

Mechanisms and structure-reactivity relationships in photosensitized reactions of some diarylcyclobutanes and quadricyclane by organic electron acceptors

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Abstract - Photosensitized ring-splitting reactions of some selected diarylcyclobutanes (1 - 5) and quadricyclane (6) by typical organic electron acceptors are described. It is shown that the triplex photosensitization involving interactions of the cyclobutanes with 1,4-dicyanonaphthalene-alkylbenzene exciplexes provides a better probe to explore relationships between reactivities and CT contributions than the exciplex photosensitization by direct interactions with the excited sensitizers. In cases of the diarylcyclobutanes, net efficiencies of the ring-splitting reactions increase with increasing CT contributions, though relative reactivities of 1 - 5 are mainly controlled by stereochemical effects on through-bond interactions between the two separate π electron systems. In the case of 6, on the other hand, the population of positive charge due to CT contributions is much less effective as a driving force of the photosensitized isomerization.

In acetonitrile, photosensitized reactions of 1, 3, and 6 proceed *via* ion-radical pairs without the dissociation into the free ion radicals, whereas the free cation radical is the reactive intermediate in the ring-splitting reaction of 5. Geminate recombination of ion radical pairs back to the ground-state molecules might depend on structures of the cyclobutanes.

INTRODUCTION

Splitting of the cyclobutane ring, which simply forms two π bonds, has received much interest in a variety of fields of chemistry, *e.g.*, as a typical prototype for theoretical predictions of chemical reaction courses (ref. 1), as a convenient probe for stereochemical aspects of reactions (ref. 2a-c), as an elegant tool for organic syntheses (ref. 2a,3), as an essential biological process in the photoreactivation of UV-induced damage of DNA (ref. 4), and as a model process for solar energy utilization (ref. 5). These versatile applications may be due to the apparent simplicity of the net reactions as well as due to remarkable susceptibilities of cyclobutanes to a variety of chemical activations. Steric and electronic properties of cyclobutanes are unique, since the cyclobutane rings are typical of small and rigid ring systems but are conformationally mobile to a small extent (unlike the cyclopropane rings (ref.6)) and since the molecular-orbital descriptions of the ring framework point small but significant π -bonding contributions (ref. 7). This means that chemical behaviours of cyclobutanes may be delicately perturbed by steric and electronic effects of substituents. In other words, ring-splitting reactions of cyclobutanes may provide an excellent probe to manifest steric and electronic factors operating in reaction courses as well as to explore the chemical and dynamic behaviours of reactive states and/or reactive intermediates involved.

In recent years, a novel type of photosensitization in the presence of electron acceptors has been applied to effect ring-cleavage reactions of various cyclobutanes (ref 8-14), in which exciplexes, ion-radical pairs, and free cation radicals are suggested to play essential roles as reactive intermediates depending on reaction conditions. Formation of these intermediates should consequently lead to the population of positive charge on cyclobutanes, which may be important for the cleavage of the cyclobutane rings. In exciplex photosensitization, reaction efficiencies of 1,2-diarylcyclobutanes increase with the increase of charge-transfer (CT) contributions (ref. 9a,10a), while CT contributions of exciplexes are suggested to play minor roles in the isomerization of quadricyclane to norbornadiene (11) (ref. 13,14). Therefore, a crucial question should arise as to why the cyclobutanes reveal different behaviors in the exciplex photosensitization. Chemical and physical decay channels of the exciplexes may depend on steric and electronic properties of the cyclobutanes. Another question is related with conflicting observations on photoelectron-transfer-induced reactions; 6 and diaryl-substituted cage compounds undergo chain ring-cleavage reactions *via* the free cation radicals (ref. 10b,11), while the rapid geminate recombination of ion-radical pairs occurs without the dissociation into free ion radicals in photosensitized reactions of similar reaction systems (ref. 9b,14b). Efficiencies of the dissociation of ion-radical pairs may depend on chemical

properties of cyclobutanes. These questions are certainly connected with major subjects in recent organic photochemistry involving exciplex formation and electron transfer. In this paper, I shall discuss mechanisms and structure-reactivity relationships in photosensitized reactions of some selected 1,2-diarylcyclobutanes (1 - 5) and quadricyclane (6) by aromatic nitriles and chloranil as typical electron acceptors (Fig. 1).

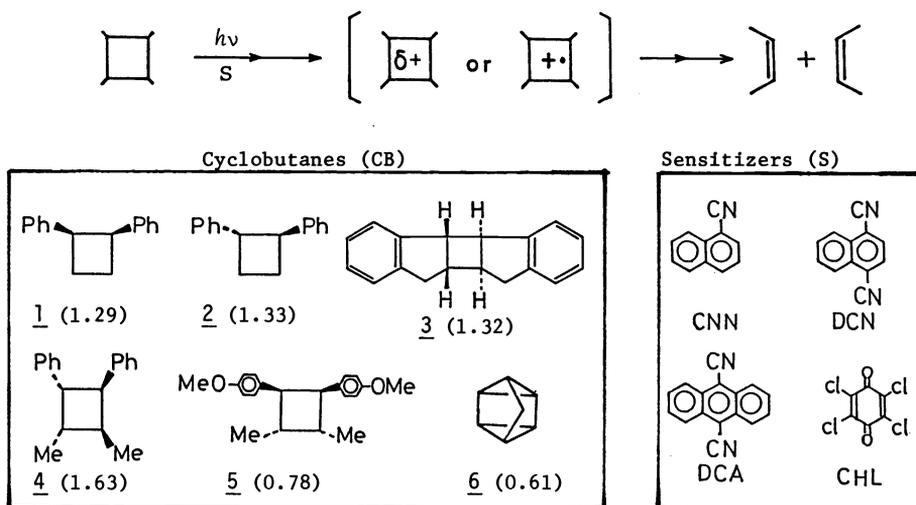
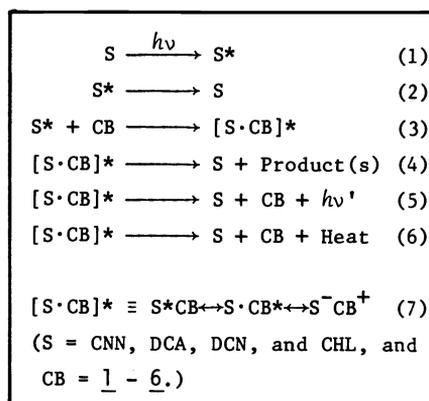


Fig. 1. The structures of the cyclobutanes and sensitizers. In parentheses are shown half-wave oxidation potentials of the cyclobutanes vs. Ag/AgNO_3 in acetonitrile.

EXCIPLEX PHOTOSENSITIZATION

The photosensitized reactions of 1 - 6 by the electron acceptors in nonpolar solvents mainly or exclusively afford the corresponding olefins, *i.e.*, styrene (7) from either 1 or 2, indene (9) from 3, anethole (10) from 5, and norbornadiene (11) from 6. In the case of 1, the trans isomer (2) and 1-phenyltetralin (8) are also formed. Interestingly, on the other hand, 4 remained virtually unchanged even upon extensive irradiation in the presence of any of the sensitizers. TABLE 1 lists the limiting quantum yields for the photosensitized olefin formation from 1, 3, and 6. Kinetic and spectroscopic studies strongly suggested that the photosensitized reactions proceed *via* either singlet exciplexes with the aromatic nitriles or triplet exciplexes with CHL (ref. 9a). Equations 1 - 6 show a simplified mechanism, where the spin state of S^* and $[S\cdot\text{CB}]^*$ is singlet for S = aromatic nitriles or triplet for S = CHL.

Electronic properties of exciplexes are approximately described by CT contributions and excitation-resonance (ER) contributions (Eq. 7), which can be qualitatively estimated by reduction potentials ($E^*(\text{red})$) and excitation energies (E^*) of S^* , respectively, for a given cyclobutane. The limiting quantum yields for the isomerization of 6 decrease with the increase of $E^*(\text{red})$, implying that CT stabilization of the exciplexes is unfavorable for the isomerization to 11. In contrast, reactivities of 1 and 3 in benzene reveal converse dependences on $E^*(\text{red})$, apparently showing that the population of positive charge on the cyclobutanes due to CT contributions is important in the chemical decay of the exciplexes. Moreover, the product distributions in the photosensitized reactions of 1 depends on the electron-accepting power of the sensitizers as well as on the spin state of the exciplexes as shown in TABLE 2.



The exciplex decay to the ground-state precursors, Eq. 6, includes a variety of channels, in which each rate constant may independently vary upon changing exciplex precursors. If this is the case, exciplex reactivities associated with CT nature can not be properly described by dependences of limiting quantum yields on redox potentials of exciplex precursors. In particular, intersystem crossing to triplet(s) is important since the rate constants remarkably depend on electronic properties and configurations of exciplexes (ref. 15,16). In this regard, it should be noted that the net efficiencies of the DCN-photosensitized reactions of 1 and 3 in *cyclohexane* are much lower than those in *benzene*, while a converse "solvent effect"

TABLE 1. Limiting quantum yields for photosensitized olefin formation.

S	E* ^b /eV	E*(red) ^c /V	$\phi_{ol}^{\infty a}$		
			<u>1</u>	<u>3</u>	<u>6</u>
CNN	3.75	1.42	0.083	0.25	0.71 ^d
DCA	2.88	1.76	0.25	0.77	0.33 ^d
DCN	3.45	2.40	0.90 (0.35)	1.3 (0.45)	0.041 (0.12) ^e

^aLimiting quantum yields in benzene unless otherwise noted.

^bExcitation energies of ¹S* (ref. 25b).

^cCalculated reductions potentials of ¹S* vs. Ag/AgNO₃ in acetonitrile.

^dReported values in heptane (ref. 14a).

^eIn cyclohexane.

TABLE 2. Photosensitized reactions of 1.

S	Solvents	Quantum Yields ^a		
		<u>7</u>	<u>2</u>	<u>8</u>
CNN	C ₆ H ₆	0.05	0.007	<10 ⁻⁴
DCA	C ₆ H ₆	0.11	0.01	0.007
DCN	C ₆ H ₁₂ ^b	0.35	0.052	0.054
	C ₆ H ₆	0.90	0.10	0.025
	C ₆ H ₅ Me	0.30	0.069	0.042
	p-C ₆ H ₄ Me ₂	0.30	0.043	0.026
	1,3,5-C ₆ H ₃ Me ₃	n.d.	0.093	0.005
CHL	C ₆ H ₆	1.0	0.18	<10 ⁻⁴

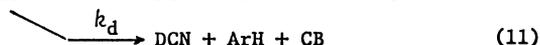
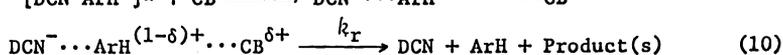
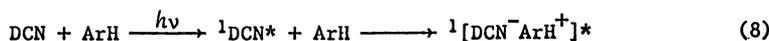
^aValues at [1] = 0.3 M; 7 = styrene and 8 = 1-phenyltetralin; n.d. = not determined.

^bC₆H₁₂ = cyclohexane.

is seen in the DCN-photosensitized isomerization of 6. Actually, the "solvent effects" mainly arise from the mechanistic origin. Although a DCN-CB exciplex is certainly the reactive intermediate in *cyclohexane*, excited-singlet DCN preferentially forms an exciplex with a solvent molecule in benzene which subsequently interacts with a CB molecule to effect the ring-cleavage reaction (*vide infra*). The DCN-1 and 3 exciplexes in cyclohexane appears to undergo efficient intersystem crossing, whereas this physical decay is minimized by a *termolecular* interaction involving a CB molecule and a DCN-benzene exciplex. Therefore, the very low quantum yields for the CNN-photosensitized reactions of 1 and 3 can not be definitely attributed to low CT contributions, unless roles of intersystem crossing in exciplex decays were firmly established.

TRIPLEX PHOTOSENSITIZATION

Excited-singlet DCN forms emissive exciplexes of typical CT nature with alkylbenzenes (ref. 16). The DCN-arene (ArH) exciplexes interact with 1 - 6 to cause the ring-cleavage reactions with one exception (4). For further discussions, the photosensitized reactions of 3, 5, and 6 will be mainly referred to. In the case of 3, the exciplex-quenching rate constants decrease with the decrease of ionization potential of ArH, whereas either 5 or 6 of low oxidation potential quenches the DCN-ArH exciplexes at or near a diffusion-controlled limit in most cases (TABLE 3). Figure 2(A) shows a linear correlation of logarithms of the quenching rate constants of 3 with the ionization potential of ArH (IP). These quenching behaviors can be easily understood according to the Caldwell's generalization on exciplex quenching (ref. 17), which predicts that an electron-donating quencher (CB in the present case) approaches the ArH⁺ side of ¹[DCN⁻ArH⁺]* as shown in Eq. 9. Such a termolecular interaction is stabilized by delocalization of the positive charge over ArH and CB. In cases of 5 and 6, the positive charge appears to be largely localized on the cyclobutanes interacting with the DCN-ArH exciplexes, i.e., $\delta \approx 1$ except for ArH=durene and pentamethylbenzene. Similarly, it can be expected that $\delta \approx 1$ for 1 and 3 interacting with the DCN-C₆H₆ exciplex because of the high ionization potential of benzene, while population densities of positive charge on 1 or 3 decrease with the decrease of IP.



Since the limiting quantum yields for the photosensitized olefin formation of the ternary reaction systems reveal dependences on IP very similar to those of k_q , both the exciplex quenching and the photosensitized reactions involve a common mechanism shown in Eqs. 8 - 11. We call this type of reaction *triplex photosensitization*, though we have no direct evidence yet for the intervention of excited *termolecular complexes having finite lifetimes*. In the triplex photosensitization, a CB molecule does not directly interact with excited DCN but with ArH⁺ of CT-stabilized DCN exciplex. It is therefore presumed that the population of positive charge on CB due to CT interactions should work as the driving force of the triplex photosensitization, while ER contributions are much less important. Since population den-

sities of positive charge on a CB can be controlled by the change of ArH with a fixed exciplex precursor being excited (DCN), roles of CT contributions in the ring-cleavage reactions can be properly assessed without either concomitant ER contributions or mechanistic confusions which may happen in exciplex photosensitization. This presumption is supported by a good correlation in Fig. 2(B) and by the independence of the quantum yields of 5 and 6 on IP. Since $\phi_{01}^{\infty}/(2 - \phi_{01}^{\infty}) = k_r/k_d$, Fig. 2(B) indicates that the reactivity of 3 increase with the increase of CT nature. Consequently, the limiting quantum yields of 1 and 3 with ArH = C₆H₆ and the quantum yields of 5 and 6 can be considered to represent the reactivities in the ring-cleavage reactions occurring by "pure" CT contributions. In conclusion, the population of positive charge due to CT interactions are effective for the ring-cleavage reactions of the diarylcyclobutanes but much less effective for the isomerization of 6.

TABLE 3. Emission maxima and lifetimes of DCN-ArH exciplexes, rate constants for quenching of exciplex emission by the cyclobutanes, and limiting quantum yields for the photosensitized olefin formation by DCN-ArH exciplexes.^a

ArH	IP/eV	$\lambda_{\max}^{\text{em}}$ /nm	τ /ns (lit ^c)	$k_q/10^9 \text{ M}^{-1}\text{s}^{-1}$			$\phi_{01}^{\infty \text{ b}}$				
				<u>3</u>	<u>5</u>	<u>6</u>	<u>3</u> A	<u>5</u> A	<u>5</u> B	<u>6</u> A	<u>6</u> B
(C ₆ H ₁₂) ^d		358	3.3 (3.4)	10	17	15	0.45		0.30		0.12
C ₆ H ₆	9.24	384	11	5.0	14	11	1.3	0.16	0.34	0.041	
C ₆ H ₅ Me	8.82	397	18	2.8	9.6	11	1.0	0.17	0.36	0.042	0.085
<i>m</i> -C ₆ H ₄ Me ₂	8.59	412	26 (19)	1.3	7.8	9.4	0.50	0.15	0.39	0.040	0.091
<i>o</i> -C ₆ H ₄ Me ₂	8.56	414	29 (20)	0.94	6.2		0.56	0.18	0.42		
<i>p</i> -C ₆ H ₄ Me ₂	8.44	419	29 (27)	0.82	10	11	0.66	0.17	0.41	0.037	0.098
1,3,5-C ₆ H ₃ Me ₃	8.41	417	39 (31)	0.28	7.1	6.6	0.63	0.17	0.41	0.037	0.093
1,2,4-C ₆ H ₃ Me ₃	8.27	433	(42)	0.31	5.8	7.0	0.29		0.38	0.030	0.078
1,2,4,5-C ₆ H ₂ Me ₄	8.04	429 ^e	(56)		5.2 ^e	6.3 ^e			0.36		0.090
C ₆ HMe ₅	7.92	436 ^e	(61)		1.6 ^e	4.8 ^e					0.073

^aObserved values in neat ArH unless otherwise noted.

^bLimiting quantum yields for the olefin formation in neat ArH (A) or in cyclohexane (B).

^cReported lifetimes in heptane (ref. 16).

^dIn cyclohexane in the absence of ArH.

^eIn cyclohexane.

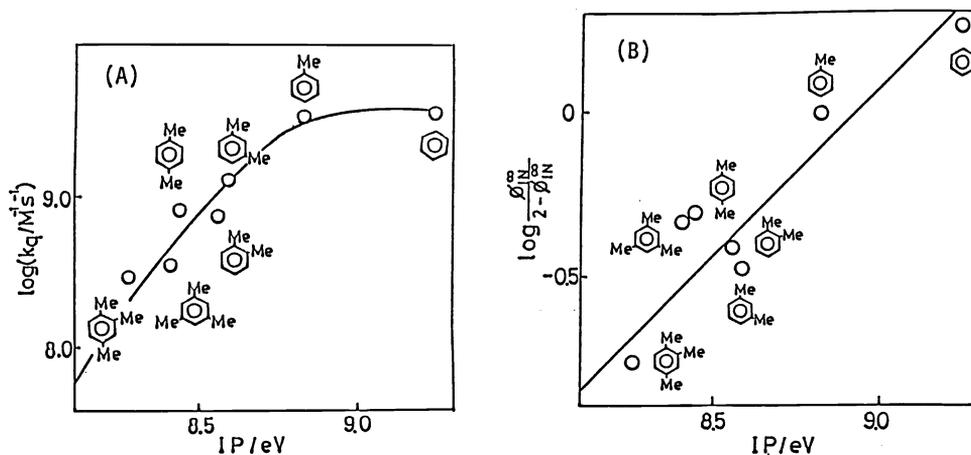
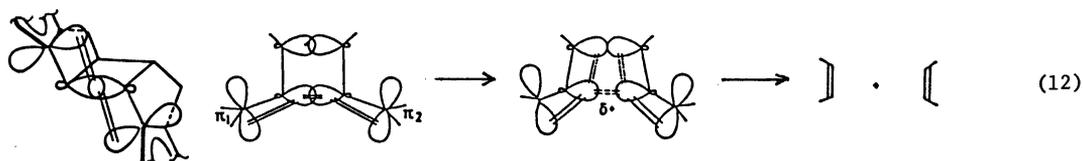


Fig. 2. Correlations of $\log k_q$ (A) and $\log [\phi_{01}^{\infty}/(2 - \phi_{01}^{\infty})]$ (B) vs. ionization potential of ArH (IP) in the photosensitized reaction of 3 by DCN-ArH exciplexes.

STRUCTURE-REACTIVITY RELATIONSHIPS ASSOCIATED WITH CHARGE-TRANSFER (CT) CONTRIBUTIONS

We previously demonstrated that through-bond interactions between vicinally substituted π or n electron systems are essential for the redox-photosensitized ring-cleavage reactions of relevant cyclobutanes which proceed *via* π complexes with the photogenerated cation radical of aromatic hydrocarbons, a typical photosensitization occurring by the population of positive charge (ref. 4f,8). For example **3** is very reactive because of the rigid head-to-head structure favorable for efficient through-bond interactions between the two separate π -electron systems, while no redox-photosensitized reaction occurs at all with the head-to-tail isomer for which through-bond interactions are configurationally disallowed. The positive charge populated on head-to-head diarylcyclobutanes is mainly localized on the π_1 -C1 σ -C2 σ - π_2 orbital array, since these basis-set orbitals constitute the HOMO of the cyclobutanes because of through-bond interactions (ref. 18). The cleavage of the cyclobutane ring can thus occur as the consequences of a specific weakening of the C1-C2 bond due to a decrease of electron density of this sigma bond as shown in Eq. 12.



The through-bond-interaction concept appears to be again valid for the interpretation of reactivities of **1** - **5** in the present photosensitized reactions. However, it should be noted that the redox-photosensitized reaction of **1** gives *only* **8** but not at all **7** and **2** (ref. 8c). The exciplex or triplex photosensitization should be regarded as the consequences of decays of *excited states or intermediates* unlike the redox-photosensitization. A crucial question is how the chemical pathways of exciplex and "triplex" intermediates are affected by either CT nature or through-bond interactions. In this regard it is of interest to note that direct photolysis of **1** exclusively gives **7** ($\phi = 0.33$) along with a small amount of **2** ($\phi = 0.014$) whereas the triplet-photosensitized reaction by acetone affords **7** and **2** in the limiting quantum yields of 0.13 and 0.04 respectively (ref. 19). In a thermal reaction, **7** and **2** are formed in a ratio of ca. 3:1 (ref. 19,20). These observations demonstrate that major chemical decay channels of the exciplex and triplex intermediates do not involve the internal conversion to form hot ground-state molecules nor the intersystem crossing to the triplet of **1**. Although **8** is formed from polar exciplexes and triplexes, this process is only minor. It is therefore reasonable to assume that the major chemistry of the exciplexes and triplexes occurs by crossing to a singlet reaction hypersurface involved in the direct photolysis of CB. Figure 3(A) shows a schematic reaction surface diagram for the singlet photochemistry of **1** - **5**, which is illustrated on the basis of the Michl's prediction concerning [2 + 2] cycloaddition and cycloreversion (ref. 21).

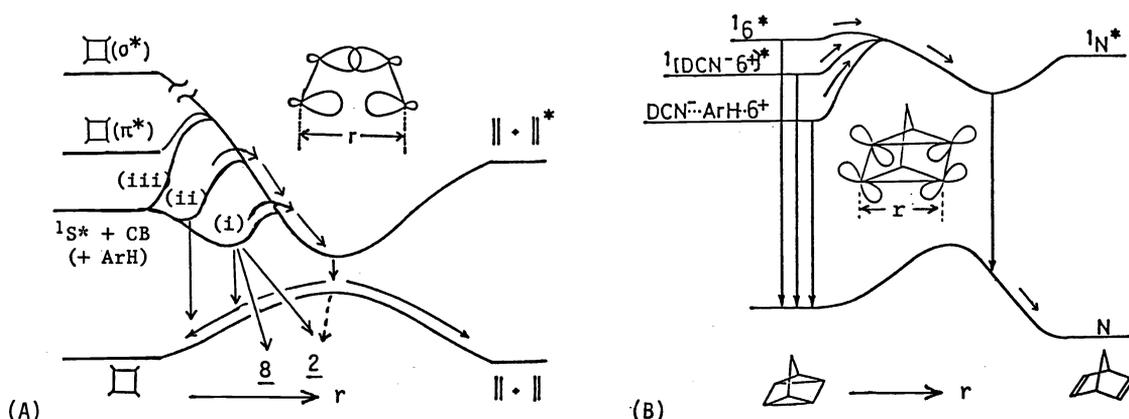
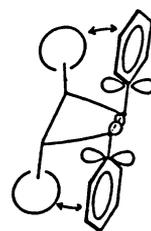


Fig. 3. (A) A schematic potential hypersurface diagram for the singlet photochemistry of the diarylcyclobutanes; (i) a highly polar state, (ii) a less polar state, and (iii) a possible reaction surface of **4**. (B) A schematic potential hypersurface diagram for the singlet photochemistry of **6**.

Perturbations by CT interactions should specifically elongate the C1-C2 bond depending on CT contributions because of through-bond interactions, thus realising closer location of exciplex and triplex states to the reaction hypersurface. Consequently, higher CT nature of the states leads to lower activation barriers for crossing to the surface. The decay of very polar exciplex or triplex states might accompany the isomerization of **1** to **2** and **8**, since the

C1-C2 bond is substantially elongated. Activation barriers for the crossing seem to be also affected by conformations that control through-bond interactions. The most reactive cyclobutane, 3, is conformationally frozen in an optimum structure for maximum π, σ -orbital overlaps, while 1 and 5 are conformationally more mobile. The other extreme cyclobutane is 4, for which through-bond interactions are conformationally disallowed because of steric repulsions between the methyl and phenyl groups as evidenced by X-ray crystallographic analyses of similar cyclobutanes (ref. 22). In this case, activation barriers should be very high because of little perturbation of the C1-C2 bond by CT interactions. On the other hand, if the exciplex and triplex states are largely stabilized by strong CT interactions, activation barriers for the crossing will become higher. This fits the case of 5. The lower quantum yields in neat ArH compared with those in cyclohexane in the triplex photosensitized reactions probably arise from greater stabilization of the triplex state by solvation with ArH which is more polar than cyclohexane as solvent.



In the case of 6, MINDO/3 calculations predict that the removal of an electron leads to elongation of the C2-C6 and C3-C5 bonds as well as to a remarkable decrease of activation barrier for the isomerization (ref. 23). It should be however pointed out that the positive charge populated on 6 is mostly delocalized over the whole cyclobutane ring. Such perturbations perhaps equally activate both the C2-C6 and C3-C5 bonds. If a concerted mechanism involving the two-bond cleavage would operate, the population of positive charge would be favorable for the isomerization of 6 to occur along a predicted reaction surface of the cation radical species. This is clearly not the case for the exciplex and triplex-photosensitized isomerization. Figure 3(B) shows a schematic reaction hypersurface diagram for the singlet photochemistry of 6 proposed by Turro (ref. 24). Since the exciplex and triplex states of high CT nature are largely stabilized, the CT-stabilized states should get rid of relatively high activation barriers for the crossing to the reaction hypersurface though ER contributions can be expected to participate, at least in part, in the exciplex photosensitization. In neat ArH, the triplex states are more stabilized by solvation than those in cyclohexane.

PHOTOSENSITIZATION BY WAY OF ION-RADICAL PAIR OR FREE CATION RADICAL

The photosensitized reactions of 1 in acetonitrile result in lower quantum yields compared with those in nonpolar solvents as well as in the lack of formation of 8 except for the case of CNN where converse solvent effects occur as shown in TABLE 4 (ref. 9b). Similar solvent effects can be seen in the photosensitized reaction of 3. All these reactions at [CB] = 0.1 M are not quenched at all by 1,3,5-trimethoxybenzene, a potential cation-radical quencher, at a low concentration (1×10^{-3} M) nor by 10%(v/v) methanol, an observation demonstrating no participation of long-lived cation radicals as the reactive species. If the ring cleavage of 3 would occur via free $3^{+\cdot}$ and/or $9^{+\cdot}$, these species could be effectively trapped by methanol to give methoxylated compounds (ref. 25). Moreover, the anion radical of DCA was not detected in a time domain of longer than 1 ns by laser-flash photolyses of the DCA-1-acetonitrile system, though the S-S absorption of DCA was rapidly quenched by 1.

An electron-transfer mechanism certainly operate in the photosensitized reactions, since the calculated free-energy changes (ΔG) associated with electron transfer are largely negative with one exception (CNN). It is therefore strongly suggested that the photoreactions in acetonitrile occur directly from ion-radical pairs without the dissociation into free ion radicals. The lower quantum yields probably arise from the rapid geminate recombination of the ion-radical pairs. This mechanism can also interpret the lack of formation of 8 in the DCA- and DCN-photosensitized reactions. Mattes and Farid suggested that the DCA-photosensitized dimerization of 1,1-diphenylethylene in acetonitrile gives tetraphenylcyclobutane via a 1,4-biradical generated by back back electron transfer from DCA $^{\cdot-}$ to the dimer cation radical of the olefin in a solvent cage, whereas a tetralin compound is formed from the free cat-

TABLE 4. Photosensitized reactions of 1 and 3 in acetonitrile.

S	$-\Delta G^a$		ϕ^{∞}			
	kJ mol $^{-1}$		<u>1</u>		<u>3</u>	
	<u>1</u>	<u>3</u>	<u>7</u>	<u>2</u>	<u>8</u>	<u>9</u>
CNN	13.4	13.7	0.53	0.029	0.01	0.40
DCA	46	47	0.11	0.005	<10 $^{-4}$	0.10
DCN	108	111	0.20	0.039	<10 $^{-4}$	0.45
CHL	115	118	0.24	0.04	<10 $^{-4}$	

^aCalculated free-energy changes for electron transfer from the cyclobutanes to the excited-singlet or triplet sensitizers.

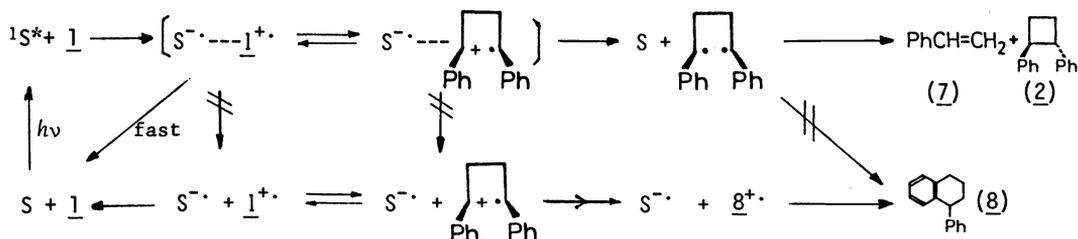
TABLE 5. Photosensitized reactions of 5 in acetonitrile

S ^a	$E^*(red)$	$-E(red)^b$	ϕ_{ol}^{∞}	
	V	V	deaerated	aerated
DCN	2.40	1.05	0.46	0.64
CNN	1.42	2.33	2.2	2.7
CAN	1.27	1.69	~ 7	~ 15
DC1A			~ 10	~ 15

^aCAN = 9-cyanoanthracene; DC1A = 9,10-dichloroanthracene.

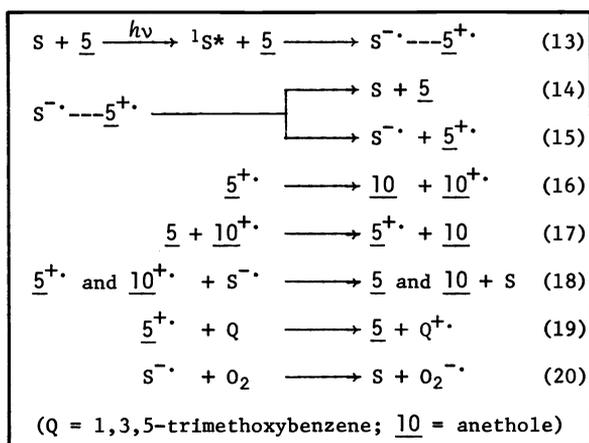
^bReduction potentials in the ground state vs. Ag/AgNO $_3$ in acetonitrile.

ion radical (ref. 26). It is therefore reasonable to assume that back electron transfer from $S^{\cdot-}$ to 1^+ and/or a ring-opened species in a solvent cage occurs to generate a 1,4-biradical, which then undergoes either the fragmentation to 7 or the ring closure to 2 and 1 but not the isomerization to 8. A similar geminate-recombination mechanism should operate in the case of 3 as well as in the triplet photosensitization by CHL though spin inversion is required to occur (ref. 12). On the other hand, the CNN-photosensitized reactions of 1 and 3 are not accommodated by this mechanism since the solvent effects are entirely different. In this case, the solvent effects can be interpreted in terms of a solvent-induced change of electronic properties of the CNN exciplexes from low CT nature in benzene to a very polar state in acetonitrile (ref. 27).

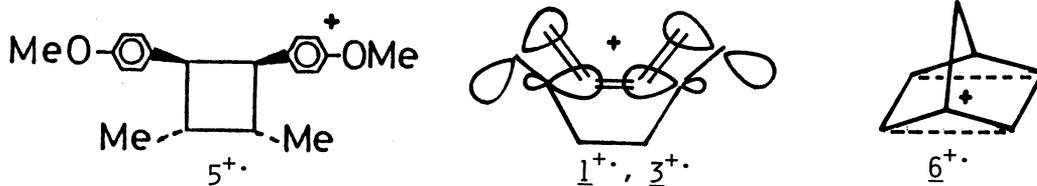


The photosensitized isomerization of 6 by aromatic nitriles in acetonitrile, which is inefficient, was also discussed in terms of the rapid geminate recombination (ref. 14b). In contrast, the free cation radical should be the reactive intermediate in the photo-

sensitized reaction of 5, since 1,3,5-trimethoxybenzene at 1×10^{-3} M completely quenched the reaction at $[5] = 0.1$ M. More strikingly, the quantum yields increase with the decrease of $E^*(red)$ of S, being much greater than two in the photosensitization by 9-cyanoanthracene (CAN) or 9,10-dichloroanthracene (DCLA) as shown in TABLE 5. These observations strongly suggest a chain-reaction mechanism involving free 5^+ and 10^+ as shown in Eqs. 13 - 20 (ref. 10b,11). The quantum yields appear to be mainly determined by efficiencies of the dissociation into the free cation radical of 5 which might depend on $E^*(red)$. The complete quenching of the reaction by Q at a low concentration indicates that no reaction significantly occurs before the dissociation of ion-radical pair and that the ring cleavage of free 5^+ should be much slower than 10^7 s $^{-1}$.



A question should emerge as to why the dissociation of ion-radical pairs is involved as an essential pathway only in the photosensitized reactions of 5 but not at all in those of the other cyclobutanes independently of S. Rate constants for the geminate recombination of ion-radical pairs that are primarily related with dissociation efficiencies reveal dependences on free-energy changes of the geminate recombination in some reaction systems as predicted by the Marcus theory (ref. 28). In the present reaction systems, however, dissociation capabilities of ion-radical pairs are not simply related with free-energy changes calculated on the basis of the redox-potentials of the precursors. As discussed in the previous section, considerable changes of structure might occur upon removal of an electron in the cases of 1 and 3 because of through-bond interactions and in the case of 6 because of the strained structure. Such perturbations would give rise to geometric changes of ion-radical pairs and solvation shell favorably for the geminate recombination. In the case of 5, the HOMO level of the methoxyphenyl group should be higher than that of the phenyl group, thus leading to less π, σ interactions compared with those of 1 and 3. In other words, the positive charge of 5^+ is mostly localized on the methoxyphenyl group to give relatively small perturbations of the cyclobutane ring.



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