet-}$ to $\mathbf{2c}^{\bullet+}$ followed by the ring cleavage of **2c** resulted in the formation of **1c**. In support of this assumption was the product distribution ratio, d_4-**1c**:d_4-**1c′**, from d_4-**4c** under PET and direct irradiation conditions as mentioned later. It is thus reasonably assumed that a similar BET process operates to form d_4-**2** in the DCA-sensitized PET degenerate Cope of d_4-**1**, completing a CRCY−DRCL mechanism as shown in Scheme 1d.

Photoacoustic Calorimetric Analysis and Energetics of the PET Degenerate Cope Rearrangement of d_4-1. The direct CR cleavage of d_4-$\mathbf{2}^{\bullet+}$ to d_4-$\mathbf{1}^{\bullet+}$ and d_4-$\mathbf{1'}^{\bullet+}$ does not compete with BET from $DCA^{\bullet-}$ to d_4-$\mathbf{2}^{\bullet+}$. A possible kinetic reason for this observation is based on the reaction thermodynamics. To determine the energetics of the CR cleavage, the enthalpy of formation, $\Delta H_{irp}([\mathbf{2}^{\bullet+}/DCA^{\bullet-}])$, of the ion radical pair [$\mathbf{2}^{\bullet+}$/$DCA^{\bullet-}$] must be measured. For this, we applied nanosecond time-resolved photoacoustic calorimetry (PAC), which is a useful technique to determine energetics of various PET reactions as have been reported previously.[40] The deconvolution of the experimental acoustic waveforms can provide the amplitude and time evolution of heat that is emitted when the excited sensitizer affords [$\mathbf{2}^{\bullet+}$/sensitizer$^{\bullet-}$]. Experiments were performed for both the **1a**−**c**−DCA−BP and **1c**−$NMQ^+PF_6^-$−TOL systems in acetonitrile according to the reported procedure.[41] In Figure 2, a schematic diagram for PAC is described for the **1**−DCA−BP system. Enthalpy of formation of [$\mathbf{2}^{\bullet+}$/$DCA^{\bullet-}$] can be expressed by eqs 1 and 2

$$\Delta H_{irp}([\mathbf{2}^{\bullet+}/DCA^{\bullet-}]) = h\nu(1 - \alpha_1 - \alpha_2)/\phi \quad (1)$$

$$\phi = h\nu(1 - \alpha_1)/E([BP^{\bullet+}/DCA^{\bullet-}]) \quad (2)$$

where $h\nu$, ϕ, and $E([BP^{\bullet+}/DCA^{\bullet-}])$ are photon energy (415 nm, 68.9 kcal/mol), 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.

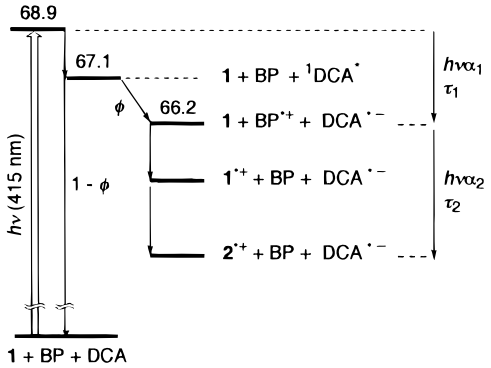


Figure 2. Schematic diagram of PAC for the **1**−DCA−BP system.

From several experiments, the deconvolution parameters, α_1, α_2, and τ_2 are determined to be 0.29 ± 0.03, 0.24 ± 0.05, and 194 ± 42 ns, respectively, for the **1c**−DCA−BP system. $\Delta H_{irp}([\mathbf{2a}-\mathbf{c}^{\bullet+}/DCA^{\bullet-}])$, i.e., energy difference between [**2a**−$\mathbf{c}^{\bullet+}$/$DCA^{\bullet-}$] and the ground states of **1a**−**c** and DCA, were thus determined to be 40.8 ± 5.3, 44.2 ± 5.4 and 43.6 ± 4.5 kcal/mol for **2a**, **2b**, and **2c**, respectively.[42] For the **1c**−$NMQ^+PF_6^-$−TOL system, the deconvolution parameters, α_1, α_2, and τ_2 were determined to be 0.57 ± 0.02, 0.27 ± 0.03, and 180 ± 55 ns, respectively. From those values and numerous calibrations, energy of the ion-radical pair [$\mathbf{2c}^{\bullet+}$/$NMQ^{\bullet}PF_6^-$] was given by the equation $\Delta H_{irp}([\mathbf{2c}^{\bullet+}/NMQ^{\bullet}PF_6^-]) = h\nu \times (1 - \alpha_1) + 9$ kcal/mol.[43] Using the α_1 value and photon energy (337 nm, 84.8 kcal/mol), $\Delta H_{irp}([\mathbf{2c}^{\bullet+}/NMQ^{\bullet}PF_6^-])$ was determined to be 45.6 ± 3.5 kcal/mol. The reliability of ΔH_{irp} values determined for both systems was verified by taking into account the difference (0.05 V) in $E^{red}_{1/2}$ between DCA[14] and $NMQ^+PF_6^-$ (−0.90 V vs SCE in acetonitrile). Energy of the ion radical pair $\Delta H_{irp}([\mathbf{2c}^{\bullet+}/NMQ^{\bullet}PF_6^-])$ can be compared with that of [$\mathbf{2c}^{\bullet+}$/$DCA^{\bullet-}$] by adding 1.2 kcal/mol. The resulting energy of the ion-radical pair, 46.8 ± 3.5 kcal/mol, approximates to 43.6 ± 4.5 kcal/mol within experimental errors. After all, $\Delta H_{irp}([\mathbf{2c}^{\bullet+}/DCA^{\bullet-}])$ was determined statistically to be 44.4 ± 4.5 kcal/mol as shown in Figure 3.

By using the redox potentials of **1c** and DCA, the free energy changes of the formation of [$\mathbf{1c}^{\bullet+}$/$DCA^{\bullet-}$] are calculated to be 60.6 kcal/mol. On the basis of our results[21] of pulse radiolysis for cyclization of *d,l*-2,5-bis(4-methoxyphenyl)-3,4-dimethyl-1,5-hexadiene CR to *trans*-1,4-bis(4-methoxyphenyl)-2,3-dimethylcyclohexane-1,4-diyl CR, the enthalpy of activation for cyclization of $\mathbf{1c}^{\bullet+}$ to $\mathbf{2c}^{\bullet+}$ was assumed to be 3∼4 kcal/mol. The energy barrier for the CR cleavage of $\mathbf{2c}^{\bullet+}$ is thus >19 kcal/mol as shown in Figure 3. This barrier seems to be too high for d_4-**1c** to undergo the degenerate Cope, especially at −80 °C, in a CRCY−CRCL mechanism, and hence, $\mathbf{2c}^{\bullet+}$ enters into the DR energy surface through the competing exothermic BET process. Because $\Delta H_{irp}([\mathbf{2c}^{\bullet+}/DCA^{\bullet-}])$ and the ΔG_{bet} for the BET from $DCA^{\bullet-}$ to $\mathbf{2c}^{\bullet+}$ are *ca.* 44.4 ± 4.5 and *ca.* 25.6 kcal/mol, respectively, diyl **2c** will lie *ca.* 18.8 kcal/mol higher in energy than **1c** and *ca.* 25.6 kcal/mol below [$\mathbf{2c}^{\bullet+}$/$DCA^{\bullet-}$].[37] The experimental PAC results demonstrate the endothermicity[4]

(37) This calculation has been done on the assumption that $E^{ox}_{1/2}$ of **2c** is comparable with that of the cumyl radical. As one of the reviewers pointed out, this estimation of ΔG_{bet} gives a lower limit because the $E^{ox}_{1/2}$ of **2c** may be more negative. This was suggested from a significant electron coupling between the cumyl cation and cumyl radical parts in $\mathbf{2c}^{\bullet+}$ that cause the remarkable red shift of $\mathbf{2c}^{\bullet+}$ in the electronic absorption spectroscopy. Unfortunately, however, it is difficult to evaluate the effect of through-bond interaction upon redox potentials.

(38) By using the following equations (3, 4)[39] and reported parameters by Farid[15c] and Kikuchi,[15d] rate constant, k_{bet}, of the BET in [$\mathbf{2c}^{\bullet+}$/$DCA^{\bullet-}$] at 20 °C was estimated to be 1.9×10^9 s^{-1} and 4.9×10^{10} s^{-1}, respectively, in acetonitrile

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

$$S = \lambda_v/h\nu \quad (4)$$

where parameters $|V|^2$, λ_s, λ_v, and ν are, respectively, an electronic matrix element squared, solvent reorganization energy, vibrational reorganization energy, and single average frequency.

(39) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057−5068. Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741−747, 748−752. Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183−197. Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358−4368.

(40) Rothberg, L. J.; Simon, J. D.; Bernstein, M.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 3464−3468. Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 1700−1701. Ci, X.; da Silva, R. S.; Goodman, J. L.; Nicodem, D. E.; Whitten, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 8548−8550. Zona, T. A.; Goodman, J. L. *Tetrahedron Lett.* **1992**, *33*, 6093−6096. LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 712−714.

(41) Rudzki, J. E.; Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 7849−7854. Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 1849−1854. Peters, K. S. In *Kinetics and Spectroscopy of Carbenes and Biradicals;* Platz, M. S., Ed.; Plenum: New York, 1990; pp 37−49. Griller, D.; Wayner, D. D. M. *Pure Appl. Chem.* **1989**, *61*, 717−724.

(42) Similarly, $\Delta H_{irp}([\mathbf{2c}^{\bullet+}/NMQ^{\bullet}PF_6^-])$ in 1,2-dichloroethane was determined to be 45.1 ± 2.3 kcal/mol by using the following parameters; $\alpha_1 = 0.32 \pm 0.02$, $\alpha_2 = 0.27 \pm 0.02$, and $\tau_2 = 233 \pm 36$ ns (averages from five runs).

(43) Goodman, J. L. unpublished results.

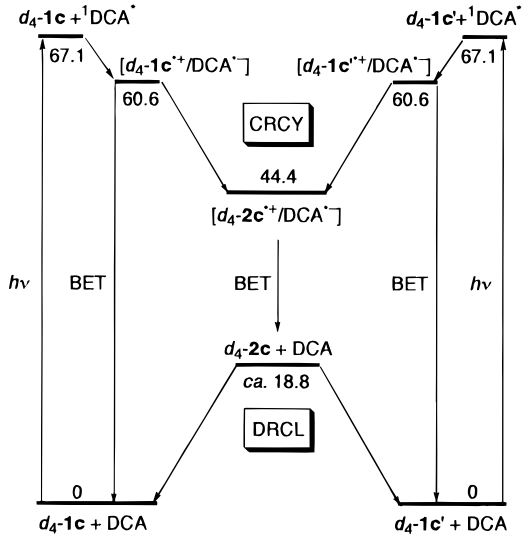
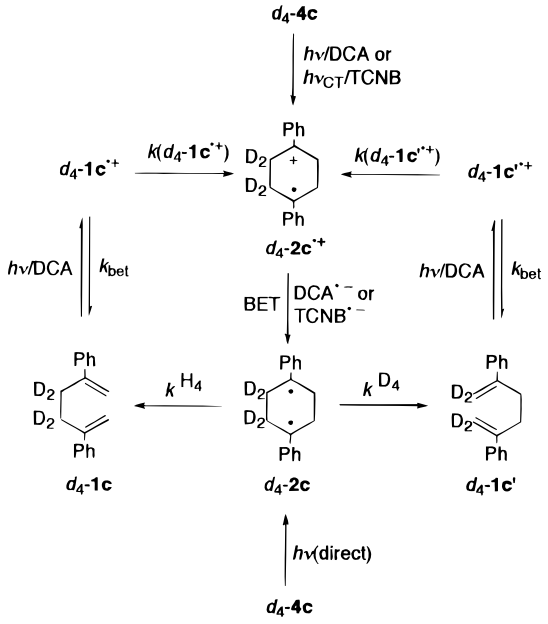


Figure 3. Energy diagram for the DCA-sensitized PET degenerate Cope rearrangement of d_4-**1c**. Relative energy was represented in kcal/mol.

Scheme 6



of the direct CR cleavage of d_4-**2c**$^{\bullet+}$ to d_4-**1c**$^{\bullet+}$ and d_4-**1c′**$^{\bullet+}$, which allows competitive BET to form d_4-**2c**.

Bond-Breaking and Bond-Making Kinetic Isotope Effects on a CRCY−DRCL Mechanism. In order to gain further insight into a CRCY−DRCL mechanism, we investigated deazetations of d_4-**4c** under various photochemical conditions. If a CRCY−DRCL mechanism is really operative in the PET degenerate Cope of d_4-**1c**, the observed PS ratio, [d_4-**1c**]ps/[d_4-**1c′**]ps = *ca.* 52/48, can be expressed by $[\Phi(d_4\text{-}\mathbf{1c'}^{\bullet+})/\Phi(d_4\text{-}\mathbf{1c}^{\bullet+})] \times [k^{\mathrm{H}}4/k^{\mathrm{D}}4]$, where $\Phi(d_4\text{-}\mathbf{1c'}^{\bullet+}) = k(d_4\text{-}\mathbf{1c'}^{\bullet+})/[k(d_4\text{-}\mathbf{1c'}^{\bullet+}) + k_{\mathrm{bet}}]$ and $\Phi(d_4\text{-}\mathbf{1c}^{\bullet+}) = k(d_4\text{-}\mathbf{1c}^{\bullet+})/[k(d_4\text{-}\mathbf{1c}^{\bullet+}) + k_{\mathrm{bet}}]$ (Scheme 6). The former is a ratio of the efficiency of the CRCY step in an ion-radical pair, whereas the latter corresponds to the bond-breaking kinetic isotope effects (DR−BBKIE) of the DRCL step. Thus, the direct determination of the DR−BBKIE of d_4-**2c** by independent generation would provide the efficiency ratio $\Phi(d_4\text{-}\mathbf{1c'}^{\bullet+})/\Phi(d_4\text{-}\mathbf{1c}^{\bullet+})$ and judge which step controls the PS ratio. Furthermore, if a mechanism for the PET deazetation of **4c** includes BET to form diyl **2c**, the product distribution ratio, d_4-**1c**:d_4-**1c′**, in the PET deazetation of d_4-**4c** should be same as that in direct photolysis of d_4-**4c** as described in Scheme 6.

Table 6. Deazetation of d_4-**4c** under PET and Direct Irradiation Conditions at 20 °C[a]

conditions	relative yields (%) d_4-**1c**	relative yields (%) d_4-**1c′**	$k^{\mathrm{H}}4/k^{\mathrm{D}}4$
$h\nu$/DCA/CD_2Cl_2[b]	52.5 ± 0.3	47.5 ± 0.3	1.10 ± 0.02
$h\nu_{\mathrm{CT}}$/TCNB/CD_2Cl_2[c]	52.3 ± 0.4	47.7 ± 0.4	1.10 ± 0.02
$h\nu$(direct)/C_6D_6[d]	52.6 ± 0.3	47.4 ± 0.3	1.11 ± 0.02

[a] The errors are 1σ. [b] λ > 410 nm, 12−32% conversion. [c] λ > 410 nm, 10−28% conversion. [d] λ > 320 nm, 45−100% conversion.

As shown in Table 6, the distribution ratio, d_4-**1c**:d_4-**1c′**, under direct irradiation conditions was nearly same as not only that under PET conditions but also the PS ratio of the PET degenerate Cope of d_4-**1c**. This observation is reasonable if the PET degenerate Cope of d_4-**1c** occurs in a CRCY−DRCL mechanism involving d_4-**2c**$^{\bullet+}$ and d_4-**2c** and deazetation of d_4-**4c** forms d_4-**2c** as a common intermediate in a cleavage step under the PET and direct irradiation conditions (Scheme 6). From the distribution ratio (d_4-**1c**:d_4-**1c′** = 52.6:47.4 at 20 °C) observed in direct irradiation of d_4-**4c** and the PS ratio (d_4-**1c**:d_4-**1c′** = 52.4:47.6 at 20 °C) of the PET degenerate Cope of d_4-**1c**, the efficiency ratio $\Phi(d_4\text{-}\mathbf{1c'}^{\bullet+})$ / $\Phi(d_4\text{-}\mathbf{1c}^{\bullet+})$ and DR−BBKIE can be calculated to be 0.99 and 1.11, respectively, at 20 °C. The fact that the distribution ratio from d_4-**2c** is nearly same as the PS ratio of the PET degenerate Cope of d_4-**1c** suggests that the DRCL step predominates the determination of the PS ratio of the PET Cope of d_4-**1c**. In fact, the bond-making kinetic isotope effects (CR−BMKIE) of the CRCY step is substantially 1.0, because $k(d_4\text{-}\mathbf{1c}^{\bullet+})$ equals $k(d_4\text{-}\mathbf{1c'}^{\bullet+})$ when $\Phi(d_4\text{-}\mathbf{1c'}^{\bullet+})/\Phi(d_4\text{-}\mathbf{1c}^{\bullet+})$ is 0.99. This indicates that there is no inverse KIE for the $sp^2 \rightarrow sp^3$ bond-making step. A plausible explanation will be that a highly exothermic CRCY process with low activation energy proceeds through an early transition state in which the σ (C-3−C-4) bond is kept intact and C-1 and C-6 keep the sp^2-like character of d_4-**1c**$^{\bullet+}$ (or d_4-**1c′**$^{\bullet+}$). In this sense, of importance is an intramolecular charge-transfer interaction[7e] between the neutral styrene unit as an electron donor and the styrene CR unit as an electron acceptor in **1c**$^{\bullet+}$. Both the CR−BMKIE and DR−BBKIE thus explain consistently the PS ratio of the PET degenerate Cope of d_4-**1c** if a CRCY−DRCL mechanism is operative.

Conclusions

The operation of the CRCY−DRCL mechanism is established for the DCA-sensitized PET degenerate Cope rearrangement of d_4-**1**. This mechanism avoids the proposed endothermicity[4] of the direct CR cleavage of d_4-**2**$^{\bullet+}$ in a CRCY−CRCL mechanism and accounts for differences in the reactivity of d_4-**2**$^{\bullet+}$ formed under PET and non-PET conditions. Accordingly, an exothermic BET process to form a low-lying diyl d_4-**2** is an important key process in PET conditions. Significant solvent effects on quantum efficiencies (Table 2) are in accord with a probable operation of the CRCY−DRCL mechanism in which BET in [**2**$^{\bullet+}$/DCA$^{\bullet-}$] efficiently operates. In connection with the directly determined DR−BBKIE of d_4-**2c**, it is of particular interest to note that the value, 1.11, is very close to the BBKIE, 1.07, determined kinetically by Gajewski for the thermal degenerate Cope of d_4-**1c** through a six-membered cyclic

transition state.[44] Interestingly, the calculations of Dewar suggested that the kinetically determined BBKIE, 1.07, can be reproducible as the BBKIE of d_4-**2c** in a stepwise CY−CL mechanism described in Scheme 1a.[3f] Of course, the DR−BBKIE determined directly from d_4-**2c** in this work cannot simply judge whether d_4-**2c** is a putative or true intermediate in the thermal degenerate Cope of d_4-**1c**. Nevertheless, the direct determination of DR−BBKIE and experimental energy evaluation of d_4-**2c** would be of basic value for further argument on a mechanism of the thermal degenerate Cope of d_4-**1c**. A mechanistic connection between CR and DR in the PET reaction is another intriguing aspect. If an efficient BET from a sensitizer anion radical to an intermediate CR is operative, the PET reaction is a useful mechanistic probe to investigate intriguing but unobservable reactive diyl intermediates in thermal reactions.

Experimental Section

General Methods. All melting and boiling points are uncorrected. Elemental analyses were performed by the Instrumental Analyses Center for Chemistry, Graduate School of Science, Tohoku University, and correct elemental analyses were obtained for all new compounds in this report. ^{1}H NMR spectra were recorded at 90 MHz on a Varian EM-390, at 200 MHz on a Varian XL-200, or at 400 MHz on a JEOL GX-400 spectrometer. Chemical shifts were reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constants (Hz). Product analyses by ^{1}H NMR were done using 1,1,2,2-tetrachloroethane or 1,1,1,2-tetrachloroethane as an internal standard. ^{13}C NMR spectra were obtained at 50 MHz on a Varian XL-200 spectrometer. MS were performed on a Hitachi M-52, a JEOL JMS-HX110, or a Hitachi M-2500 mass spectrometer under electron ionization. Redox potentials ($E^{ox}_{1/2}$ and $E^{red}_{1/2}$; V vs SCE) were measured on a Yanaco P-1000 voltammetric analyzer by cyclic voltammetry (Pt electrode, scan rate 100 mV/s) in CH_3CN containing Et_4NClO_4 (0.1 M) as a supporting electrolyte. Because all of substrates gave irreversible waves, their $E^{ox}_{1/2}$ values were obtained as E_{ap} (anodic peak potential) − 0.03 V, assuming a one-electron oxidation process. Fluorescence spectra were recorded on a Hitachi MPF-4 or on a Hitachi F-4010 fluorescence spectrophotometer. Nanosecond absorption spectroscopy was carried out by using a Continuum Surelite-10 YAG laser system (Nd, THG, $\lambda_{ex} = 355$ nm, 55 mJ) for the DCA−BP cosensitization or Lumonics EX600 excimer laser (XeCl, $\lambda_{ex} = 308$ nm, 100 mJ) for the $NMQ^+BF_4^-$−TOL cosensitization and a pulsed Xe arc lamp (150 W) as a monitoring light source. A PRA nitrogen laser LN 1000 was used for photoacoustic calorimetry experiments done in the NSF Center for Photoinduced Charge Transfer at the University of Rochester. Ethereal solvents were dried and distilled from $LiAlH_4$. CH_3CN was dried and distilled from P_2O_5 and then CaH_2. C_6H_6 and CH_2Cl_2 were dried and distilled from CaH_2. Deuterated solvents for photoreactions, CD_3CN (99.6% deuterated), C_6D_6 (99.6%), $CD_3C_6D_5$ (99.6%), and CD_2Cl_2 (99.3%) were dried over molecular sieves 4A prior to use. Merck silica gel 60 (230−400 mesh) was used for column chromatography. Aminium salt, $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$, (Aldrich) was washed with dry ether and dried in vacuo prior to use. Preparative thick-layer chromatography (PTLC) was performed on 0.5 mm × 20 cm × 20 cm plates (E. Merck, silica gel 60 PF_{254}).

Syntheses of Substrates Shown in Scheme 2. See the Supporting Information.

DCA Fluorescence Quenching. The DCA fluorescence quenching experiments were carried out under air, monitoring the changes in the intensity of fluorescence at $\lambda_{max} = ca.$ 436 and 460 nm as a function of concentration of quencher. The slope of I^0/I vs [quencher] in the Stern−Volmer plot, which equals $k_q\tau$, was determined by the least-squares method. Quenching efficiencies, Q_e, at [**1**] = 10 mM and quenching rate constants, k_q, calculated from known τ are shown in Tables 7 and 1, respectively.

Table 7. Quenching Efficiencies (Q_e) for ^{1}DCA* with **1** and Quantum Yields (Φ) for the PET Degenerate Cope Rearrangements of d_4-**1** at 20 °C[a]

	Q_e				Φ		
sub	CD_3CN	CD_2Cl_2	C_6D_6	sub	CD_3CN	CD_2Cl_2	C_6D_6
1a	0.732	0.644	0.545	d_4-**1a**	n.a.[b]	0.088	0.21
1b	0.662	0.543	0.361	d_4-**1b**	0.14	0.18	0.17
1c	0.623	0.295	0.0616	d_4-**1c**	0.21	0.13	0.031
1d	0.595	0.249	0.0293	d_4-**1d**	0.20	0.089	0.010

[a] [**1**] = [d_4-**1**] = 10 mM. [b] No attempt.

Analyses of Time-Dependent Change of Product Ratios for the DCA-Sensitized Photoreactions of d_4-1a−d and 4c. A typical procedure: A 0.1 M solution (0.5 mL) containing 0.05 mmol of d_4-**1c** or **4c** and 2−3 mg of DCA in CD_3CN, CD_2Cl_2, or C_6D_6 was irradiated with a 2 kW Xe lamp through a Toshiba cutoff filter L-39 ($\lambda > 360$ nm) for d_4-**1c** or Y-44 ($\lambda > 410$ nm) for d_4-**4c** under N_2 at 20 ± 1 °C. Taking into account the 98% deuterium incorporation in d_4-**1c**, the d_4-**1c**:d_4-**1c′** ratios in the photoreaction of d_4-**1c** were determined by 200 MHz ^{1}H NMR analyses as follows: d_4-**1c**:d_4-**1c′** = $(I_1 - \alpha)$:$(I_2 - \alpha)$, $\alpha = (I_1 + I_2) - (I_1 + I_2)/1.02$, where I_1 and I_2 are integration intensities of olefin protons (2 H + 2 H) (d_4-**1c**: δ 5.05 and 5.28 in $CDCl_3$) and methylene protons (4 H) (d_4-**1c**: δ 2.65 in $CDCl_3$), respectively. Similarly, the d_4-**4c**:d_4-**1c**:d_4-**1c′** ratios in the photoreaction of d_4-**4c** (97% deuteration) were determined by 200 MHz ^{1}H NMR analyses as follows: d_4-**4c**:d_4-**1c**:d_4-**1c′** = I_3 / 1.03:$(I_1 - \alpha)$:$(I_2 - \alpha)$, where I_3 is integration intensities of methylene protons (2 H + 2 H) (δ 1.53 and 2.20 in $CDCl_3$), $\alpha = (I_1 + I_2) - (I_1 + I_2)/1.03$. Results are shown in Table 2.

Quantum Yield Determinations. A typical procedure: A CH_3CN, CH_2Cl_2, or C_6H_6 solution (3 mL) containing 0.03 mmol of d_4-**1c** (10 mM) and DCA (0.19 mM in CH_3CN; 0.47 mM in CH_2Cl_2; or 0.68 mM in C_6H_6) was irradiated with light of wavelength at $\lambda_{max} = 368 \pm 24$ nm under N_2 at 20 ± 1 °C. Light of this wavelength was obtained from a 500 W Hg-Xe lamp through an aqueous $CuSO_4$ solution filter, a Toshiba cutoff filter UV-35, and an interference filter ($\lambda_{max} = 363$ nm). Aberchrome 540 was used as an actinometer. The conversion was 5−15% in all cases. After irradiation and removal of solvent in the dark, the photolysate was analyzed by ^{1}H NMR. Thus, there is at least *ca.* 2% of the experimental error in eash case. Taking into account the 98% deuterium incorporation, the true conversion percentage, *C* (%), was determined as $C\ (\%) = [1.02 \times [I_2/(I_1 + I_2)] - 0.02]/0.98 \times 100$. Uncorrected Φ and corrected Φ_{cor} are summarized in Tables 7 and 2, respectively.

DCA-Sensitized Photoreactions of 1a−d under O_2. A typical procedure: A 5 mL solution containing 0.05 mmol of **1c** (0.01 M) and 2−3 mg of DCA in CH_3CN, CH_2Cl_2, or C_6H_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, PTLC, followed by recrystallization from CH_2Cl_2−ether afforded cyclic peroxide **3c**. Results are shown in Table 3. Physical data for **3a**−**d** are shown in the Supporting Information.

Photoreaction of 4c in the Absence of DCA with Wavelength λ > 400 nm and Reaction of 4c in the Presence of DCA in the Dark. A 5 mL C_6H_6 solution containing 6.6 mg (0.025 mmol) of **4c** was irradiated for 2 h with a 2 kW Xe lamp through a Toshiba cutoff filter Y-44 ($\lambda > 410$ nm) under N_2 at 20 ± 1 °C. Removal of C_6H_6 and ^{1}H NMR analysis showed the quantitative recovery of **4c**. Similarly, a 5 mL CH_2Cl_2 solution containing 13.1 mg (0.05 mmol) of **4c** was irradiated for 10 h. ^{1}H NMR analysis showed only 2% conversion of **4c** to **1c**. A 5 mL CH_2Cl_2 solution containing 13.1 mg (0.05 mmol) of **4c** was stirred under N_2 at 20 ± 1 °C in the dark. Removal of CH_2Cl_2 and ^{1}H NMR analysis showed the quantitative recovery of **4c**.

DCA-Sensitized Photoreaction of 4c. A solution of **4c** (13.1 mg, 0.05 mmol) and DCA (7.7 mg, 0.034 mmol) in CH_3CN (150 mL) 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. Removal of solvent followed by PTLC afforded **1c** quantitatively. Similarly, **1c** was quantitatively

(44) (a) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 6269−6270. (b) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693−6704. (c) Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142−148. (d) Gajewski, J. J. *Hydrocarbon Thermal Isomerization*; Academic: New York, 1981.

afforded upon irradiation of a 5 mL CH_2Cl_2 or C_6H_6 solution containing **4c** (13.1 mg, 0.05 mmol in CH_2Cl_2 or 6.6 mg, 0.025 mmol in C_6H_6) and DCA (1.1 mg, 0.005 mmol).

Photoexcitation of the CT Complex of 4c and TCNB. A 5 mL CH_2Cl_2 solution containing 13.1 mg (0.05 mmol, 0.01 M) of **4c** and 8.9 mg (0.05 mmol) of TCNB was irradiated for 5 h with a 2 kW Xe lamp through a Toshiba cutoff filter Y-44 (λ > 410 nm) under N_2 at 20 ± 1 °C. Removal of solvent followed by PTLC afforded **1c** quantitatively and ^{1}H NMR analysis showed the quantitative recovery of TCNB.

Photoexcitation of the CT Complex of 4c and TCNE. A 5 mL CH_2Cl_2 solution containing 13.1 mg (0.05 mmol, 0.01 M) of **4c** and 6.4 mg (0.05 mmol) of TCNE was irradiated for 2 h with a 2 kW Xe lamp through a Toshiba cutoff filter Y-44 (λ > 410 nm) under N_2 at 20 ± 1 °C. Removal of solvent followed by ^{1}H NMR analysis showed the formation of **1c** (40%) along with the recovered **4c** (8%). The recovery of TCNE in photolysate was determined to be 28% by the reaction of TCNE and α-terpinene which occurs quantitatively.

CAN-Catalyzed Reaction of 1a under O_2. A two-necked flask containing a solution of **1a** (14.7 mg, 0.05 mmol) in dry CH_3CN (50 mL) was replaced with O_2. To this solution, CAN (27.4 mg, 0.05 mmol) was added in one portion under stirring and the mixture was stirred for 20 min. After addition of water, the reaction mixture was extracted with ether. The combined extract was washed with water and brine and dried over Na_2SO_4. Removal of solvent followed by PTLC afforded **3a** (63%) and **10a** (9%) along the recovered **1a** (20%).

CBN-Catalyzed Reaction of 1a under O_2. A two-necked flask containing a solution of **1a** (29.4 mg, 0.1 mmol) in dry CH_3CN (100 mL) was replaced with O_2. To this solution was added CBN (99.7 mg, 0.1 mmol) in one portion under stirring, and the mixture was stirred for 30 min. The same workup as that for the CAN-catalyzed reaction of **1a** under O_2 followed by PTLC afforded **3a** (58%) and **10a** (10%) along with the recovered **1a** (20%).

CAN-Catalyzed Reaction of d_4-1a under N_2. A two-necked flask containing a solution of d_4-**1a** (14.9 mg, 0.05 mmol) in dry CH_3CN (50 mL) was replaced several times with N_2. To this solution was added CAN (27.4 mg, 0.05 mmol) in one portion, and the mixture was stirred for 20 min under N_2. After addition of water, the reaction mixture was extracted with ether. The same workup as that for the CAN-catalyzed reaction of **1a** under O_2 followed by ^{1}H NMR analysis showed the formation of 2′,3′-dideuterio-4,4″-dimethoxy-*p*-terphenyl (d_2-**10a**) (4%) along with the recovered d_4-**1a** (72%).

CBN-Catalyzed Reaction of d_4-1a under N_2. A two-necked flask containing a solution of d_4-**1a** (14.9 mg, 0.05 mmol) in dry CH_3CN (50 mL) was replaced several times with N_2. To this solution was added CBN (54.7 mg, 0.05 mmol) in one portion, and the mixture was stirred for 1 h under N_2. After addition of water, the reaction mixture was extracted with ether. The same workup as that for the CAN-catalyzed reaction of **1a** under O_2 followed by ^{1}H NMR analysis showed the formation of d_2-**10a** (5%) along with the recovered d_4-**1a** (60%).

CBN-Catalyzed Reaction of 4c under N_2. A two-necked flask containing a solution of diazene **4c** (13.1 mg, 0.05 mmol) in dry CH_2Cl_2 (5 mL) was replaced several times with N_2. To this solution was added CBN (54.7 mg, 0.05 mmol) in one portion, and the mixture was stirred for 1 h under N_2. After addition of water, the reaction mixture was extracted with CH_2Cl_2. The same workup as that for the CAN-catalyzed reaction of **1a** under O_2 followed by ^{1}H NMR analysis showed the formation of **7c** (11%), **10c** (4%), and **13c** (3%) along with recovered **4c** (45%).

(4-BrC_6H_4)$_3N^{\bullet+}SbCl_6^-$-Catalyzed Reaction of 4c under N_2. A two-necked flask containing diazene **4c** (13.1 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) was replaced several times with N_2. To this solution was added (4-BrC_6H_4)$_3N^{\bullet+}SbCl_6^-$ (40.8 mg, 0.05 mmol) in one portion, and the mixture was stirred under N_2. When the blue color of aminium salt faded, aminium salt was added twice (20.4 mg each) further, and the reaction mixture was stirred for 1 h. After addition of 28% NaOMe/MeOH (1 mL) and water, the mixture was extracted with CH_2Cl_2. The same workup as that for the CAN-catalyzed reaction of **1a** under O_2 followed by ^{1}H NMR analysis showed the formation of **10c** (29%) along with the recovered **4c** (60%).

Electrode-Catalyzed Reaction of 4c. A CH_2Cl_2 solution (20 mL) containing 13.1 mg (0.05 mmol) of diazene **4c** and 0.05 M Et_4NClO_4 in an electrolytic cell was subjected to the anodic oxidation on a Pt electrode at +1.25 V under N_2 for 18 h. A saturated calomel electrode (SCE) was used as a reference electrode. Washing with water, drying over Na_2SO_4, removal of solvent followed by ^{1}H NMR analysis showed the formation of **10c** (11%) along with the recovered **4c** (61%).

Direct Irradiation of d_4-4c. A 5 mL C_6H_6 solution containing 6.7 mg (0.025 mmol) of d_4-**4c** was irradiated for 5 h with a 2 kW Xe lamp through a Toshiba cutoff filter UV-35 (λ > 320 nm) under N_2 at 20 ± 1 °C. The d_4-**1c**:d_4-**1c**′ ratios were determined by 200 MHz ^{1}H NMR analyses (*vide supra*).

Energy Determination by Time-Resolved PAC. The details of the PAC experiment has been described previously.[41] A chart of the PAC waveforms for **1c**−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 three separate runs, and errors are within 1 σ.

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Supporting Information Available: Synthetic details of Scheme 2, PAC experiment, a chart of the PAC waveforms for the **1c**−DCA−BP system, and lists of deconvolution fitting parameters for experimental waveforms in each PAC experiment (13 pages). See any current masthead page for ordering and Internet access instructions.

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