

## Photoinduced electron-transfer reactions of the cope and related systems

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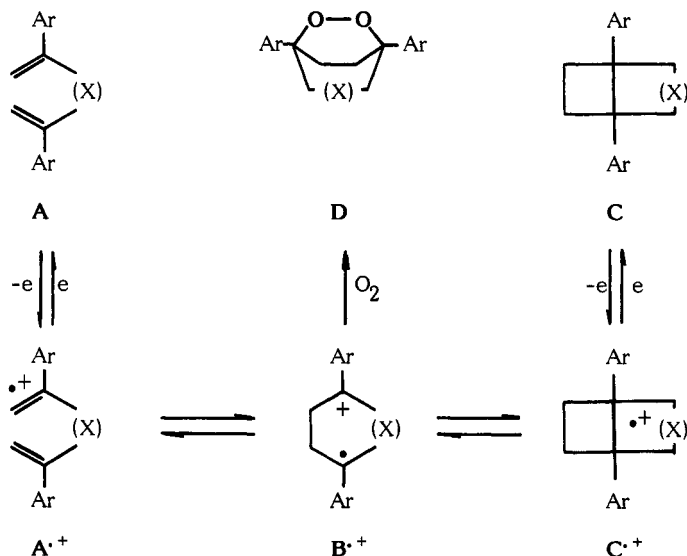
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**Abstract** - The 9,10-dicyanoanthracene-sensitized electron-transfer photoreactions of 2,5-diaryl-1,5-hexadienes and 3,6-diaryl-2,6-octadienes were investigated in order to prove a cyclohexa-1,4-diyl cation radical intermediate in the cation radical Cope rearrangement. Stereochemical results of rearrangements and oxygenation reactions provided evidences that cation radicals of these Cope systems initially cyclize to chair cyclohexa-1,4-diyl cation radicals, through which the cation radical Cope rearrangements stereospecifically occur in a cyclization-cleavage mechanism. Similar electron-transfer photoreactions of 1,4-diarylbicyclo[2.2.0]hexanes further supported this mechanism.

### INTRODUCTION

Electron-transfer photoreactions of acyclic dienes (**A**), in which two styryl functions are linked at the  $\alpha$  position by X, would provide simple but unique intramolecular reactions as shown in Scheme I. When photogenerated diene cation radicals (**A** $^{\cdot+}$ ) intramolecularly cyclize, we can expect generation of various types of cyclic 1,4-diyl cation radical intermediates (**B** $^{\cdot+}$ ), by changing X. Two competitive processes such as cleavage to **A** $^{\cdot+}$  and reclosure to **C** $^{\cdot+}$  then would be expected as subsequent reactions of **B** $^{\cdot+}$ . Among various types of **B** $^{\cdot+}$  we were particularly interested in a cyclohexa-1,4-diyl cation radical intermediate (**B** $^{\cdot+}$ ) (X=-CH<sub>2</sub>CH<sub>2</sub>-), because the reversible processes between **A** $^{\cdot+}$  and **B** $^{\cdot+}$  can be formulated as the hitherto unknown Cope rearrangement which occurs in a cyclization-cleavage mechanism (ref. 1). However, there must be experimentally accessible evidence for a cyclohexa-1,4-diyl cation radical intermediate in order to demonstrate a cyclization-cleavage mechanism. We assumed that the direct capture of **B** $^{\cdot+}$  (X=-CH<sub>2</sub>CH<sub>2</sub>-) as **D** by molecular oxygen and investigations of stereochemical courses of oxygenation and rearrangement would provide direct evidence for structures of intermediates because stereochemical integrity obtained in the initial cyclization of **A** $^{\cdot+}$  to **B** $^{\cdot+}$  can be conserved throughout oxygenation and rearrangement.

Scheme I



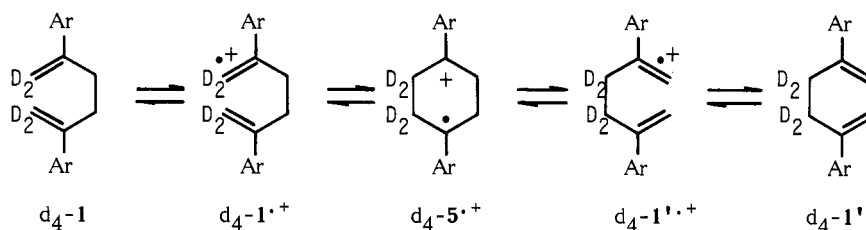
In order to uncover a cyclization-cleavage mechanism of the cation radical Cope rearrangement, we thus investigated electron-transfer photoreactions of 2,5-diaryl-1,5-hexadienes (**1**), 1,1,6,6-tetradeuterio-2,5-diaryl-1,5-hexadienes ( $d_4$ -**1**), 3,6-diaryl-2,6-octadienes (EE-**2**, EZ-**2** and ZZ-**2**), 2,5-diaryl-3,4-dimethyl-1,5-hexadienes (dl-**3** and meso-**3**) and 1,4-diaryl-2,3-dimethylbicyclo[2.2.0]hexanes (tBH-**4**) under the 9,10-dicyanoanthracene-sensitized conditions. The electron-transfer photoreactions of 2,6-diaryl-1,6-heptadienes were also investigated in order to test the generality of a cyclization-cleavage mechanism through  $B^+$ . The present paper summarizes recent results from our laboratory.

## 1. ELECTRON-TRANSFER PHOTOREACTIONS OF 2,5-DIARYL-1,5-HEXADIENES

### (A) The degenerate cation radical Cope rearrangement (ref. 2)

The thermal unimolecular Cope rearrangement of 2,5-diphenyl-1,5-hexadiene (**1b**) has been investigated by Dewar and co-workers in terms of the possible intermediacy of a cyclohexa-1,4-diyl intermediate (ref. 3). Although they found the enhancement of the rearrangement rate by phenyl substituents at the C-2 and C-5 positions of **1b**, they explained that the enhancement is caused by significant C-3-C-4 bond weakening in a transition state rather than in a cyclohexa-1,4-diyl intermediate. Similarly, the thermochemical-kinetic arguments by Gajewski precluded the possible intermediacy of a cyclohexa-1,4-diyl intermediate in the thermal unimolecular Cope rearrangement (ref. 4). However, if a cyclization-cleavage mechanism operates in the cation radical Cope according to Scheme I, we expected that electron-transfer photoreactions of 2,5-diaryl-1,5-hexadienes would most likely generate a stable 1,4-diaryl-cyclohexa-1,4-diyl cation radical intermediate. Thus, we synthesized three 2,5-diaryl-1,5-hexadiene derivatives (**1a-1c**) and their 1,1,6,6-tetradeuterio derivatives ( $d_4$ -**1a-1c**). The fluorescence of 9,10-dicyanoanthracene (DCA) was efficiently quenched in acetonitrile and benzene by **1a-1c** as shown in Table 1.

Scheme II



a: Ar=p-MeOC<sub>6</sub>H<sub>4</sub>; b: Ar=C<sub>6</sub>H<sub>5</sub>; c: Ar=p-ClC<sub>6</sub>H<sub>4</sub>

Table 1. Oxidation potentials, fluorescence quenching rate constants and photostationary ratios

| substrate | solvent                         | $E_{1/2}^{ox}$<br>(V vs SCE) | $10^{10}k_q$<br>(M <sup>-1</sup> s <sup>-1</sup> ) | irrad.<br>time<br>(min) <sup>a</sup> | ratio <sup>b</sup><br>$d_4-1/1'$ | m. b.<br>(%) <sup>c</sup> |
|-----------|---------------------------------|------------------------------|--|--------------------------------------|----------------------------------|---------------------------|
| $d_4-1a$  | CH <sub>3</sub> CN              | 1.27                         | 2.0  | 60                                   | 50/50                            | 38                        |
|           | CD <sub>2</sub> Cl <sub>2</sub> |                              | 1.5  | 30                                   | 52/48                            | 63                        |
|           | C <sub>6</sub> D <sub>6</sub>   |                              | 1.0  | 10                                   | 50/50                            | 93                        |
| $d_4-1b$  | CH <sub>3</sub> CN              | 1.68                         | 1.2  | 240                                  | 49/51                            | 44                        |
|           | CD <sub>2</sub> Cl <sub>2</sub> |                              | 0.36   | 30                                   | 48/52                            | 89                        |
|           | C <sub>6</sub> D <sub>6</sub>   |                              | 0.059  | 60                                   | 48/52                            | 92                        |
| $d_4-1c$  | CH <sub>3</sub> CN              | 1.71                         | 1.1  | 30                                   | 49/51                            | 87                        |
|           | CD <sub>2</sub> Cl <sub>2</sub> |                              | 0.24   | 60                                   | 47/53                            | 76                        |
|           | C <sub>6</sub> D <sub>6</sub>   |                              | 0.027  | 120                                  | 46/54                            | 100                       |

<sup>a</sup>the time reached to a photostationary state. <sup>b</sup>determined by 200 MHz nmr.  
<sup>c</sup>material balance.

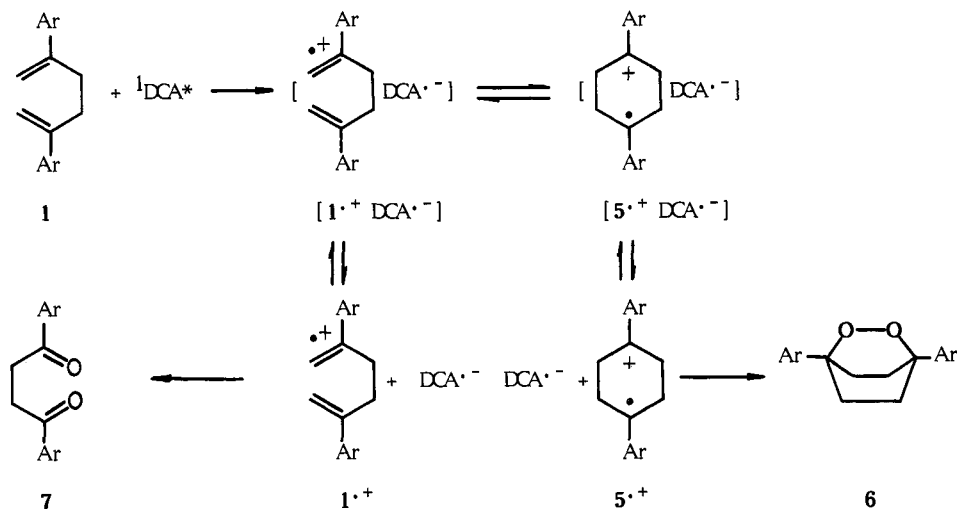
Upon separate irradiation (>390-nm) of DCA with  $d_4-1a$ ,  $d_4-1b$  or  $d_4-1c$  in acetonitrile- $d_3$ , dichloromethane- $d_2$  or benzene- $d_6$  under Ar, the degenerate Cope rearrangements were observed as summarized in Table 1. Significant solvent and substituent effects were not observed for photostationary ratios of  $d_4-1$  and  $d_4-1'$ . However, irradiation time reached to a photostationary state were found to depend on substituents and solvent polarity. If DCA-fluorescence quenching rate constants are close, the more electron-donative substrates such as  $d_4-1a$  and  $d_4-1b$  reach to a photostationary state much faster in the less polar solvents than in acetonitrile. Interestingly, in acetonitrile, the less electron-donative  $d_4-1c$

reaches to a photostationary state much faster than the more electron-donative  $d_4$ -**1a** and  $d_4$ -**1b**. These facts suggest that the degenerate Cope may occur prior to separation of ion pairs in the more polar acetonitrile and dichloromethane and through exciplexes in non-polar benzene. The degenerate Cope rearrangement seems to be most likely explained by a sequential cyclization-cleavage mechanism through a cyclohexa-1,4-diyl cation radical intermediate ( $d_4$ -**5<sup>+</sup>**) as shown in Scheme II. In support of this mechanism was the oxygenations of **1** leading to 1,4-diaryl-2,3-dioxabicyclo[2.2.0]octanes.

### (B) Photooxygenations of **1** under the DCA-sensitized conditions (ref. 2)

If cyclohexa-1,4-diyl cation radical intermediates intervene in the degenerate Cope rearrangements of **1**, these would be captured by molecular oxygen as a trimethylenemethane cation radical intermediate in the degenerate cation radical methylenecyclopropane rearrangement was captured (ref. 5). Upon irradiation of DCA with **1a** in oxygen-saturated acetonitrile for 5 min, **6a** was quantitatively isolated. The irradiation in oxygen-saturated dichloromethane for 5 min gave **6a** in 37% yield together with 63% of recovered **1a**, but the irradiation for 20 min resulted in the quantitative formation of **6a**. The irradiation in benzene, however, did not afford **6a** at all. Neither **1b** nor **1c**, likewise **1a**, was oxygenated in non-polar benzene. On the other hand, the irradiation of DCA with the less electron-donative **1b** for 20 min in oxygen-saturated acetonitrile afforded **6b** and diketone **7b** only in 10 and 3%, respectively, along with 58% recovered **1b**. Similarly, **1c** afforded **6c** and **7c** in 14 and 4% yields, respectively, along with 70% recovered **1c** after 20 min irradiation in oxygen-saturated acetonitrile. Experimental evidence that oxygenation rates significantly depend on the electron-donative nature of substrates may suggest that the intramolecular CT interaction between the charged and neutral styryl units, namely the cyclization rate, decreases with a decrease in the electron-donative nature of substrates. Thus, in the case of the more electron-donative **1a**, the cyclization of [**1a<sup>+</sup>** DCA<sup>-</sup>] to [**5a<sup>+</sup>** DCA<sup>-</sup>] occurs much faster than diffusion of [**1a<sup>+</sup>** DCA<sup>-</sup>] to **1a<sup>+</sup>** and DCA<sup>-</sup> in the more polar acetonitrile. Molecular oxygen then efficiently captures **5a<sup>+</sup>**. In contrast, in the case of the less electron-donative **1c**, the cyclization rate of [**1c<sup>+</sup>** DCA<sup>-</sup>] to [**5c<sup>+</sup>** DCA<sup>-</sup>] decreases so that the separation to **1c<sup>+</sup>** from [**1c<sup>+</sup>** DCA<sup>-</sup>] competes that to **5c<sup>+</sup>** from [**5c<sup>+</sup>** DCA<sup>-</sup>]. Molecular oxygen captures both **1c<sup>+</sup>** and **5c<sup>+</sup>** to give **7c** and **6c**, respectively. In benzene, **1<sup>+</sup>** and **5<sup>+</sup>** are reluctant to separate from ion pairs and exciplexes, and thereby **1a-1c** are not oxygenated at all. Observed results in (A) and (B), for the first time, demonstrate a cyclization-cleavage mechanism through a cyclohexa-1,4-diyl cation radical intermediate.

Scheme III



a: Ar=p-MeOC<sub>6</sub>H<sub>4</sub>; b: Ar=C<sub>6</sub>H<sub>5</sub>; c: Ar=p-ClC<sub>6</sub>H<sub>4</sub>

## 2. ELECTRON-TRANSFER PHOTOREACTIONS OF 3,6-DIARYL-2,6-OCTADIENES AND 2,5-DIARYL-3,4-DIMETHYL-1,5-HEXADIENES

### (A) Stereochemistry of oxygenation reactions

The famous studies done by Doering and Roth had concluded that the thermal unimolecular Cope rearrangement stereospecifically occurs through the six-membered chair transition state (ref. 6). However, the possible intermediacy of a cyclohexa-1,4-diyl is theoretically still controversial (ref. 7). In contrast, our study revealed that the cation radical Cope rearrangement of 2,5-diaryl-1,5-hexadienes involves a cyclohexa-1,4-diyl intermediate.

Theoretical support for a cyclohexa-1,4-diyl cation radical intermediate is the calculation done by Bauld and co-workers which suggested that the cyclization of 1,5-hexadiene cation radical to cyclohexa-1,4-diyl cation radical would be a low energy pathway (ref. 8). In addition, the initial cyclization of  $1^{+\cdot}$  to  $5^{+\cdot}$  is consistent with the cyclization of the parent 1,5-hexadiene cation radical to cyclohexa-1,4-diyl cation radical observed in ESR-matrix isolation studies by Williams and co-workers, though the parent cyclohexa-1,4-diyl cation radical did not undergo the Cope rearrangement in low temperature matrices (ref. 9). However, these theoretical and spectroscopic studies could not determine the conformation of cyclohexa-1,4-diyl cation radical. Our next studies were then directed toward the stereochemical determination of a 1,4-diarylcyclohexa-1,4-diyl cation radical intermediate. Because, as mentioned previously, the stereochemical integrity obtained in the initial cyclization step can be conserved throughout oxygenation and rearrangement, the oxygenation reactions of the Cope systems with stereochemical labels are essential. For this purpose, we synthesized stereochemically pure three isomers of 3,6-diaryl-2,6-octadienes (EE-, ZZ- and EZ-2) by the Wittig reaction of 1,4-diaryl-1,4-butanedione (7). NOE examinations provided correct stereochemical assignments of these isomers. *dl*-2,5-Diaryl-3,4-dimethyl-1,5-hexadienes (*dl*-3) were similarly derived from *dl*-1,4-diaryl-2,3-dimethyl-1,4-butanediones prepared according to the known procedure. The *meso*-isomers (*meso*-3) were successfully prepared from *meso*-1,4-diaryl-2,3-dimethyl-1,4-butanediones which were derived from *dl*-isomers by a base-catalyzed simultaneous isomerization-crystallization method, utilizing poorer solubility of *meso*-1,4-butanediones than *dl*-butanediones.

## Scheme IV

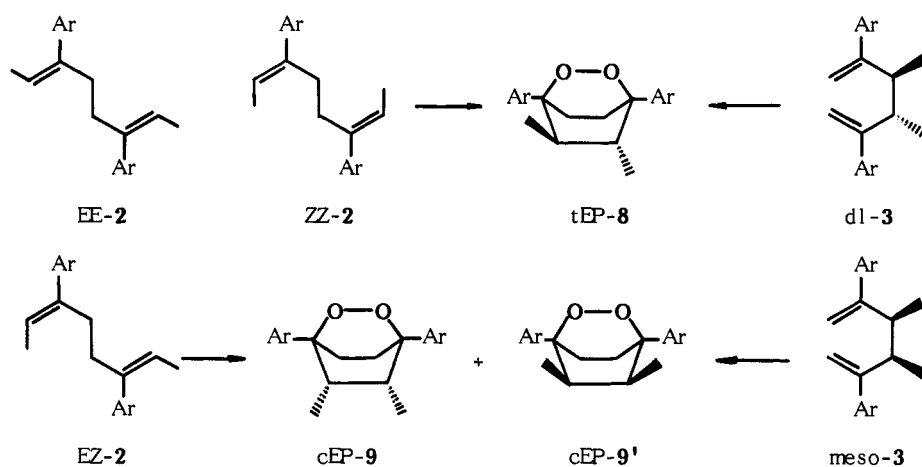


Table 2. Solvent and substituent effects on oxygenation reactions of ZZ-2

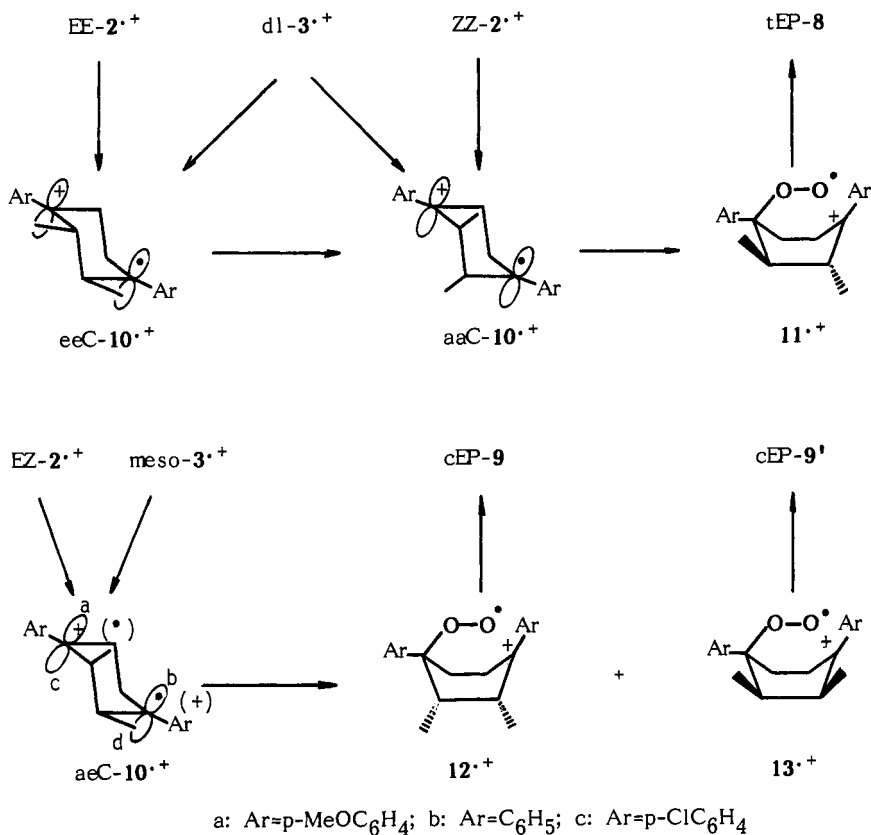
| substrate | solvent                         | $E_{1/2}^{ox}$<br>(V vs SCE) | $10^{10}k_q$<br>(M <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup> | irrad.<br>time<br>(min) | tEP-8      | dl-3 | ZZ-2 | tBH-4 |
|-----------|---------------------------------|------------------------------|---|-------------------------|------------|------|------|-------|
|           |                                 |                              |   |                         | yields (%) |      |      |       |
| ZZ-2a     | CH <sub>3</sub> CN              | 1.11                         | 1.9   | 1                       | 94         | 0    | 0    | 0     |
|           | CH <sub>2</sub> Cl <sub>2</sub> |                              | 1.8   | 5                       | 67         | 0    | 33   | 0     |
|           | C <sub>6</sub> H <sub>6</sub>   |                              | 1.3   | 10                      | 0          | 15   | 43   | 0     |
| ZZ-2b     | CH <sub>3</sub> CN              | 1.46                         | 1.6   | 1                       | 13         | 11   | 36   | 2     |
| ZZ-2c     | CH <sub>3</sub> CN              | 1.52                         | 1.4   | 5                       | 7          | 15   | 12   | 5     |

<sup>a</sup>DCA fluorescence quenching rate constant.

Upon irradiation (>360-nm) of DCA with EE-2a in oxygen-saturated acetonitrile, tEP-8a rapidly precipitated and was quantitatively isolated after irradiation for 1 min. Similar sensitized irradiations of ZZ-2a and dl-3a resulted in quantitative formations of tEP-8a. On the other hand, oxygenations of EZ-2a and meso-3a were slow, but both gave a 4:1 mixture of cEP-9a and cEP-9a', in 96 and 89% yields, respectively. The structure of cEP-9 was unequivocally determined by X-ray crystallographic analysis, and stereochemical assignments for tEP-8a and cEP-9a' were obtained by comparisons of the NMR spectrum of cEP-9a with those of tEP-8a and cEP-9a'. Solvent and substituents effects on oxygenation reactions were investigated for ZZ-2 and results were summarized in Table 2. Yields of tEP-8 decreased as the electron-donative nature of substrates decreases. Instead rearrangements of ZZ-2 to dl-3 and formations of small amounts of tBH-4 were observed in acetonitrile for the

less electron-donative ZZ-2b and ZZ-2c. As shown in Table 2, yields of tEP-8 decreased with a decrease in solvent polarity. Interestingly, in non-polar benzene, the rearrangement of ZZ-2a to dl-3a was a major pathway. These substituent and solvent effects on oxygenation further supplement previous assumption that the Cope rearrangement predominantly occurs within ion pairs or exciplexes, while oxygenation occurs after separation of ion pairs. Observed stereochemical results can be most likely accounted for by the initial stereospecific formations of the chair cyclohexa-1,4-diyli cation radicals as shown in Scheme V. The initial cyclization of EE-2<sup>•+</sup> and ZZ-2<sup>•+</sup> give eeC-10<sup>•+</sup> and aaC-10<sup>•+</sup>, respectively, while dl-3<sup>•+</sup> could cyclize to both. Molecular oxygen then captured either eeC-10<sup>•+</sup> or aaC-10<sup>•+</sup>, giving rise to the same product tEP-8. However, as we mention later, eeC-10<sup>•+</sup> which places two methyl groups equatorial seems to be thermodynamically less stable than aaC-10<sup>•+</sup> because of severe syn-coplanar steric repulsion between the methyl and aryl groups. Thus, ZZ-2<sup>•+</sup> and dl-3<sup>•+</sup> predominantly give aaC-10<sup>•+</sup>, through which oxygenations occur. EE-2<sup>•+</sup> initially cyclize to eeC-10<sup>•+</sup>, but oxygenations occur through aaC-10<sup>•+</sup> after the conformational change. Similarly both EZ-2<sup>•+</sup> and meso-3<sup>•+</sup> cyclize to aeC-10<sup>•+</sup>. Molecular oxygen can capture aeC-10<sup>•+</sup> at four different sites, i.e., a and/or b, recyclizes to give cEP-9 as a major product, while 13<sup>•+</sup> captured at the more hindered site, i.e., c and/or d, give cEP-9' as a minor product.

Scheme V



### (B) Stereochemistry of the cation radical Cope rearrangements

Because oxygenations of these Cope systems occur through aaC-10<sup>•+</sup> or aeC-10<sup>•+</sup> as a common intermediate, these Cope systems should stereospecifically interconvert through aaC-10<sup>•+</sup> or aeC-10<sup>•+</sup> in the Cope rearrangement. The rearrangement of ZZ-2 to dl-3 observed in oxygenation reactions is one of expected pathways. We further investigated a stereochemical course of the cation radical Cope rearrangement in detail. Upon irradiation of DCA with ZZ-2a under Ar in dichloromethane, ZZ-2a gradually decreased along with the formation of dl-3a. After 10 hrs irradiation, a photostationary mixture including ZZ-2a (42%), EE-2a (2%) and dl-3a (52%) was formed with 92% material balance. The isolated dl-3a was proved to be identical with that independently synthesized. Similar sensitized reaction of dl-3a gave nearly the same photostationary mixture after 4 hrs irradiation. On the other hand, the reaction of EE-2a was very slow so that the reaction did not reach to a photostationary state even after 20 hrs as shown in Table 3, but the ratio of ZZ-2a and dl-3a was nearly same as that in photostationary mixtures from ZZ-2a and dl-3a. Solvent polarity did not significantly change a photostationary ratio of ZZ-2a and dl-3a, but a material balance in

the more polar acetonitrile became poor and ZZ-2a formed small amounts of tBH-4a in non-polar benzene. Photoreactions of EZ-2a and meso-3a were simple and both gave nearly the same photostationary mixture in dichloromethane. Meso-3a from EZ-2a was also proved to be identical with that independently synthesized.

### Scheme VI

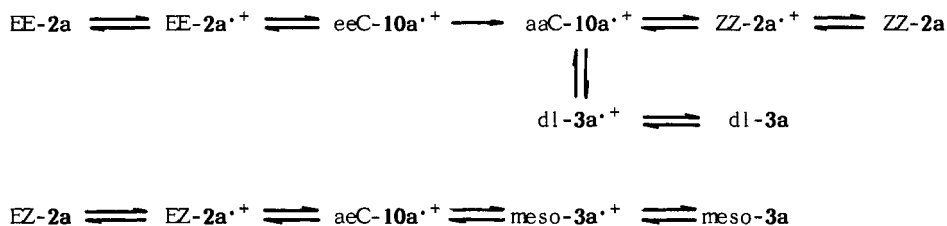


Table 3. Relative yields of Cope products in a photostationary state

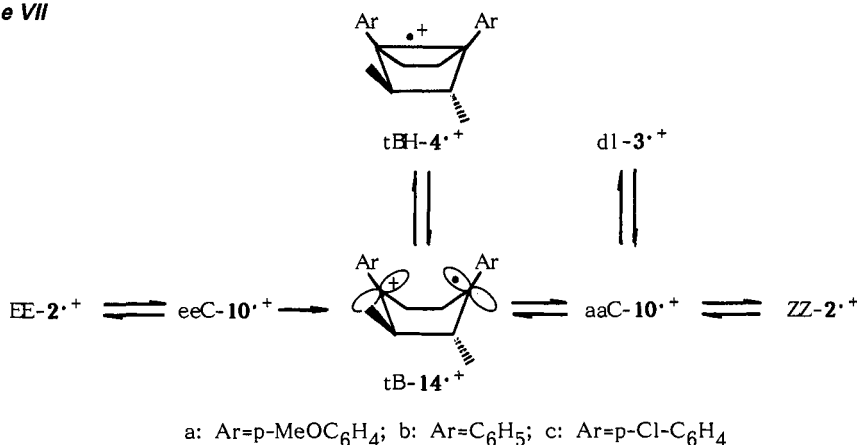
| substrate          | solvent                         | 10k <sub>q</sub><br>(M <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup> | irrad.<br>time<br>(hr) <sup>b</sup> | relative yields<br>(%) |       |       |       |         | M.B. <sup>c</sup><br>(%) |
|--------------------|---------------------------------|---|-------------------------------------|------------------------|-------|-------|-------|---------|--------------------------|
|                    |                                 |   |                                     | ZZ-2a                  | EE-2a | EZ-2a | dl-3a | meso-3a |                          |
| ZZ-2a              | CH <sub>3</sub> CN              | 1.9   | 4                                   | 48                     | 0     | 0     | 52    | 0       | 58                       |
|                    | CD <sub>2</sub> Cl <sub>2</sub> | 1.8   | 10                                  | 42                     | 2     | 0     | 55    | 0       | 92                       |
| EE-2a <sup>d</sup> | CD <sub>2</sub> Cl <sub>2</sub> | 1.5   | 20                                  | 19                     | 51    | 0     | 30    | 0       | 57                       |
| EZ-2a              | CD <sub>2</sub> Cl <sub>2</sub> | 1.6   | 8                                   | 0                      | 0     | 80    | 0     | 20      | 83                       |
| dl-3a              | CD <sub>2</sub> Cl <sub>2</sub> | 1.4   | 4                                   | 40                     | 2     | 0     | 57    | 0       | 87                       |
| meso-3a            | CD <sub>2</sub> Cl <sub>2</sub> | 1.5   | 10                                  | 0                      | 0     | 80    | 0     | 20      | 77                       |

<sup>a</sup>DCA-fluorescence quenching rate constant. <sup>b</sup>time reached to a photostationary state. <sup>c</sup>material balance. <sup>d</sup>not a photostationary mixture.

Stereochemical results observed in the Cope rearrangements of these systems can be rationalized by the same mechanism proposed for oxygenation. As shown in Scheme VI, ZZ-2a and EE-2a cyclize to aaC-10a<sup>·+</sup> and eeC-10a<sup>·+</sup>, respectively. However, eeC-10a<sup>·+</sup> undergoes the irreversible conformational change to aaC-10a<sup>·+</sup> and dl-3a predominantly cyclizes to aaC-10a<sup>·+</sup>. This is the reason why EE-2a is excluded from a photostationary mixture of ZZ-2a and dl-3a. The stereochemical result of the cation radical Cope rearrangement from dl-3a to ZZ-2a and that of the thermal unimolecular Cope rearrangement from dl-3,4-dimethyl-1,5-hexadiene to (E,E)-2,6-octadienes (ref. 6) are reversed, indicating significant steric repulsion between the methyl and p-anisyl groups in eeC-10a<sup>·+</sup>. We will further discuss about this point later in electron-transfer photoreactions of bicyclo[2.2.0]hexanes. Similarly, EZ-2a and meso-3a cyclize to aeC-10a<sup>·+</sup>, through which the reversible Cope between EZ-2a and meso-3a occurs. Experimental evidence for the initial cyclization to the chair form is consistent with that obtained from ESR-matrix isolation studies done by Williams (ref. 10).

Major rearrangement pathways of the cation radical Cope can be described as Scheme VI, but this mechanism can not explain the formations of small amounts of tBH-4 in the oxygenation reactions of ZZ-2b and ZZ-2c as shown in Table 2. In fact, the DCA-sensitized reaction of ZZ-2b in dichloromethane under Ar gave a photostationary mixture of ZZ-2b, dl-3b, and tBH-4b in 4:64:27 ratio. One rationale for the formation of tBH-4 is the intervention of the boat cyclohexa-1,4-diyl cation radical (tB-14<sup>·+</sup>) between eeC-10<sup>·+</sup> and aaC-10<sup>·+</sup>. If this assumption is correct, a mechanism shown in Scheme VI can be reformed as Scheme VII. In this mechanism, tBH-4<sup>·+</sup> leaves and enters a Cope rearrangement channel through tB-14<sup>·+</sup>. The ring cleavage of tB-14<sup>·+</sup> does not occur because of poor overlap of the C-2-C-3 bond with the spin and charge orbitals, and the ring flip between eeC-10<sup>·+</sup> and tB-14<sup>·+</sup> is irreversible, while that between tB-14<sup>·+</sup> and aaC-10<sup>·+</sup> is reversible. Under these circumstances, if rates of reversible processes between tBH-4<sup>·+</sup> and tB-14<sup>·+</sup> are comparable, tBH-4 can survive in a photostationary mixture of ZZ-2 and dl-3. The ring cleavage of tBH-4<sup>·+</sup> is assumed to be facilitated significantly by the electron-donative substituent such as the p-anisyl group. This may be the reason why tBH-4a is not included in photostationary mixtures from ZZ-2a, while a photostationary mixture from ZZ-2b includes tBH-4b. In order for this mechanism to operate, difference of free-energies between boat and chair cyclohexa-1,4-diyl cation radicals must be much smaller than that between boat and chair cyclohexanes so that appreciable amounts of the boat 1,4-diyl cation radical can be in equilibrium with the chair 1,4-diyl cation radical. However, at present, there is no available data to estimate this. For the experimental confirmation of this mechanism, electron-transfer photoreactions of *trans*-1,4-diaryl-2,3-dimethylbicyclo[2.2.0]hexanes were investigated.

Scheme VII



### 3. ELECTRON-TRANSFER PHOTOREACTIONS OF TRANS-1,4-DIARYL-2,3-DIMETHYLBICYCLO 2.2.0 HEXANE

The independent generation of tB-14<sup>•+</sup> is essential to gain insights into the role of the boat cyclohexa-1,4-diyli cation radical intermediate in the main Cope rearrangement pathway. Three derivatives (tBH-4a, tBH-4b and tBH-4c) were prepared from 1,2-diaryl-cyclobutenes. The DCA-sensitized photoreaction of tBH-4a in dichloromethane under Ar gave a photostationary mixture of ZZ-2a and dl-3a in 39:61 ratio, which is nearly the same ratio as those in photostationary mixtures from ZZ-2a and dl-3a shown in Table 3. This result clearly indicates that tB-14<sup>•+</sup> does not cleave to EZ-2a to meso-3a, but flips predominantly to the more stable aaC-10<sup>•+</sup>, through which the reversible Cope rearrangement of ZZ-2a and dl-3a occurs, supporting a mechanism shown in Scheme VII.

Table 4. Oxidation potentials, DCA-fluorescence quenching rate constants and oxygenations of tBH-4

| substrate | solvent            | $E_{1/2}^{ox}$<br>(V vs SCE) | $10^{10}k_q$<br>(M <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup> | irrad.<br>time<br>(min) | tEP-8 | 7 | ZZ-2 | dl-3 | tBH-4 |
|-----------|--------------------|------------------------------|---|-------------------------|-------|---|------|------|-------|
| tBH-4a    | CD <sub>3</sub> CN | 1.00                         | 1.6   | 0.25                    | 34    | 0 | 0    | 0    | 64    |
|           |                    |                              |   | 1                       | 100   | 0 | 0    | 0    | 0     |
| tBH-4b    | CD <sub>3</sub> CN | 1.54                         | 1.0   | 60                      | 4     | 2 | 0    | 3    | 86    |
|           |                    |                              |   | 180                     | 6     | 8 | 0    | 1    | 46    |
| tBH-4c    | CD <sub>3</sub> CN | 1.59                         | 0.97  | 180                     | 5     | 7 | 0    | 1    | 36    |

<sup>a</sup>DCA fluorescence quenching rate constant

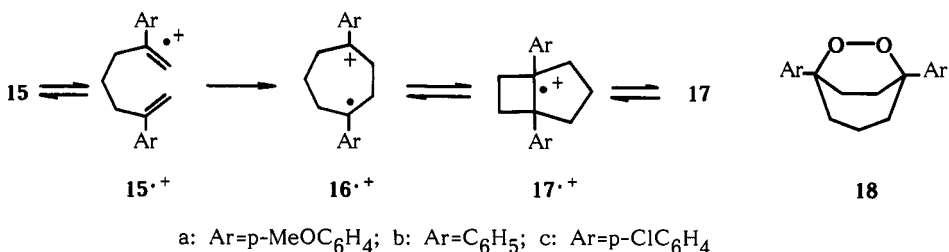
The DCA-sensitized oxygenation reactions of tBH-4 provided experimental evidence for the facility in the ring cleavage of the more electron-donative tBH-4a. As shown in Table 4, three derivatives of tBH-4 stereospecifically gave tEP-8, through a common intermediate aaC-10<sup>•+</sup>. However, combined yields of oxygenation (7 and tEP-8) and rearranged (dl-3) products from tBH-4b and tBH-4c are markedly low as compared with that from tBH-4a. This result can not be explained by difference in DCA-fluorescence quenching rate constants, but should be ascribed to difference in the electron-donative nature of substrates. Similar to the initial cyclization of 2,5-diaryl-1,5-hexadiene cation radicals, the separation of charge and spin due to the C-1-C-4 bond cleavage of tBH-4<sup>•+</sup> is presumably facilitated by the more electron-donative p-anisyl group. Although kinetics of other processes in Scheme VII must be taken into account, difference in the facility in the ring cleavage of tBH-4<sup>•+</sup> is important for the inclusion of tBH-4 in a photostationary mixture. Thus, the less electron-donative substrates provide the Cope rearrangement involving the formation of the bicyclo[2.2.0]hexane system.

### 4. ELECTRON-TRANSFER PHOTOREACTIONS OF 2,6-DIARYL-1,6-HEPTADIENES

A cyclization-cleavage mechanism in other systems was tested in electron-transfer photoreactions of 2,6-diaryl-1,6-heptadienes (15). Upon irradiation of DCA with 15a ( $E_{1/2}^{ox}=1.19$  V vs SCE in acetonitrile) in acetonitrile, dichloromethane or benzene, 17a, a formal [2+2]-

cycloadduct, was quantitatively isolated. Under similar sensitized conditions, **17a** ( $E_{1/2}^{\text{ox}}=1.01$  V) did not cyclorevert to **15a**. However, the DCA-sensitized oxygenations of **15a** and **17a** quantitatively gave **18a**, indicating the intervention of cyclohepta-1,4-diyl cation radical **16a<sup>+</sup>** as an intermediate. The less electron donative **15b** ( $E_{1/2}^{\text{ox}}=1.75$  V) and **15c** ( $E_{1/2}^{\text{ox}}=1.84$  V) similarly gave **17b** ( $E_{1/2}^{\text{ox}}=1.57$  V) and **17c** ( $E_{1/2}^{\text{ox}}=1.65$  V) in quantitative yields, respectively, in acetonitrile, dichloromethane or benzene, but **17b** and **17c** did not cyclorevert to **15b** and **15c**, respectively, in acetonitrile. Interestingly, neither **15b** nor **15c** was oxygenated even in acetonitrile. Observed results suggest that the cyclization of **15<sup>+</sup>** to **16<sup>+</sup>** and subsequent reclosure of **16<sup>+</sup>** to **17<sup>+</sup>** rapidly occur within ion pairs regardless of the electron-donative nature of substrates and solvent polarity, but the C-1-C-5 bond cleavage of **17<sup>+</sup>** to **16<sup>+</sup>** significantly depends on substrates. Although the fact that **17b** and **17c** were not oxygenated in acetonitrile does not necessarily indicate that **17b<sup>+</sup>** and **17c<sup>+</sup>** do not undergo the C-1-C-5 bond cleavage, the C-1-C-5 bond cleavage of **17<sup>+</sup>** is apparently facilitated by the electron-donative substituent such as the p-anisyl group. The trend of facility in the bond cleavage of **17<sup>+</sup>** is thus similar to that of tBH-4<sup>+</sup>. A failure of the C-2-C-3 bond cleavage in **16<sup>+</sup>** should be ascribed to poor overlap of the C-2-C-3 bond with the spin with charge orbitals in the most stable twist chair conformer. This is a major difference between the chair cyclohexa-1,4-diyl and twist chair cyclohepta-1,4-diyl cation radicals.

Scheme VIII



## CONCLUSION

Our present study, for the first time, experimentally demonstrates the cation radical Cope rearrangement which not only occurs in a cyclization-cleavage mechanism through the chair cyclohexa-1,4-diyl cation radical intermediate but also involves the formation of the bicyclo[2.2.0]hexane system through the boat cyclohexa-1,4-diyl cation radical, revealing all processes shown in Scheme I.

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