

Electron-transfer photoreactions of small-ring compounds: nature and role of cation-radical intermediates

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ABSTRACT - Rearrangement sequences of electron-transfer reactions of small-ring compounds such as methylenecyclopropanes, methylenespiropentanes, spiropentanes and bicyclo[2.2.0]hexanes are characteristic of photogenerated cation radicals. Unlike the thermal unimolecular rearrangements of the corresponding neutral molecules, key intermediates such as trimethylenemethane, allylically stabilized 1,4-, cyclopropylbiscarbonyl, and cyclohexa-1,4-diyl cation radical intermediates were chemically captured. The polarity of the reaction solvent, electron-donating nature of the substrates and the degree of donor acceptor interaction were found to be important in these cation radical rearrangements. For instance, solvent polarity changed the rearrangement pathway of the cation radical spiropentane-methylenecyclobutane rearrangement. Significant substituent effects on electron-transfer photoreactions of 1,4-diarylbicyclo[2.2.0]hexanes and various 2,5-diaryl-1,5-hexadienes provided an unprecedented Cope rearrangement which involves the bicyclo[2.2.0]hexane system.

INTRODUCTION

Because energy barriers of internal rotation and closure of short-lived biradicals are low, identification of true biradical intermediates in thermal unimolecular rearrangements of neutral molecules is often difficult. In fact, there are many thermal unimolecular rearrangements known as hypothetical biradical pathways in which biradical intermediates eluded direct chemical capture (ref. 1). The degenerate methylenecyclopropane and methylenespiropentane-biscyclopropylidene rearrangements via trimethylenemethane biradicals, the degenerate methylenecyclobutane and spiropentane-methylenecyclobutane rearrangements via allylically stabilized 1,4- and cyclopropylbiscarbonyl biradicals, and the Cope rearrangement via cyclohexa-1,4-diyl are among the famous and intriguing cases in point. We have investigated electron-transfer photoreactions of these systems from the viewpoint of cation radical chemistry. One unique feature of cation radical chemistry is that key cation radical intermediates formed from photogenerated ion radical pairs can be directly captured by conventional reagents such as molecular oxygen. The credibility of individual intermediates in these cation radical rearrangements was then evaluated by combination of such chemical capture with stereochemical analyses of the products and the rearrangement pathways. In the case of the cation radical degenerate methylenecyclopropane rearrangement, the CIDNP technique provided strong evidence for the stereochemical identification of an intermediate. We also investigated these rearrangements in terms of solvent and substituent effects, which are important not only for the initial electron-transfer process but also for stabilization of the intermediate ion radical species. By changing solvent polarity, divergent rearrangement pathways were found in the cation radical spiropentane-methylenecyclobutane rearrangement. Substituent effects on the ring cleavage of 1,4-diarylbicyclo[2.2.0]hexanes uncovered an unprecedented Cope rearrangement which involves the bicyclo[2.2.0]hexane system. Plausible mechanisms of these cation radical rearrangements are discussed, focussing on the nature and the role of cation radical intermediates.

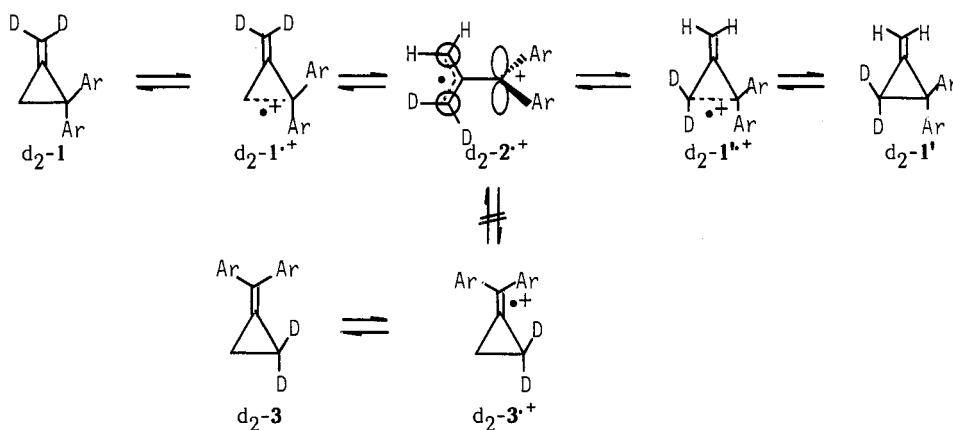
1. TRIMETHYLENEMETHANE CATION RADICAL INTERMEDIATES GENERATED FROM METHYLENOCYCLOPROPANE AND METHYLENESPIROPENTANE CATION RADICALS

(A) Electron-transfer photoreactions of 2,2-diaryl-1-methylenecyclopropanes

The thermal structural isomerizations of methylenecyclopropanes were first observed by Ullman in the thermal reactions of Feist's esters (ref. 2). Since then, many examples of the methylenecyclopropane rearrangement have been found. Although many stereochemical and kinetic experiments have been carried out to demonstrate a postulated trimethylenemethane biradical intermediate, recent elegant studies of Berson established the substantiality of both singlet and triplet trimethylenemethane biradicals (ref. 3). We were interested in the structure and reactivity of the cation radical variant and investigated electron-transfer photoreactions of 2,2-diaryl-1-methylenecyclopropanes (1) which thermally undergo the dege-

nerate methylenecyclopropane rearrangement (ref. 4), but do not undergo it photochemically (ref. 5). Under the *p*-chloranil (CA, $E_{1/2}^{\text{red}} = +0.01$ V vs. SCE)- or anthraquinone (AQ, $E_{1/2}^{\text{red}} = -0.94$ V)-sensitized conditions in acetonitrile, d_2 -**1a-d** undergo the degenerate methylenecyclopropane rearrangement. The phenanthraquinone (PQ, $E_{1/2}^{\text{red}} = -0.66$ V)-sensitized reactions of d_2 -**1c** ($E_{1/2}^{\text{ox}} = +1.65$ V) and d_2 -**1d** ($E_{1/2}^{\text{ox}} = +1.35$ V) involved the degenerate rearrangement, but less electron-donating d_2 -**1a** ($E_{1/2}^{\text{ox}} = +1.88$ V) and d_2 -**1b** ($E_{1/2}^{\text{ox}} = +1.83$ V) did not undergo the degenerate rearrangement, indicating that the degenerate rearrangement occurs via an electron-transfer process. The intermediacy of a trimethylenemethane cation radical was substantiated by oxygenation reactions to give dioxolanes (ref. 6). Under the sensitized conditions which involve the degenerate rearrangement, **1a-d** were oxygenated. The formation of CA-adducts in acetonitrile under Ar also supports the intermediacy of 2^+ (ref. 7). Similar oxygenations of **1** took place when the electron donor-acceptor complexes of **1** and tetracyanoethylene were irradiated in polar solvents under O_2 (ref. 8). One intriguing feature of this electron-transfer reaction is that **1** did not rearrange to the thermodynamically more stable **3**. The latter remained unchanged under various sensitized conditions, indicating that cation radicals 1^+ and 3^+ are different species in terms of their reactivities.

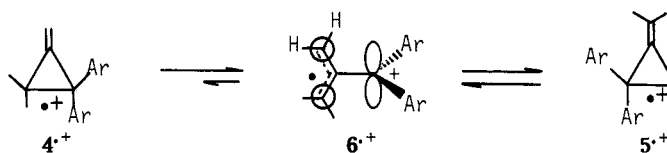
Scheme I



a: Ar=4-ClC₆H₄; b: Ar=C₆H₅; c: Ar=4-CH₃C₆H₄; d: Ar=4-CH₃OC₆H₄

Direct evidence for the structures of 2^+ and 3^+ was obtained from CIDNP experiments of **1d** and **3d** (ref. 7). The observed polarization patterns from the photoreaction of **1d** and CA in acetone- d_6 suggested that 2^+ is a bisected species in which the spin density primarily localized in the allyl moiety, while the charge is primarily localized in the diarylmethylene group. On the other hand, similar photoreaction of **3d** suggested that 3^+ is in essence a diarylmethylene cation radical. Thus, the different photoreactivities of **1** and **3** can be ascribed to their different structures. In cation radical 3^+ , the spin and the charge which are localized only in the π -system do not interact with the cyclopropane Walsh orbitals and thereby 3^+ resists the ring cleavage. The bisected trimethylenemethane cation radical 2^+ can be generated from 1^+ in a least motion pathway by rotation of the less bulky methylene group. 1^+ is then reorganized again by the rotation of the methylene group and not of the bulkier diphenylmethylene group. In support of the successive rotations of the less bulky group in the reorganization of methylenecyclopropane is the irreversible rearrangement of **4** to **5**. The 9,10-dicyanoanthracene (DCA)-sensitized irradiation of **4** in chloroform under Ar gave **5**, while similar irradiation of **5** did not give **4**. However, evidence that the DCA-sensitized irradiations of **4** and **5** in oxygen-saturated acetonitrile gave dioxolanes indicates that 6^+ is formed from both 4^+ and 5^+ by rotations of the less bulky dimethylmethylene and methylene groups, respectively. If the successive rotation of the less bulky methylene group of 6^+ occurs much faster than that of the dimethylmethylene group, 6^+ can predominantly give 5^+ .

Scheme II



(Ar=4-CH₃OC₆H₄)

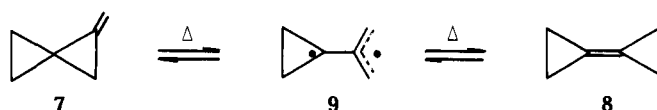
The difference in reactivity between the two types of methylenecyclopropane cation radicals

was theoretically rationalized by recent theoretical calculations of Borden. The ring cleavage of the σ -type cation radical corresponding to 1^+ would occur without energy barrier, while the ring cleavage of the π -type cation radical corresponding to 3^+ requires higher activation energy (ref. 9).

(B) Electron-transfer photoreactions of 2,2-diaryl-1-methylenespiropentanes

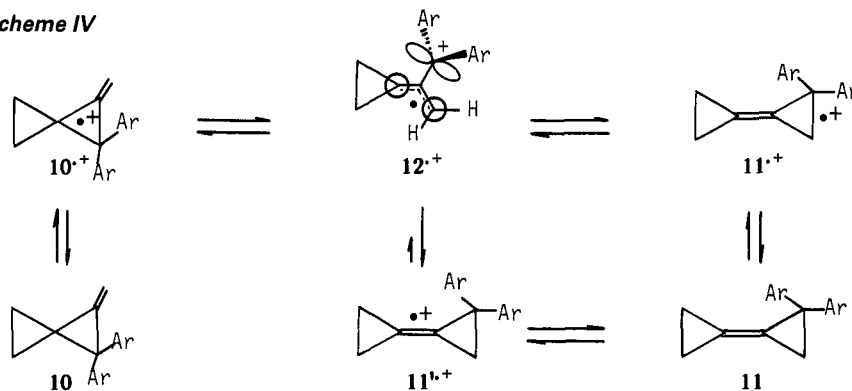
Because methylenespiropentane (**7**) and bicyclopropylidene (**8**) possess the methylenecyclopropane moiety, the ring cleavage at the C_2 - C_3 bond of **7** and C_1 - C_2 bond of **8** can generate biradical (**9**), through which the degenerate rearrangement of **7** and the reversible methylenespiropentane-bicyclopropylidene rearrangement between **7** and **8** are expected to occur.

Scheme III



However, upon pyrolysis at 320°C **7** rearranges to 1,2- and 1,3-bismethylenecyclobutanes, respectively, through the tetramethyleneethane and allylic-vinyl biradical intermediates, while at 210°C **8** irreversibly rearranges to **7**. The reason why **7** did not rearrange to **8** is ascribed to serious instability of **8** under the pyrolysis conditions (ref. 10). In order to search for the reversible methylenespiropentane-bicyclopropylidene rearrangement, electron-transfer photoreactions of 2,2-diaryl-1-methylenespiropentanes (**10**) were investigated.

Scheme IV



a: Ar=C₆H₅; b: Ar=4-CH₃C₆H₄; c: Ar=4-CH₃C₆H₄ and C₆H₅;

d: Ar=4-CH₃OC₆H₄ and 4-CH₃C₆H₄; e: Ar=4-CH₃OC₆H₄

Table 1. Photostationary ratios (**11/10**) observed in the DCA- and TRCA-sensitized photoreactions of **10** in acetonitrile at 10°C^a

	10a	10b	10c	10d	10e
DCA	6.9	3.4	2.3	1.9	1.5
TRCA	4.0	3.2	1.8	1.7	1.4

^aReduction potentials of DCA and TRCA are -0.98 and -0.70 V vs. SCE, respectively. Oxidation potentials of **10a-e** are 1.71, 1.55, 1.32, 1.31 and 1.23 V vs. SCE, respectively and those of **11a**, **11c** and **11e** are 1.71, 1.32 and 1.23 V vs. SCE, respectively.

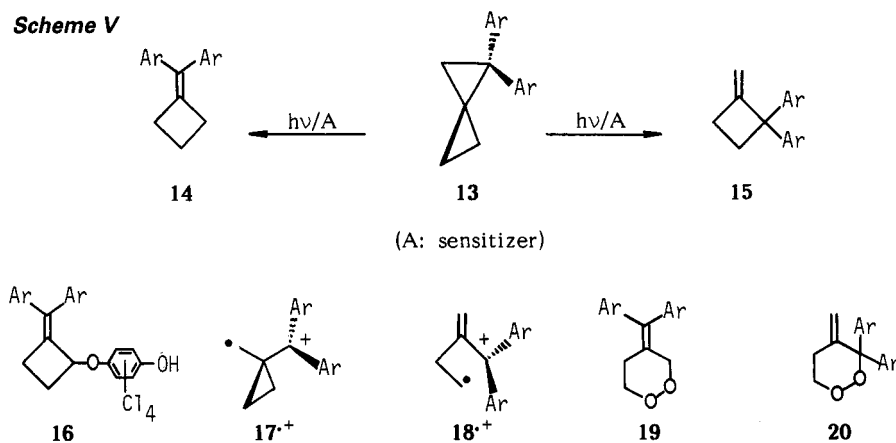
The 9,10-dicyanoanthracene (DCA)-sensitized electron-transfer reaction of **10a** in acetonitrile at 10°C gave a 6.9:1 photostationary mixture of **11a** and **10a**. Similar photoreaction of **11a** resulted in the formation of a 6.5:1 photostationary mixture. The 2,9,10-tricyanoanthracene (TRCA)-sensitized reactions of **10a** and **11a** also gave nearly the same photostationary mixture of **10a** and **11a**. As expected from the thermal rearrangement of **8** to **7**, **11a** rearranged to **10a** upon heating at 80°C. The explanation for the predominant formation of **11a** is that the methylene group of $12a^+$ rotates faster than the cyclopropyl group when **10a** and **11a** are reorganized. This explanation, however, is not sufficient to account for substituent effects on the photostationary ratios shown in Table 1. The yield of **10** increases with an increase in electron-donating nature of diaryl substituents, though the formation of **11**

is still favored even for dianisyl derivative **10d** which has the lowest oxidation potential. Because the DCA-fluorescence quenching rate constants and the oxidation potentials of **10** and **11** are nearly the same, the initial electron-transfer process to form $10^{\bullet+}$ or $11^{\bullet+}$ is assumed to be unimportant in determining the photostationary ratio. We assume that the nature of cation radical **11** would be rather important. Biscyclopropylidene has a low ionization potential (IP 8.93 eV) (ref. 11), which is much lower than that of methylenecyclopropane (9.60 eV) (ref. 12) but comparable with that of phenylcyclopropane (8.71 eV) (ref. 13). Thus, two types of cation radicals, i.e., the σ -type $11^{\bullet+}$ and π -type $11^{\bullet+}$ would be generated from **11**. Because the electron-donating nature of the diaryl substituents is of primary importance for the generation of $11^{\bullet+}$, a more electron-donating substituent such as the anisyl group will increase the contribution of $11^{\bullet+}$ which, like $1^{\bullet+}$, will readily undergo the ring cleavage. By contrast, as the oxidation potential increases, the contributions of $11^{\bullet+}$ decreases and that of the more stable $11^{\bullet+}$ relatively increases. The predominant formation of **11** is consistent with the predominant contribution of $11^{\bullet+}$ which, like $3^{\bullet+}$, will be reluctant to undergo the ring cleavage.

2. DIVERGENT REARRANGEMENT PATHWAYS IN THE CATION RADICAL SPIROPENTANE-METHYLENOCYCLOBUTANE REARRANGEMENT

Doering had proposed that the thermal unimolecular rearrangement of spiro-pentane to methylenecyclobutane occurs via two successive bond cleavages. First, the C₁-C₂ bond cleavage gives the cyclopropyl-1,1-biscarbonyl biradical which is successively converted to the allylically stabilized 1,4-biradical. The latter biradical is known as an intermediate in the thermal degenerate methylenecyclobutane rearrangement (ref. 14). However, the possibility of a symmetry-allowed concerted rearrangement was proposed in the rearrangements of 1-carbomethoxy-2,4-dimethylspiro-pentanes (ref. 15). We investigated electron-transfer photoreactions of 1,1-diarylspiropentanes and found that two independent pathways compete in the cation radical spiro-pentane-methylenecyclobutane rearrangement (ref. 16), i.e., the rearrangement to 1-(diarylmethylene)cyclobutane occurs predominantly in a concerted manner, whereas the rearrangement to the thermodynamically less stable 2,2-diaryl-1-methylenecyclobutane occurs in a stepwise manner, involving cyclopropyl-1,1-biscarbonyl and allylic 1,4-cation radical intermediates (ref. 17).

Scheme V



a: Ar=4-ClC₆H₄; b: Ar=C₆H₅; c: Ar=4-CH₃C₆H₄; d: Ar=4-CH₃OC₆H₄

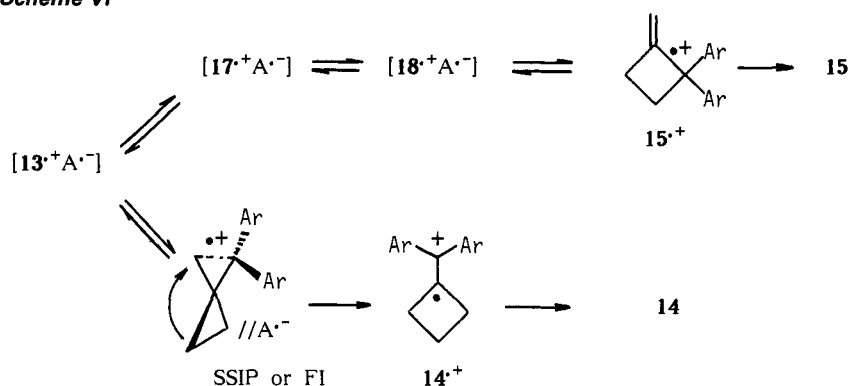
The phosphorescence of anthraquinone (AQ, $E_{1/2}^{\text{red}} = -0.94$ V vs SCE) was efficiently quenched by **13a** ($E_{1/2}^{\text{ox}} = 1.72$ V), **13b** ($E_{1/2}^{\text{ox}} = 1.67$ V), **13c** ($E_{1/2}^{\text{ox}} = 1.42$ V) and **13d** ($E_{1/2}^{\text{ox}} = 1.17$ V) in acetonitrile. Upon irradiation of AQ with **13d** in acetonitrile, **14d** and **15d** were isolated in 33 and 26% yields, respectively, after 79% conversion of **13d**. The formation of **14d** and **15d** was also observed in less polar solvents such as dichloromethane, chloroform and benzene, though the yields decreased. When 2,4,7-trinitrofluorenone (TNF, $E_{1/2}^{\text{red}} = -0.42$ V) or *p*-chloroanil (CA, $E_{1/2}^{\text{red}} = +0.01$ V) was used as an electron-acceptor sensitizer, **14d** and **15d** were similarly formed. However, under the CA-sensitized conditions large amounts of **16d** were isolated as a secondary CA-adduct in acetonitrile and dichloromethane. Experimental results for **13d** obtained under various sensitized conditions are shown in Table 2 together with those for the less electron-donating **13a**, **13b** and **13c**. An intriguing feature of electron-transfer photoreactions of **13** is that the **14/15** ratio depends significantly on solvent polarity and the sensitizer. The **14/15** ratio increases with an increase in solvent polarity. The CA-sensitized photoreactions in acetonitrile gave exclusively the thermodynamically more stable **14**, while the AQ- and TNF-sensitized photoreactions gave **14** together with comparable amounts of **15**. Similar solvent effects were also observed in the 9,10-dicyanoanthracene (DCA)-sensitized photoreactions of **13** as shown in Table 2.

Table 2. Yields of **14** and **15** in the AQ-, TNF-, CA- and DCA-sensitized photoreactions of **13**^a

sens.		yields and conversions (%)											
		acetonitrile				dichloromethane				benzene			
		13a	13b	13c	13d	13a	13b	13c	13d	13a	13b	13c	13d
AQ	14	12	13	19	33	0	b	13	17	0	0	0	12
	15	19	29	29	26	9	18	31	41	0	2	4	44
	conv.	45	59	61	79	16	28	59	68	0	4	13	86
TNF	14	8	14	18	31	0	7	9	13	0	0	6	8
	15	13	12	20	20	12	14	23	34	4	10	23	32
	conv.	23	30	51	61	21	29	41	67	8	17	41	51
CA	14	7	18	8	3	4	6	18	6	0	5	0	0
	15	4	4	b	2	19	13	10	b	22	31	32	40
	16 ^c	34	49	72	45	63	47	44	12	b	5	0	0
	conv.	100	100	100	100	96	100	99	94	86	100	100	97
DCA	14	21	40	33	45	19	23	25	4	b	6	10	0
	15	9	14	4	8	16	34	28	27	5	12	52	39
	conv.	60	77	56	89	45	68	60	72	13	19	95	54

^a A 5ml solution of **13** (0.08 mmol) and AQ (0.01 mmol), TNF (0.01 mmol) or CA (0.08 mmol) was irradiated for 30 min (AQ), 20 min (TNF) and 60 min (CA); ^bless than 2%; ^cIrradiations in acetonitrile and dichloromethane gave additionally a 2:1 CA-**13** adduct in 40 and 58% yields, respectively.

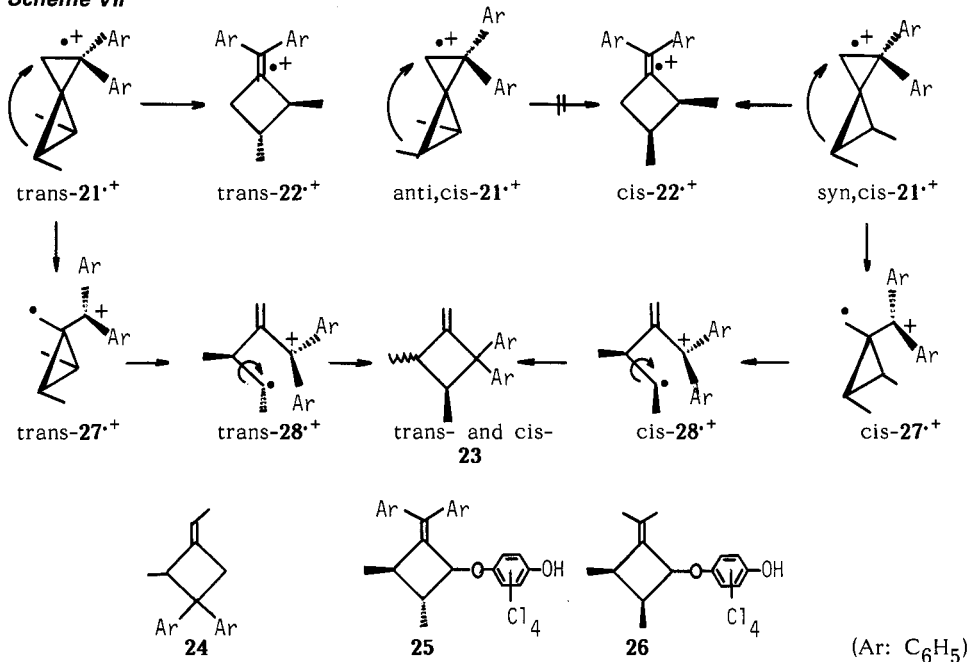
Scheme VI



Because **14** and **15** failed to interconvert under these sensitized conditions, the observed solvent effects on the product ratio **14/15** can not be explained by a single mechanism through a common intermediate such as 17^+ or 18^+ , but rather suggest that two independent processes are operative for the formation of **14** and **15**. Assuming that the separation of photogenerated ion radical pairs is facilitated by an increase in solvent polarity, the fact that the **14/15** ratio increases with an increase in solvent polarity would suggest that **14** and **15** are generated before and after the separation of the ion radical pairs, respectively. On the basis of this assumption, a plausible mechanism is shown in Scheme VI. Solvents of higher dielectric constant facilitate the separation of the contact ion radical pairs $[13^+A^-]$ to solvent separated ion radical pairs (SSIP) or free ion radicals (FI), in which the C_1-C_2 bond of **13** is weakened, but not cleaved completely. The direct C_4 to C_2 bond migration then occurs so as to give 14^+ which is thermodynamically more stable than 15^+ . Because ion radical pairs $[13^+CA^-]$ are more polar than $[13^+TNF^-]$ and $[13^+AQ^-]$ in which the spin and charge localize over two or three benzene rings, the separation of $[13^+A^-]$ would be most facilitated for the combination of 13^+ with CA^- in which the spin and charge localize only in one benzene ring. The exclusive formation of **14** in acetonitrile under the CA-sensitized conditions can be accounted for by this mechanism. By contrast, $[13^+A^-]$ subsequently collapse to $[17^+A^-]$ and $[18^+A^-]$ within ion radical pairs, keeping a tight ion pair interaction which is important for stabilization of ion radical pairs in the less polar solvents. Because the bulkier diarylmethylene group of 18^+ is orthogonal to the C_2-C_3 bond, the formation of the thermodynamically less stable 15^+ requires only the rotation of the C_4 methylene group, but not of the diarylmethylene group. Evidence that oxygenation products such as **19** and **20** are formed only under conditions where **15** is formed in moderate yields support 18^+ as the direct precursor of 15^+ . This sequential process resembles the cation radical degenerate methylenecyclopropane rearrangement of d_2-1 . The yield of **15** thus increases as solvent polarity decreases. If these

mechanisms are operative, the rearrangement to 1-(diarylmethylene)cyclobutanes would occur with high stereoselectivity, whereas stereorandomization would be expected for the formation of 2,2-diaryl-1-methylenecyclobutanes. In order to determine the stereochemistry of rearrangements, electron-transfer photoreactions of *trans*-, *anti,cis*- and *syn,cis*-1,1-diphenyl-4,5-dimethylspiropentanes (**21**) were investigated. Three isomers were prepared by the procedure reported (ref. 18). The reaction of the 2,2-diphenylcyclopropyl carbene with *trans*-2-butene gave *trans*-**21**, while the reaction with *cis*-2-butene gave a 8:1 mixture of *anti,cis*-**21** and *syn,cis*-**21**. *Anti,cis*-**21** and *syn,cis*-**21** were separated and the minor *syn,cis*-**21** was independently prepared from *cis*-2,3-dimethyl-1-diphenylmethylenecyclopropane.

Scheme VII

Table 3. CA- and DCA-sensitized photoreactions of *trans*-, *anti,cis*- and *syn,cis*-**21**

21	sens.	solvent	irrad. time (min) ^a	22		yields (%) 23		24	25	26	conv.
				<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>				
<i>trans</i>	DCA	CH ₃ CN	180	37	0	2	b	27	--	--	86
		CH ₂ Cl ₂	100	43	0	8	3	20	--	--	82
		C ₆ H ₆	100	19	0	5	3	15	--	--	55
	CA	CH ₃ CN	30	30	0	0	0	17	10	--	100
		C ₆ H ₆	30	0	0	8	2	7	17	--	100
<i>anti,cis</i>	DCA	CH ₃ CN	260	0	4	0	0	62	--	--	94
		CH ₂ Cl ₂	100	0	b	b	b	98	--	--	100
		C ₆ H ₆	200	0	0	b	b	77	--	--	77
<i>syn,cis</i>	CA	CH ₃ CN	15	0	66	0	0	0	--	--	100
		C ₆ H ₆	15	0	0	11	4	0	--	8	90

^aphotolyzed by using a 2kW xenon lamp; ^bless than 1%

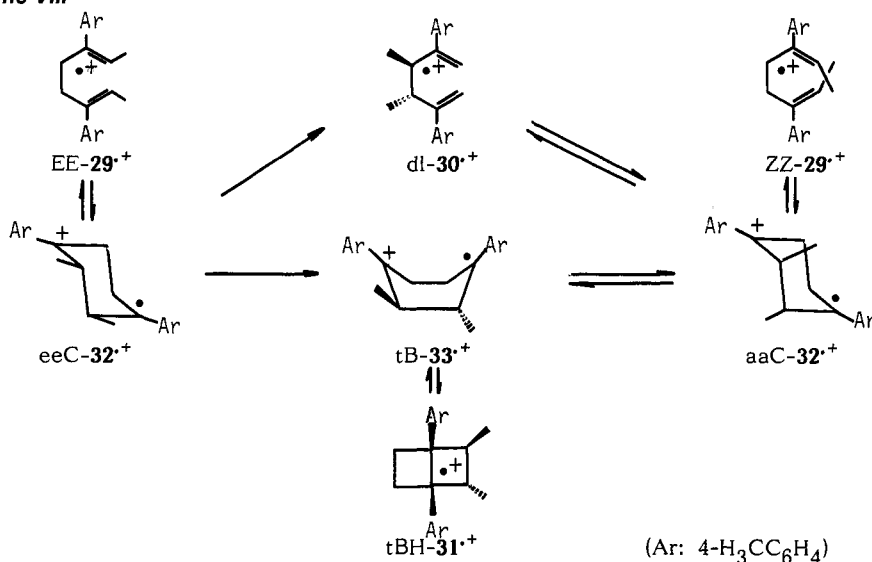
As shown in Table 3, *trans*-**22** and *cis*-**22** were stereospecifically formed from *trans*-**21** and *syn,cis*-**21**, respectively, as a major product in acetonitrile, while the formation of **23** from *trans*-**21** and *syn,cis*-**21** is nonstereospecific. Interestingly, *anti,cis*-**21** gave neither *trans*-**22** nor *cis*-**22**, but exclusively gave **24**, which was also formed from *trans*-**21**. The stereospecific formations of *trans*-**22** and *cis*-**22** can be well accounted for by the concerted [$\sigma_{2a}+\sigma_{2s}$] pathway with retention at C₂ and retention at C₄ (ref. 15) in *trans*-**21**⁺ and *syn,cis*-**21**⁺. The retention pathway at C₂ and C₅ in *trans*-**21**⁺ can also afford *trans*-**22**, but this process does not operate because of significant steric repulsion. In fact, *anti,cis*-**21**⁺ does not give *cis*-**22**, but instead the successive C₁-C₃ and C₄-C₅ bond cleavages (ref. 19) led to **24**. The formation of a mixture of *trans*-**23** and *cis*-**23** which is favored in less polar solvents can be explained by a sequential mechanism through **27**⁺ and **28**⁺.

These results provide an example of characteristic rearrangements of cation radicals in which the rearrangement sequence is changed by the degree of the donor-acceptor interaction in the photogenerated ion radical pairs.

3. CHAIR AND BOAT CYCLOHEXA-1,4-DIYL CATION RADICAL INTERMEDIATES IN THE CATION RADICAL COPE REARRANGEMENT

Thermochemical-kinetic arguments have denied a mechanistic connection between the 1,5-hexadiene and bicyclo[2.2.0]hexane systems in the Cope rearrangement (ref. 20). The energy of the cyclohexa-1,4-diyl generated from bicyclo[2.2.0]hexane (ref. 21) is about 5 kcal/mol higher than that of the six-membered cyclic transition state. Thus, the cyclohexa-1,4-diyl does not serve as an intermediate in the thermal unimolecular Cope rearrangement, though the process is still theoretically argued (ref. 22). In contrast, we previously demonstrated the chair cyclohexa-1,4-diyl cation radical intermediate in the cation radical Cope rearrangement of 3,6-diaryl-2,6-octadienes (ref. 23). We further investigated the cation radical Cope rearrangements in terms of substituent effects and found that the rearrangements of the tolyl derivatives are accompanied by the formation of the bicyclo[2.2.0]hexanes. We synthesized stereochemically pure 3,6-bis(4-methylphenyl)-2,6-octadienes (EE-, ZZ- and EZ-**29**), 2,5-bis(4-methylphenyl)-3,4-dimethyl-1,5-hexadienes (dl- and meso-**30**) and *trans*-1,4-bis(4-methylphenyl)-2,3-dimethylbicyclo[2.2.0]hexane (tBH-**31**). Upon irradiation of DCA with ZZ-**29** under Ar in dichloromethane, a photostationary mixture of ZZ-**29** (9%), dl-**30** (40%) and tBH-**31** (50%) was formed. Separate irradiation of DCA with EE-**29** or dl-**30** gave nearly the same photostationary mixture. The photoreaction of tBH-**31** slowly afforded a similar mixture. On the other hand, EZ-**29** gave a photostationary mixture of EZ-**29** (65%), meso-**30** (19%) and cBH-**31** (16%). Meso-**30** and cBH-**31** similarly gave nearly the same photostationary mixture in excellent yields. Molecular oxygen trapping of the intermediates gave the same stereochemical results as those reported previously (ref. 23). One characteristic feature in these electron-transfer photoreactions is that the bicyclo[2.2.0]hexane system is in equilibrium with the Cope system, which is unprecedented in the Cope rearrangement. By combining these results the mechanism shown in Scheme VIII can be proposed to account for the stereospecific rearrangements of EE-**29**, ZZ-**29**, dl-**30** and tBH-**31**.

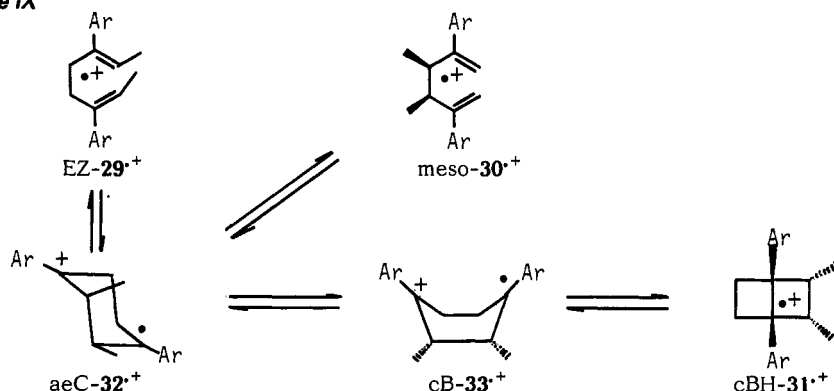
Scheme VIII



The initial cyclizations of ZZ-**29**⁺ and EE-**29**⁺ afford, respectively, aaC-**32**⁺ and eeC-**32**⁺, while dl-**30**⁺ could cyclize to either. However, eeC-**32**⁺ is probably less stable than aaC-**32**⁺ because of steric repulsion between the methyl and the tolyl group. Thus, dl-**30**⁺ predominantly cyclizes to aaC-**32**⁺, and eeC-**32**⁺ irreversibly rearranges to aaC-**32**⁺ through tB-**33**⁺ or undergoes the ring cleavage to give dl-**30**⁺. These processes and the ring cleavage of aaC-**32**⁺ result in the reversible Cope between ZZ-**29** and dl-**30** and the irreversible Cope from EE-**29** to ZZ-**29** and dl-**30**. On the other hand, because tB-**33**⁺ does not incorporate flagpole hydrogens, the energy difference between aaC-**32**⁺ and tB-**33**⁺ would be much smaller than that between chair and boat cyclohexanes. Thus, tB-**33**⁺ can survive as a long-lived intermediate comparable to aaC-**32**⁺. If the rate of the C₁-C₄ bond cleavage of tBH-**31**⁺ is comparable with that of reclosure of tB-**33**⁺ to tBH-**31**⁺, tB-**33**⁺ is no longer a masked intermediate in the Cope rearrangement pathway. tBH-**31**⁺ enters and leaves a Cope rearrangement channel through tB-**33**⁺. Similar arguments taking account of acC-**32**⁺ and cB-**33**⁺ can rationalize the formation of a photostationary mixture of EZ-**29**,

meso-**30** and cBH-**31** as shown in Scheme IX. Our experiments verified the intermediacy of not only the chair (ref. 24) but also of the boat cyclohexa-1,4-diyli cation radical intermediates in the Cope rearrangement pathway.

Scheme IX



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REFERENCES

1. J. A. Berson, in "Rearrangements in Ground and Excited States" P. de Mayo ed., Vol. 1, p.311, Academic Press, New York, 1980 and references cited.
2. E. F. Ullman, *J. Am. Chem. Soc.*, **81**, 5386-5392 (1959).
3. J. A. Berson, in "Diradicals", W. T. Borden ed, p.151, John Wiley & Sons, New York, 1982 and references cited.
4. J. C. Gilbert and J. R. Butler, *J. Am. Chem. Soc.*, **92**, 2168-2169 (1970).
5. A. S. Kende, Z. Goldschmidt, and R. F. Smith, *J. Am. Chem. Soc.*, **92**, 7606-7607 (1970).
6. Y. Takahashi, T. Miyashi, and T. Mukai, *J. Am. Chem. Soc.*, **105**, 6511-6513 (1983).
7. T. Miyashi, Y. Takahashi, T. Mukai, H. D. Roth, and M. L. M. Schilling, *J. Am. Chem. Soc.*, **107**, 1079-1080 (1985).
8. T. Miyashi, M. Kamata, and T. Mukai, *J. Am. Chem. Soc.*, **108**, 2755-2757 (1986) and **109**, 2780-2788 (1987).
9. P. Du and W. T. Borden, *J. Am. Chem. Soc.*, **109**, 5330-5336 (1987).
10. W. R. Dolbier, Jr., *Tetrahedron Lett.*, 393-396 (1968). W. R. Dolbier, Jr. and H. Alonso, *J. Am. Chem. Soc.*, **95**, 4421-4423 (1973).
11. R. Gleiter, R. Haider, J.-M. Conia, and J. -P. Barnier, *J. Chem. Soc., Chem. Commun.*, 130-132 (1979).
12. G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, *Helv. Chim. Acta*, **60**, 2213-2233 (1977).
13. P. Bruckman and M. Klessinger, *Chem. Ber.*, **107**, 1108-1125 (1974).
14. W. von E. Doering and J. C. Gilbert, *Tetrahedron, Suppl.* **7**, 397-414 (1966).
15. J. J. Gajewski, L. T. Burka, *J. Am. Chem. Soc.*, **94**, 8865-8875 (1972).
16. K. Ushida, T. Shida, and J. C. Walton, *J. Am. Chem. Soc.*, **108**, 2805-2807 (1986).
17. T. Miyashi, Y. Takahashi, H. Ohaku, K. Yokogawa, S. Morishima, and T. Mukai, *Tetrahedron Lett.*, **31**, 2411-2414 (1990).
18. W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754-2759 (1963).
19. J. J. Gajewski and L. T. Burka, *J. Am. Chem. Soc.*, **93**, 4952-4953 (1971).
20. J. J. Gajewski and N. D. Conrad, *J. Am. Chem. Soc.*, **100**, 6268-6269 and 6269-6270 (1978).
21. M. J. Goldstein and M. S. Benzon, *J. Am. Chem. Soc.*, **94**, 5119-5121 and 7147-7149 (1972).
22. M. J. S. Dewar and C. Jie, *J. Am. Chem. Soc.*, **109**, 5893-5904 (1987). K. Morokuma, W. T. Borden, and D. A. Hrovat, *J. Am. Chem. Soc.*, **110**, 4474-4475 (1988). D. A. Hrovat, W. T. Borden, R. L. Vance, N. G. Rondan, K. N. Houk, and K. Morokuma, *J. Am. Chem. Soc.*, **112**, 2018-2019 (1990).
23. T. Miyashi, A. Konno, and Y. Takahashi, *J. Am. Chem. Soc.*, **110**, 3676-3677 (1988). T. Miyashi, H. Ikeda, A. Konno, O. Okitsu, and Y. Takahashi, *Pure and Appl. Chem.*, **62**, 1531-1538 (1990).
24. Q-X. Guo, X-G. Qin, J. T. Wang, and F. Williams, *J. Am. Chem. Soc.*, **110**, 1974-1976 (1988). F. Williams, Q-X. Guo, D. C. Bebout, and B. K. Carpenter, *J. Am. Chem. Soc.*, **111**, 4133-4134 (1989).