

Photoinduced Electron-Transfer Intramolecular Cyclization of Acyclic Dienes with Two Styrene Units

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Introduction

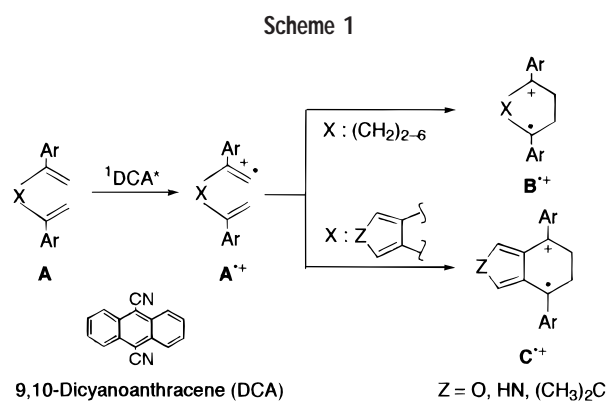
Electron transfers from substrate olefins to photoexcited electron acceptors initiate intermolecular cycloadditions of olefins. Dimerizations of styrene derivatives initiated by photoinduced electron transfer were among the most extensively investigated.^{1,2} In these reactions, 1,4-diarylbutane-1,4-diyl cation radical intermediates are initially formed by the intermolecular coupling of styrene cation radicals and neutral styrenes at the β -carbon. Our research group has concentrated on the study of the intramolecular version of this process, i.e., electron-transfer photoreactions of substrates of type **A**, in which two styrene units are linked at the α -carbon by spacers **X** (Scheme 1). Intramolecular cyclization of cation radical **A**^{•+} would form several mechanistically intriguing cation radical intermediates.

Among various cyclic 1,4-cation radicals expected from acyclic dienes **A** [**X** = (CH₂)_{2–6}], 1,4-diphenylcyclohexane-1,4-diyl cation radical [**B**^{•+}, **X** = (CH₂)₂, **Ar** = Ph] is the

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Yasutake Takahashi was born in Iwate, Japan, and educated at Iwate University (B.Eng.) and Tohoku University (M.Sc. and D.Sc.). After he received a D.Sc. under the direction of Professor Toshio Mukai, he carried out postdoctoral studies at Wayne State University (Professor A. Paul Schaap) and University of Houston (Professor Jay K. Kochi) from 1984 to 1987. He joined the faculty as an assistant professor in the group of Professor Miyashi in 1987 and moved to Mie University in 1996, where he is currently an associate professor. His research interests are related to organic photochemistry.



most intriguing intermediate. This is a cation radical variant of a putative and controversial 1,4-diphenylcyclohexane-1,4-diyl intermediate in the thermal Cope rearrangement of 2,5-diphenyl-1,5-hexadienes [**A**, **X** = (CH₂)₂, **Ar** = Ph].^{3–6} From 3,4-bis(α -styryl)furan, 3,4-bis(α -styryl)pyrrole, and 2,3-bis(α -styryl)-5,5-dimethylcyclopentadiene, in which two styrene units in **A** are linked by spacer **X**, such as furan, pyrrole, and 5,5-dimethylcyclopentadiene, respectively, we also expected the formation of tetramethyleneethane cation radical derivatives **C**^{•+}, which are cyclic cation radical variants of dimethylenefuran,^{7a–c} dimethylenepyrrole,^{7a,d,e} and dimethylenecyclopentadiene,^{7a,f} respectively.

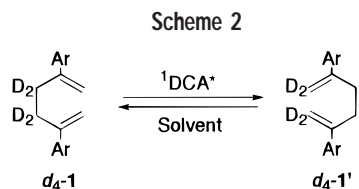
Electron-transfer photoreactions of substrates **A** to form **B**^{•+} and **C**^{•+} successfully take place under 9,10-dicyanoanthracene (DCA)-sensitized conditions. From acyclic dienes **A** [**X** = (CH₂)_{2–5}], 6–9-membered cyclic cation radical intermediates **B**^{•+} are formed. As expected, electron-transfer photoreactions of 2,5-diaryl-1,5-hexadienes **A** [**X** = (CH₂)₂] induce stepwise Cope rearrangements, involving both 1,4-diaryl-1,4-diyl cation radical and 1,4-diaryl-1,4-diyl intermediates. We also have found an unprecedented Cope rearrangement accompanied by the formation of the bicyclo[2.2.0]hexane derivative in a Cope photostationary mixture. In this Account, we describe our studies of the electron-transfer photoreactions of acyclic dienes **A** [**X** = (CH₂)_{2–5}], focusing on the photoinduced electron-transfer Cope rearrangement of 2,5-diaryl-1,5-hexadiene derivatives.

I. Electron-Transfer Photoreaction of 2,5-Diaryl-1,5-hexadienes

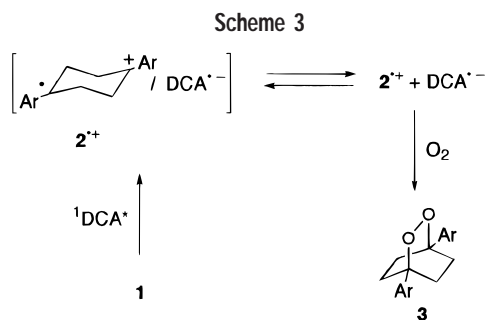
(a) The Photoinduced Electron-Transfer Degenerate Cope Rearrangement. When **X** in **A** is (CH₂)₂, the system is the well-known 1,5-hexadiene system, for which the mechanism of the thermal Cope rearrangement is still argued.^{3–6} We investigated electron-transfer photoreactions of 2,5-diaryl-1,5-hexadienes (**d**₁–**d**), expecting to observe a stepwise Cope rearrangement through a distinct intermediate.^{8,9} These 1,5-hexadienes efficiently quench

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a: Ar = 4-MeOC₆H₄, b: Ar = 4-MeC₆H₄, c: Ar = C₆H₅, d: Ar = 4-ClC₆H₄
 Solvent: acetonitrile, dichloromethane, benzene
 Average photostationary ratio: [d₄-1]/[d₄-1'] = 52/48
 $\Phi_{\text{cor}} = 0.14 - 0.50$

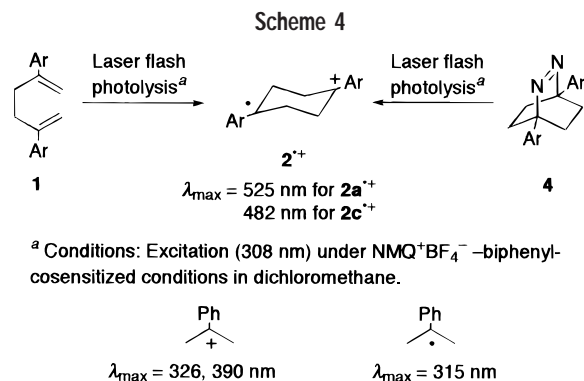


a: Ar = 4-MeOC₆H₄, b: Ar = 4-MeC₆H₄, c: Ar = C₆H₅, d: Ar = 4-ClC₆H₄

the fluorescence of DCA in acetonitrile, dichloromethane, and benzene. As expected, irradiation (>360 nm) of mixtures of DCA and d₄-1a–d at ambient temperatures in the three solvents leads to the degenerate Cope rearrangement, giving rise to a photostationary mixture of d₄-1a–d and d₄-1'a–d (Scheme 2). In dichloromethane, the degenerate Cope rearrangement occurs at temperatures as low as –80 °C.

The photostationary ratio d₄-1a–d:d₄-1'a–d is relatively constant, regardless of solvent polarity and the electron-donating nature of the substrates. One intriguing feature is that the average observed photostationary ratio, 52:48, is different from the equilibrium ratio, 63:37, of the thermal Cope rearrangement of d₄-1c.^{4b,5a,b} In contrast, the quantum efficiency is sensitive to solvent polarity and tends to increase with a decrease in solvent polarity. For instance, the quantum efficiency (Φ_{cor} , corrected for the quenching efficiency) for the degenerate Cope rearrangement of d₄-1c is 0.34, 0.42, and 0.50 in acetonitrile, dichloromethane, and benzene, respectively, suggesting an important role of an in-cage process within a contact or solvent separated ion-radical pair.

(b) Intervention of the 1,4-Diarylcyclohexane-1,4-diyl Cation Radical Intermediate. Since chemical capture of various cation radical intermediates by molecular oxygen is well documented,¹³ it was quite expedient to carry out the electron-transfer photoreaction of **1** under oxygen. In fact, oxygenation to give 1,4-diaryl-2,3-dioxabicyclo[2.2.2]octane (**3**) occurs readily (Scheme 3).^{8a,b} The yield of peroxide **3**, however, depends significantly on solvent polarity. Unlike the solvent effects on Φ_{cor} , the yield decreases with a decrease in solvent polarity. For example, **3a** is formed with excellent yields in acetonitrile and dichloromethane, but **1a** is recovered quantitatively in benzene, where the degenerate Cope rearrangement occurs efficiently. The observation that the one-electron



^a Conditions: Excitation (308 nm) under NMQ⁺BF₄[–]–biphenyl-cosensitized conditions in dichloromethane.

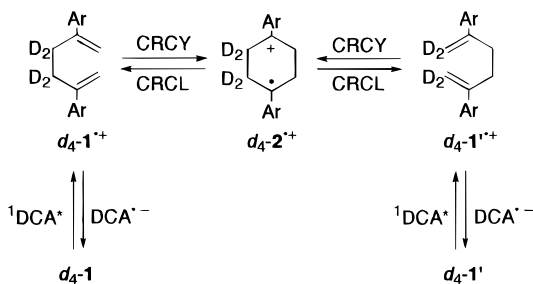
oxidation of **1a** with cerium(IV) ammonium nitrate [Ce(NH₄)₂(NO₃)₆, CAN] under oxygen gives **3a** clearly supports the interpretation that the cage-escaped cation radical 2^{•+} is captured by molecular oxygen under DCA-sensitized electron-transfer conditions.

Nanosecond laser flash photolysis of **1a** under DCA-sensitized conditions in acetonitrile in the presence of biphenyl as a cosensitizer¹⁵ affords an intense transient absorption with λ_{max} at 508 nm due to 2a^{•+}, which is relatively stable under argon but quickly decays under oxygen.^{8a} The λ_{max} of 2a^{•+} observed under *N*-methylquinolinium tetrafluoroborate (NMQ⁺BF₄[–])–toluene-cosensitized conditions is red-shifted to 525 nm in dichloromethane. Similar laser flash photolysis of **1c** gives a transient of 2c^{•+} with λ_{max} at 482 nm, which is also detected by laser flash photolysis of **4c** (Scheme 4). It is noteworthy that the λ_{max} of 2c^{•+} is significantly red-shifted as compared with those of the cumyl cation ($\lambda_{\text{max}} = 326, 390 \text{ nm}$ in FSO₃H–SbF₅ at –60 °C)¹⁷ and cumyl radical ($\lambda_{\text{max}} = 315 \text{ nm}$ in cyclohexane).¹⁸ Orbital interaction theory¹⁹ and a preliminary *ab initio* calculation suggest a through-bond interaction between the cumyl cation and cumyl radical parts in 2c^{•+} through the C₂–C₃ and C₅–C₆ σ -bonds in the chair conformation.²⁰ Similar through-bond interaction was proposed for the parent cyclohexane-1,4-diyl cation radical.^{11e} Although 2^{•+} is detected directly, nanosecond absorption spectroscopy does not give us any information about the processes involved before and after 2^{•+} is formed. Nevertheless, it is clear that 2^{•+} is an intermediate in the Cope rearrangement sequence.

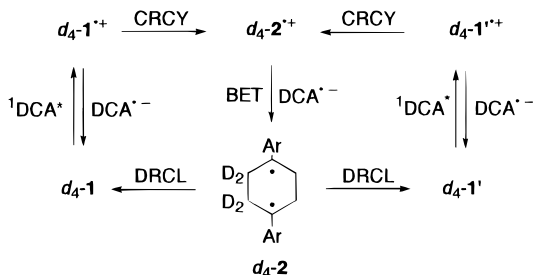
(c) Intervention of the 1,4-Diarylcyclohexane-1,4-diyl Intermediate and a CRCY–DRCL Mechanism. We previously proposed a cation radical cyclization (CRCY)–cation radical cleavage (CRCL) mechanism (Scheme 5a) for the photoinduced electron-transfer degenerate Cope rearrangement, leaving the question open as to whether 2^{•+} is the sole intermediate in the Cope rearrangement sequence.^{8b} In fact, this mechanism is inconsistent with several experimental observations. Cyclohexane-1,4-diyl cation radicals do not undergo cleavage to 1,5-hexadienes when generated by nonphotoinduced electron-transfer reactions such as the CAN-catalyzed reaction^{10b} and γ -ray irradiation¹¹ in a Freon matrix. The mechanism also cannot be used to explain the solvent effects on Φ_{cor} .^{8a} A

Scheme 5^a

(a) A CRCY–CRCL Mechanism



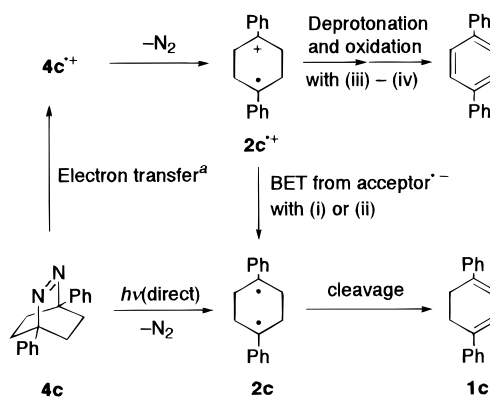
(b) A CRCY–DRCL Mechanism


^a Ar = 4-MeOC₆H₄, ^b Ar = 4-MeC₆H₄, ^c Ar = C₆H₅, ^d Ar = 4-ClC₆H₄
^a Abbreviation: CRCY, cation radical cyclization; CRCL, cation radical cleavage; DRCL, diradical cleavage; BET, back electron transfer.

key to solving these problems is the proposed intervention of a second intermediate, diradical **2**, which can be generated by the back electron transfer from DCA^{•-} to **2**^{•+} as shown in a cation radical cyclization (CRCY)–diradical cleavage (DRCL) mechanism (Scheme 5b). The back electron transfer from DCA^{•-} to **2**^{•+} is estimated to be 25.6 kcal/mol exothermic, as calculated by using the oxidation potential of the cumyl radical²¹ and the reduction potential of DCA. On the other hand, the back electron transfer from Ce(III) to **2**^{•+} is an endothermic reaction, with $\Delta G = +16.7$ kcal/mol. This implies that the formation of diradical **2** is feasible under DCA-sensitized electron-transfer conditions, but not under nonphotoinduced electron-transfer conditions. In addition, if back electron transfer occurs preferentially within an ion-radical pair [**2**^{•+}/DCA^{•-}], it is likely to be the key to increasing the quantum efficiency of the reaction in less polar solvents. A useful reaction with which to test this hypothesis is the electron-transfer deazetation reaction of **4c**. We predicted that the DCA-sensitized electron-transfer photoreaction of **4c** would produce **1c**, unlike the CAN-catalyzed reaction^{10b} of **4c**.

Like the direct irradiation²² of **4c**, both the DCA-sensitized photoreaction (>410 nm) of **4c** and photoexcitation (>410 nm) of the electron donor–acceptor (EDA) complex of **4c** and 1,2,4,5-tetracyanobenzene (TCNB) afford **1c** quantitatively.^{8a,d} In contrast, *p*-terphenyl is produced instead of **1c** in the cerium(IV) tetra-*n*-butylammonium nitrate [Ce(*n*-Bu₄N)₂(NO₃)₆]⁻ and tris(4-bromophenyl)aminium hexachloroantimonate [(4-BrC₆H₄)₃N⁺-SbCl₆⁻]-catalyzed deazetations^{8a,d} of **4c** as well as in the CAN-catalyzed deazetation.^{10b} Since the results of laser flash photolysis studies of **4c** demonstrate the presence

Scheme 6


^a Conditions: (i) ¹DCA[•], (ii) *h*_νEDA/TCNB, (iii) Ce(NH₄)₂(NO₃)₆, (iv) Ce(*n*-Bu₄N)₂(NO₃)₆, (v) (4-BrC₆H₄)₃N⁺SbCl₆⁻

of **2c**^{•+} as an intermediate, then back electron transfer to form diradical **2** must be responsible for the formation of **1c**. Thus, it is reasonable to assume that a similar back electron-transfer process operates to form **d₄-2** in the DCA-sensitized degenerate Cope rearrangement of **d₄-1**, supporting a CRCY–DRCL mechanism. Diradical **2** cannot be observed directly by laser flash photolysis. However, we recently found that a similar back electron-transfer process occurs in the photoinduced electron-transfer degenerate methylenecyclopropane rearrangement^{23,24} and that both trimethylenemethane cation radical and trimethylenemethane diradical intermediates can be detected spectroscopically.²⁴ A mechanistic connection among the deazetation reactions of **4c** mentioned above is described in Scheme 6.

(d) Energetics of a CRCY–DRCL Mechanism. In a CRCY–DRCL mechanism, the direct cleavage of **d₄-2**^{•+} to give **d₄-1**^{•+} and **d₄-1**^{•+} is too slow to compete with the back electron transfer from DCA^{•-}. To verify that the direct cleavage process is endothermic, the enthalpy of formation, $\Delta H_{\text{irp}}[\mathbf{2}^{\bullet+}/\text{DCA}^{\bullet-}]$, of the ion-radical pair [**2**^{•+}/DCA^{•-}] must be determined. We used nanosecond time-resolved photoacoustic calorimetry^{25,26} for the **1c**–DCA–biphenyl and **1c**–NMQ⁺PF₆⁻–toluene systems in acetonitrile and determined that the enthalpies of formation were $\Delta H_{\text{irp}}[\mathbf{2}^{\bullet+}/\text{DCA}^{\bullet-}] = 43.6 \pm 4.5$ kcal/mol and $\Delta H_{\text{irp}}[\mathbf{2}^{\bullet+}/\text{NMQ}^{\bullet+}\text{PF}_6^{\bullet-}] = 45.6 \pm 3.5$ kcal/mol.^{8a} The energy of the ion-radical pair [**2**^{•+}/NMQ⁺PF₆⁻] is comparable with that of [**2**^{•+}/DCA^{•-}] when 1.2 kcal/mol is added by taking into account the difference (0.05 V) in reduction potentials between DCA and NMQ⁺PF₆⁻. The resulting value, 46.8 ± 3.5 kcal/mol, is within the limits of experimental error of the value measured for $\Delta H_{\text{irp}}[\mathbf{2}^{\bullet+}/\text{DCA}^{\bullet-}]$, 43.6 ± 4.5 kcal/mol. Thus, we use the statistical value, 44.4 ± 4.5 kcal/mol, for $\Delta H_{\text{irp}}[\mathbf{2}^{\bullet+}/\text{DCA}^{\bullet-}]$, as shown in Figure 1. Since the calculated free energy change in the enthalpy of formation of [**1c**^{•+}/DCA^{•-}] is 60.6 kcal/mol, the direct cleavage of **d₄-2**^{•+} to **d₄-1**^{•+} and **d₄-1**^{•+} is apparently highly endothermic. Thus, the highly exothermic back electron transfer from DCA^{•-} to **d₄-2**^{•+} takes place preferentially

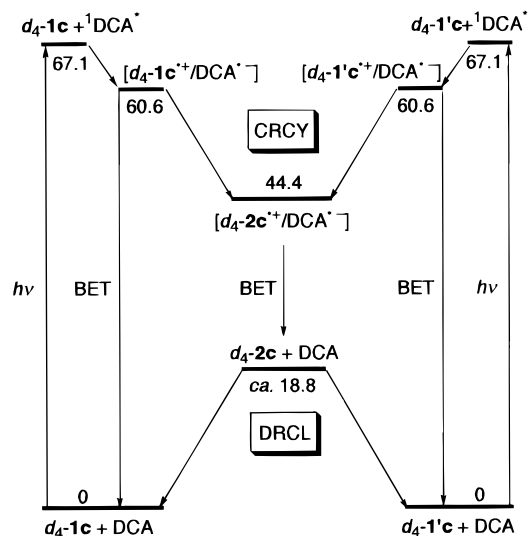
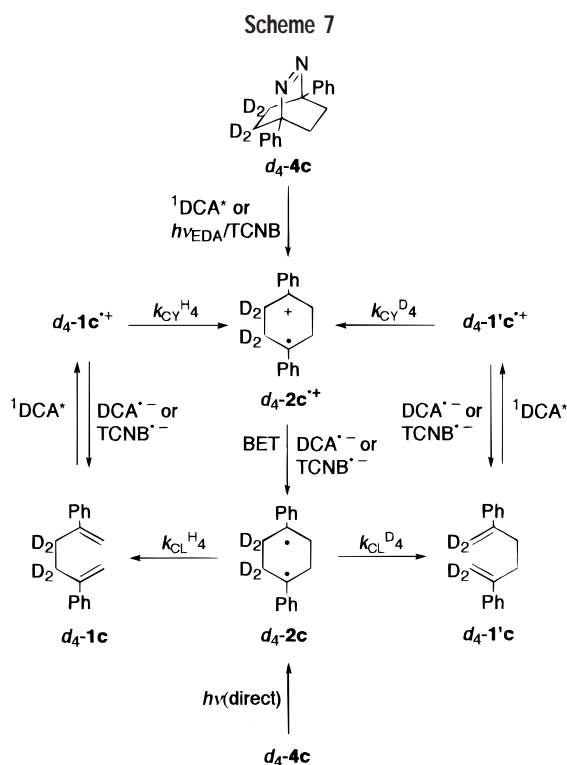


FIGURE 1. Energy diagram for the DCA-sensitized photoinduced electron-transfer degenerate Cope rearrangement of $d_4\text{-1c}$. Relative energy is represented in kilocalories per mole.



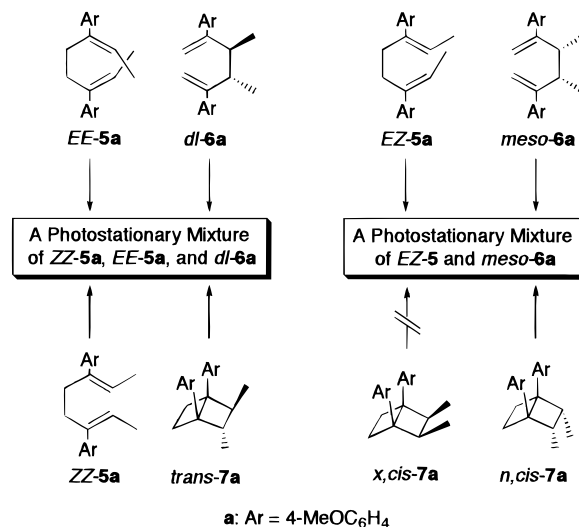
to form $d_4\text{-2}$, which is estimated to have about 19 kcal/mol more potential energy than the ground states of $d_4\text{-1c}$ or $d_4\text{-1'c}$ and DCA.

(e) BMKIE and BBKIE in a CRCY–DRCL Mechanism.

To further confirm the operation of a CRCY–DRCL mechanism and to directly determine the bond-breaking kinetic isotope effects (BBKIE = $k_{\text{CL}}^{\text{H}_4}/k_{\text{CL}}^{\text{D}_4}$) of diradical $d_4\text{-2}$ at the DRCL step, we synthesized the immediate precursor, $d_4\text{-4c}$ (Scheme 7). If the back electron transfer from DCA^- to $d_4\text{-2}^{+\cdot}$ actually occurs in the DCA-sensitized electron-transfer deazetation, then the direct irradiation and DCA-sensitized photoreaction of $d_4\text{-4c}$ should give a mixture of $d_4\text{-1c}$ and $d_4\text{-1'c}$ in the same ratio.

The experimental results are in accord with this hy-

Scheme 8



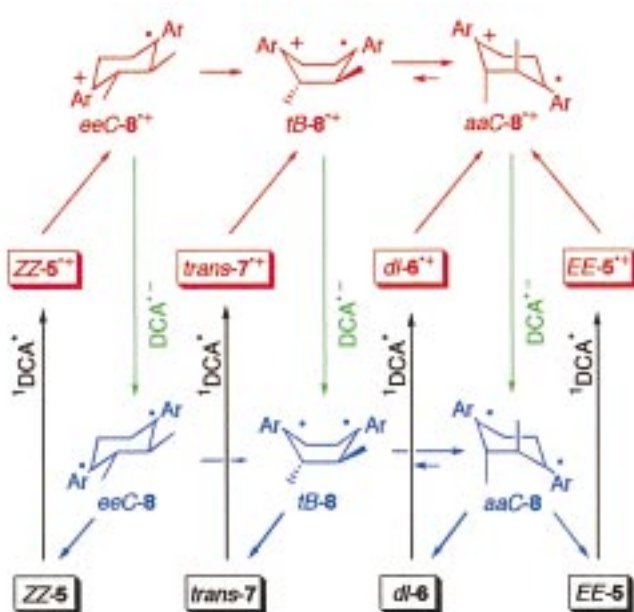
pothesis. Both the direct irradiation and DCA-sensitized photoreactions give a mixture of $d_4\text{-1c}$ and $d_4\text{-1'c}$, with ratios of 52.6:47.4 and 52.5:47.5, respectively.^{8a} Interestingly, the observed product ratios are nearly the same as the photostationary ratio, 52.6:47.4, seen with the degenerate Cope rearrangement of $d_4\text{-1c}$. Using the observed distribution ratio and the average photostationary ratio, the BBKIE and the bond-making kinetic isotope effects (BMKIE = $k_{\text{CY}}^{\text{H}_4}/k_{\text{CY}}^{\text{D}_4}$) at the CRCY step are determined to be 1.11 and almost unity, respectively. Thus, the BBKIE predominantly determines the photostationary ratio. A reasonable explanation for the relatively small BMKIE is that the highly exothermic CRCY proceeds through an early transition state, in which the $\text{C}_3\text{-C}_4$ bond is kept intact and C_1 and C_6 keep a sp^2 -like character. Both the BMKIE and BBKIE are reasonable if a CRCY–DRCL mechanism is operative.

II. Electron-Transfer Photoreactions of 3,6-Diaryl-2,6-octadienes and 2,5-Diaryl-3,4-dimethyl-1,5-hexadienes

(a) Stereospecific Formation of Chair Intermediates in the CRCY Step. Since the thermal Cope rearrangement of 1,5-hexadienes involves the simultaneous formation of the $\text{C}_1\text{-C}_6$ bond and cleavage of the $\text{C}_3\text{-C}_4$ bond through the chair six-membered transition state, it would not be surprising if both the CRCY and DRCL steps proceed through the chair conformation. Nevertheless, experimental confirmation of the stereochemical course of the reaction would lend support to the mechanistic argument. We therefore synthesized the three isomers of 3,6-diaryl-2,6-octadiene (*EE-5*, *ZZ-5*, and *EZ-5*) and two isomers of 2,5-diaryl-3,4-dimethyl-1,5-hexadiene (*dl-6* and *meso-6*) (Scheme 8).^{8b,c,23c,27}

Under DCA-sensitized conditions in dichloromethane, *EE-5a* and *dl-6a* give nearly the same photostationary mixture of *ZZ-5a*, *EE-5a*, and *dl-6a* in a 2:42:55 ratio at 20 °C, with excellent yields.²⁷ Diene *ZZ-5a* is a minor component of the photostationary mixture. The photoreaction of *ZZ-5a* is unexpectedly slow but gives

Scheme 9

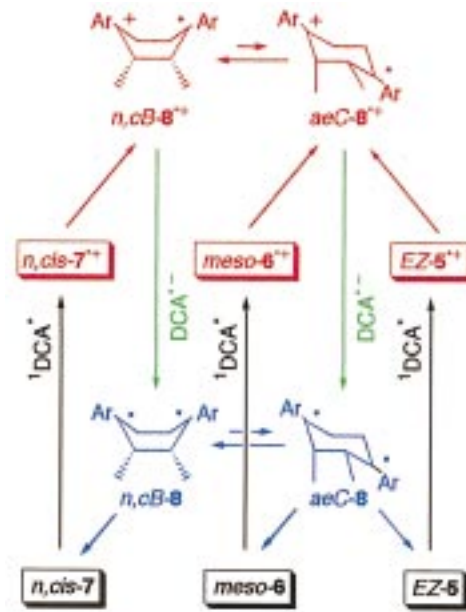


a mixture of *ZZ-5a*, *EE-5a*, and *dl-6a*. Interestingly, the relative ratio of *dl-6a* in the photostationary mixture increases as the temperature is lowered.²⁸ At $-80\text{ }^{\circ}\text{C}$, the ratio of *dl-6a* reaches an almost maximum value of 96%. Similar photoreactions of *EZ-5a* and *meso-6a* result in the formation of an 80:20 photostationary mixture of *EZ-5a* and *meso-6a* at ambient temperatures. The rearrangement sequence for the *dl*-family dienes (*ZZ-5a*, *EE-5a*, and *dl-6a*) is shown in Scheme 9 for a CRCY–DRCL mechanism.²⁷ Photostationary mixtures in this series include predominantly *EE-5a* and *dl-6a* for the following reasons: (1) both *EE-5a*⁺ and *dl-6a*⁺ preferentially cyclize to form the more stable *aaC-8a*⁺, even though *dl-6a*⁺ may cyclize to both *aaC-8a*⁺ and *eeC-8a*⁺; (2) ring-flip of *aaC-8a*⁺ to form the less stable *eeC-8a*⁺ occurs quite slowly, and therefore the population of *eeC-8a*⁺ and *eeC-8a* in a rearrangement cycle becomes quite low when starting with *EE-5a* and *dl-6a*; (3) *ZZ-5a*⁺ cyclizes to *eeC-8a*⁺, but back electron transfer may occur more quickly in *eeC-8a*⁺ than ring flip to *aaC-8a*⁺; and (4) the resulting *eeC-8a* is preferentially cleaved to *ZZ-5a* rather than *dl-6a*.

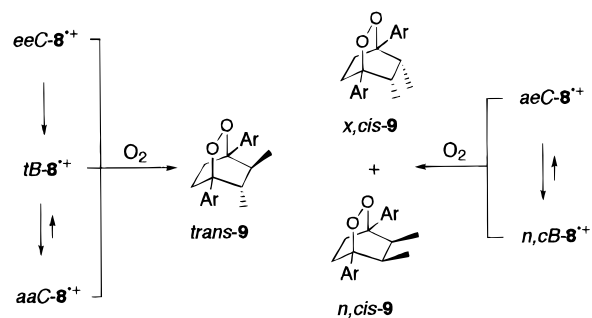
The rearrangement sequence for the *meso*-family dienes (*EZ-5a* and *meso-6a*) is similarly explained with the common intermediates *aeC-8a*⁺ and *aeC-8a*, as shown in Scheme 10.²⁷ The participation of boat intermediates, *tB-8a*⁺ and *n,cB-8a*⁺, is substantiated by the independent electron-transfer photoreactions of *trans-7a* and *n,cis-7a*, respectively. Because the *exo* isomer *x,cis-7a* behaves differently²⁷ from *n,cis-7a* under DCA-sensitized conditions, *x,cis-7* can be excluded from the Cope rearrangement sequence for the *meso*-family dienes. Observed stereospecific rearrangements clearly demonstrate that both CRCY and DRCL proceed via the chair conformation.

(b) Direct Capture of Chair Intermediates by Molecular Oxygen. Since cation radicals of *dl*- and *meso*-family dienes cyclize in the chair conformation, their stereo-

Scheme 10



Scheme 11

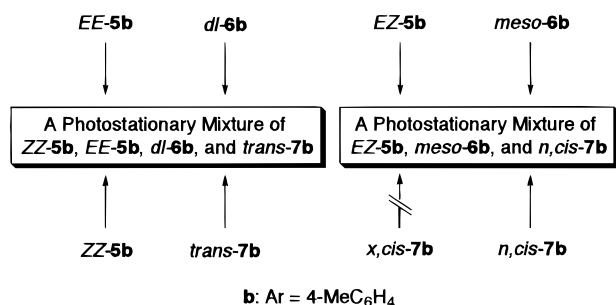


a: Ar = 4-MeOC₆H₄, **b:** Ar = 4-MeC₆H₄, **c:** Ar = C₆H₅

chemical integrity at the CRCY step should be conserved throughout the oxygenation reaction, no matter which conformational isomer is captured by molecular oxygen. In fact, *EE-5a*, *ZZ-5a*, and *dl-6a* as well as *trans-7a* all give *trans-1,4-bis(4-methoxyphenyl)-5,6-dimethyl-2,3-dioxabicyclo[2.2.2]octane* (*trans-9a*) stereoselectively in excellent yields under DCA-sensitized conditions in oxygen-saturated acetonitrile.^{8b,c,27} Similar oxygenation reactions of *EZ-5a* and *meso-6a* as well as *n,cis-7a* result in the quantitative formation of a mixture of *x,cis-9a* and *n,cis-9a* in a 4:1 ratio. As shown in Scheme 11, the stereochemical results of oxygenation unambiguously confirm that cyclizations of the *dl*- and *meso*-family diene cation radicals occur in the chair conformation.

(c) Direct Capture of Boat Intermediates and an Unusual Cope Rearrangement Accompanied by the Formation of the Bicyclo[2.2.0]hexane Derivative. The independent electron-transfer photoreactions of *trans-7a* and *n,cis-7a* strongly suggest the participation of boat intermediates (*tB-8a*⁺ and *n,cB-8a*⁺) and their diradical analogues in the Cope rearrangement sequence, though these boat intermediates never play an important role in the CRCY and DRCL processes. However, the rearrangement sequences shown in Schemes 9 and 10 indicate that

Scheme 12



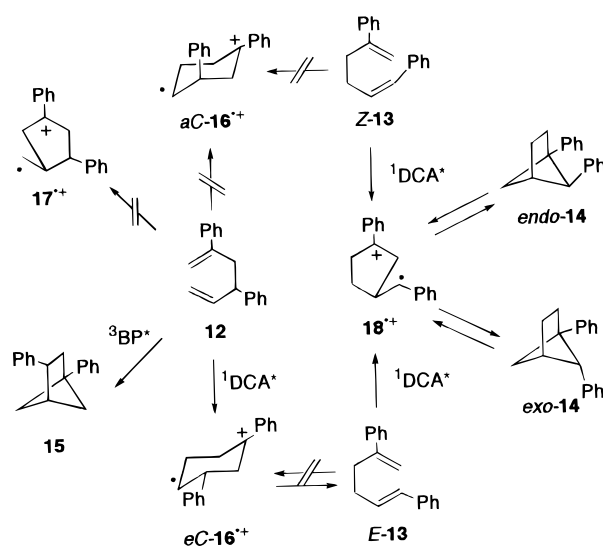
trans-7 and *n,cis-7* must be in equilibrium at the photostationary state with the *dl*- and *meso*-family dienes if *trans-7* and *n,cis-7* are stable enough to persist under DCA-sensitized conditions. We uncovered masked intermediacy of boat intermediates in electron-transfer photoreactions of weakly electron-donating 4-methylphenyl derivatives of the *dl*- and *meso*-family dienes.²⁷ The DCA-sensitized photoreactions of *ZZ-5b*, *EE-5b*, and *dl-6b* give a photostationary mixture of *EE-5b*, *dl-6b*, and *trans-7b* in ratios of approximately 9:40:50 and 9:76:15 in dichloromethane and benzene, respectively (Scheme 12). The similar photoreaction of *EZ-5b* does not form a clear photostationary mixture but gives a 53:14:33 mixture of *EZ-5b*, *meso-6b*, and *n,cis-7b* in dichloromethane. Starting with *meso-6b*, a 67:18:15 photostationary mixture of *EZ-5b*, *meso-6b*, and *n,cis-7b* is obtained in dichloromethane. In agreement with our previous hypothesis, *x,cis-7b* is not seen in photostationary mixtures formed from *EZ-5b* and *meso-6b*.

Since the formation and ring cleavage of the bicyclo[2.2.0]hexane derivatives occurs repeatedly in the Cope rearrangement sequence at the diradical and cation radical energy stages, respectively, then solvent polarity and electron-donating nature of the substrates will affect the cation radical cleavage step more significantly. The strongly electron-donating 4-methoxyphenyl derivatives such as *trans-7a* and *n,cis-7a* must be too labile to persist under DCA-sensitized conditions in acetonitrile. Since bicyclo[2.2.0]hexanes are essentially thermolabile, thermal reactions of 1,5-hexadienes never afford bicyclo[2.2.0]hexanes other than the usual Cope rearrangement products, although the thermally stable 1,5-diphenylbicyclo[3.2.0]heptane (**11c**, Scheme 14) is known to be formed upon pyrolysis of 2,6-diphenyl-1,6-heptadiene (**10c**).^{3b} Thus, the Cope rearrangement accompanied by the formation of the bicyclo[2.2.0]hexane derivative is the most unique aspect of the photoinduced electron-transfer Cope rearrangements of 2,5-diaryl-1,5-hexadienes.

III. Electron-Transfer Photoreactions of 2,4-Diphenyl- and 1,5-Diphenyl-1,5-hexadienes: Substitution Effects on the Photoinduced Electron-Transfer Cope Rearrangement

One of the key processes in the photoinduced electron-transfer Cope rearrangement is the initial cyclization to form **2^{•+}**, in which two aryl groups stabilize the unpaired electron and positive charge. Hence, a change of the aryl-

Scheme 13



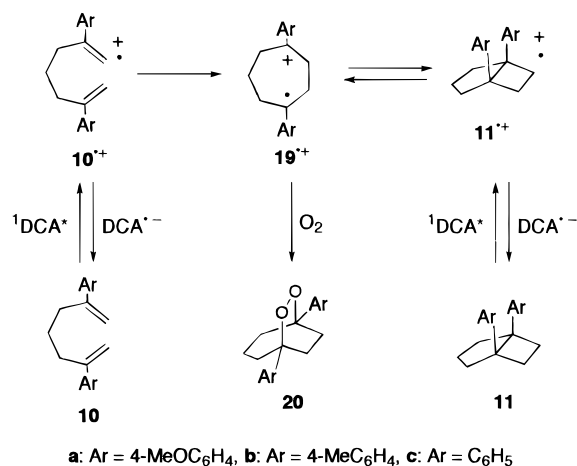
substitution position may alter the cyclization mode of aryl-substituted 1,5-hexadiene cation radicals. We tested the aryl-substitution effects in the DCA-sensitized photoreactions of 2,4-diphenyl-1,5-hexadiene (**12**) and (*E*- and *Z*)-1,5-diphenyl-1,5-hexadienes (*E-13* and *Z-13*) (Scheme 13).²⁹

The DCA-sensitized photoreaction of **12** gives the Cope rearrangement product *E-13*, together with a mixture of *endo*- and *exo*-1,5-diphenylbicyclo[2.1.1]hexane (*endo-14* and *exo-14*), while the benzophenone (BP)-sensitized photoreaction of **12** gives 1,3-diphenylbicyclo[2.1.1]hexane (**15**) exclusively. Either *E-13* or *Z-13* is not rearranged to form **12**, but forms a mixture of *endo-14* and *exo-14* under similar DCA-sensitized conditions. These results can be accounted for by the regioselective cyclization of diene cation radicals to give the more stable cyclic cation radical intermediates. Cation radical **12^{•+}** preferentially cyclizes to *eC-16^{•+}*, which is either sterically or thermodynamically more stable than *aC-16^{•+}* and **17^{•+}**. The Cope rearrangement of **12** occurs through *eC-16^{•+}*. In contrast, *E-13^{•+}* and *Z-13^{•+}* cyclize to form **18^{•+}** rather than *eC-16^{•+}* and *aC-16^{•+}*, respectively, because of thermodynamic preference. Apparently, the photoinduced electron-transfer Cope rearrangement requires the appropriate substitution for the aryl groups to induce the regioselective cyclization to a cyclohexane-1,4-diyl cation radical intermediate.

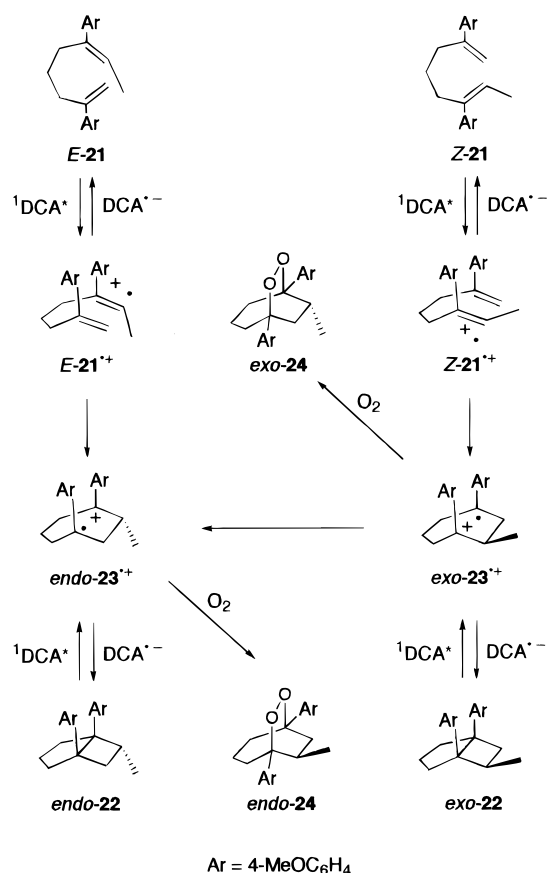
IV. Electron-Transfer Photoreactions of 2,6-Diaryl-1,6-heptadienes and Higher Homologues

The seven-, eight-, and nine-membered cyclic 1,4-cation radicals are also generated from the corresponding acyclic dienes under photoinduced electron-transfer conditions. The DCA-sensitized photoreaction of 2,6-diaryl-1,6-heptadiene (**10**) results in the formation of **11** in acetonitrile under argon (Scheme 14).^{30,31} Under DCA- or 2,6,9,10-tetracyanoanthracene-sensitized conditions in oxygen-saturated acetonitrile, 1,4-diarylcycloheptane-1,4-diyl cat-

Scheme 14



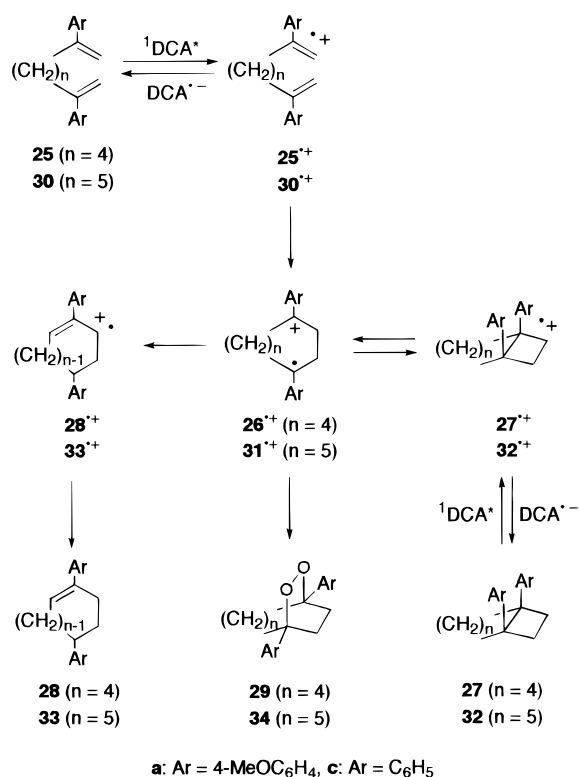
Scheme 15



ion radicals ($19^{+\bullet}$) are captured as the cyclic peroxide 20 ,^{30,31} which is reported to have antimalarial activity.³² Unlike *trans-7* and *n,cis-7*, 11 does not undergo cyclization to 10 under argon, but gives 20 under DCA-sensitized conditions in oxygen-saturated acetonitrile, suggesting that $19^{+\bullet}$ is in equilibrium with $11^{+\bullet}$. Of the three aryl derivatives, the 4-methoxyphenyl derivative $11a^{+\bullet}$ is most easily cleaved and oxygenated to $20a$.

The stereochemical course of cyclization of $10^{+\bullet}$ was tested by the electron-transfer photoreactions of *E-21* and *Z-21* (Scheme 15).³³ The DCA-sensitized photoreaction of *E-21* gives *endo-22* quantitatively at ambient temperatures in acetonitrile, whereas *Z-21* gives a 63:37 mixture of *exo-*

Scheme 16



22 and *endo-22* under similar conditions. While the photoreaction of *Z-21* appears to be nonstereoselective, cyclization of $Z-21^{+\bullet}$ is potentially stereoselective. Control experiments indicate that the nonstereoselective formation of *exo-22* and *endo-22* is ascribed to the irreversible rearrangement of *exo-22* to *endo-22* through $exo-23^{+\bullet}$ and $endo-23^{+\bullet}$ at ambient temperatures. Thus, the *exo-22*:*endo-22* ratio increases to 96:4 at -35 °C. Apparently, the ring-flip converting $exo-23^{+\bullet}$ to $endo-23^{+\bullet}$ becomes significantly slower at this temperature. The oxygenations of *E-21* and *Z-21* proceed in a similar manner. The oxygenations of *E-21* and *Z-21* form *endo-24* exclusively and a mixture of *exo-24* and *endo-24*, respectively, at ambient temperatures, whereas at -35 °C *exo-24* is formed exclusively from *Z-21*. The stereochemical results suggest that, in cyclizations of $E-21^{+\bullet}$ and $Z-21^{+\bullet}$, two styrene units approach each other in a nearly parallel configuration, maintaining the *syn*-like orientation of the two aryl groups.

2,7-Diaryl-1,7-octadiene (25) and 2,8-diaryl-1,8-nona-diene (30) produce the corresponding eight- and nine-membered cyclic cation radicals $26^{+\bullet}$ and $31^{+\bullet}$, respectively, when irradiated in the presence of DCA (Scheme 16).^{31,34} However, because of their flexible structures, $26^{+\bullet}$ and $31^{+\bullet}$ behave differently from $2^{+\bullet}$ and $19^{+\bullet}$. The DCA-sensitized photoreaction of $25a$ gives $28a$ quantitatively in acetonitrile and dichloromethane, whereas in benzene a 67:33 mixture of $27a$ and $28a$ is obtained quantitatively. The *cis*-configuration of $27a$ was confirmed directly by X-ray crystallography. Like *trans-7a* and *n,cis-7a*, the strongly electron-donating $27a$ cannot survive under DCA-sensitized conditions in acetonitrile. Ready cleavage to $26a^{+\bullet}$ followed by the H-shift results in the exclusive

formation of **28a** in acetonitrile and dichloromethane. On the other hand, the weakly electron-donating **25c** gives rise to a mixture of **27c** and **28c** in acetonitrile and dichloromethane. The intermediacy of **26a⁺** is substantiated by oxygenation to form **29a**. The reactivity of the 1,4-diarylcyclononane-1,4-diyl cation radical (**31⁺**) resembles that of **26⁺**, but yields of **32**, **33**, and **34** are substantially lower due to oligomerization of **30⁺**. A similar electron-transfer photoreaction of 2,9-diaryl-1,9-decadiene fails to give any cyclic product.

Conclusions

Photoinduced electron-transfer intramolecular cyclizations of acyclic dienes **A** [$X = (\text{CH}_2)_{2-6}$] proceed efficiently when $X = (\text{CH}_2)_{2-4}$, they proceed reluctantly when $X = (\text{CH}_2)_5$, and they are completely suppressed when $X = (\text{CH}_2)_6$. Cyclization of two styrene units is not restricted to those on acyclic systems, but it also occurs when two styrene units are vicinal on a benzene ring, five-membered heteroaromatic rings such as furan and pyrrole, and 5,5-dimethylcyclopentadiene. From 1,2-bis(α -styryl)benzene, the ¹H NMR-capturable bicyclic *o*-quinodimethane is formed.³⁵ As mentioned previously, electron-transfer photoreactions of 3,4-bis(α -styryl)furan,³⁶ 3,4-bis(α -styryl)pyrrole,^{36,37} and 2,3-bis(α -styryl)-5,5-dimethylcyclopentadienes³⁷ form cyclic tetramethyleneethane derivatives, which are diradical variants of cation radicals **C⁺** in Scheme 1. Like diradical **2**, these diradical species must be formed by back electron transfer from a sensitizer anion radical. Thus, back electron transfer to form a diradical species will be an important process, especially in electron-transfer photoreactions in which distonic cation radicals are initially formed as intermediates. When such a back electron-transfer process operates, photoinduced electron-transfer reactions serve as useful mechanistic probes to investigate diyl intermediates which are unobservable in the thermal reaction.

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