Cycloreversion of 1,5-Diarylcyclobutene in a Photosensitized Reaction
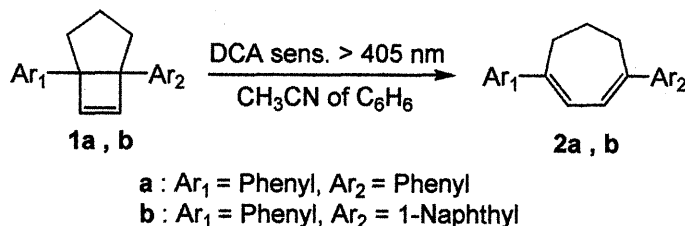
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Abstract

9,10-Dicyanoanthracene (DCA)-sensitized cycloreversion of 1,5-diphenylbicyclo-[3.2.0]hept-6-ene (**1a**) and 5-(1-naphthyl)-4-phenyl bicyclo[3.2.0] hept-6-ene (**1b**) to 1,4-diphenylcyclohepta-1,3-diene (**2a**) and 1-(1-naphthyl)-4-phenylcyclohepta-1,3-diene (**2b**), respectively, occurred with high quantum yield in acetonitrile or benzene at room temperature. The mechanism is discussed in terms of electron transfer from **1** to the excited singlet state of DCA. The cycloreversion of radical cation of **1** (**1**[+]) occurred rapidly even at 77K in pulse radiolysis and γ-radiolysis. It is suggested that cycloreversion of **1**[+] occurs in the mechanism involving cleavage of C_1-C_5 σ-bond and cyclic reaction of C_1-C_5 σ-orbitals and C_6-C_7 π-orbitals.

Introduction

Cycloreversions of small ring compounds via photochemical electron transfer reaction have received much attention from mechanistic and synthetic points of view.[1] Because of their low oxidation potentials, highly strained cyclobutene derivatives can be utilized as good electron donor molecules. The reaction of cyclobutene redical cations has been extensively investigated by mass spectroscopic technique[2] or frozen media.[3] However, little is known about the cycloreversion of aryl substituted cyclobutenes via photoinduced electron transfer reaction.[4] In order to develop the study of selective and efficient cycloreversion of aromatic cyclobutenes, in this paper, we attempted the cycloreversion of 1,5-Diarylbicyclo[3.2.0]hept-6-ene (**1a**; 1,5-Diphenyl- bicyclo[3.2.0]hept- 6-ene and **1b**; 5-(1-naphthyl)-1-phenylbicyclo[3.2.0]hept-6-ene[5] to 1,4-diarylcyclohepta- 1,3-diene (**2a**; 1,4-diphenylcyclohepta- 1,3-diene and **2b**; 4-(1-naphthyl)-1-phenylcyclohepta-1,3-diene) by photo-sensitization with 9,10-dicyanoanthracene (DCA) in acetonitrile or benzene solution (Scheme 1).

$$\text{Ar}_1 \overset{}{\underset{}{\bigsqcup}} \text{Ar}_2 \quad \xrightarrow[\text{CH}_3\text{CN of C}_6\text{H}_6]{\text{DCA sens. > 405 nm}} \quad \text{Ar}_1 \overset{}{\underset{}{\bigcirc}} \text{Ar}_2$$

1a , b   **2a , b**

a : Ar_1 = Phenyl, Ar_2 = Phenyl
b : Ar_1 = Phenyl, Ar_2 = 1-Naphthyl

Scheme 1

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In addition, we carried out the direct observation of redical cation of substrates by use of 77K matrix γ-irradiation and pulse radiolysis in dichloroethane (DCE).[6]

Experiment

Materials. Syntheses of **1** and **2** were performed according to the literature method and the products were purified by repeated recrystallizations from ethanol. 9,10-Dicyanoanthracene(DCA) was purified by repeated recrystallizations from benzene. Spectroscopic grade acetonitrile and benzene were used without further purification.

Instruments. Products analysis was carried out by HPLC on a Shimadzu LC10AD HPLC using a Wakosil AR as a column (eluent; hexane and ether). The fluorescence quenching experiments were performed for degassed acetonitrile or benzene solutions (3 ml) containing DCA (2×10^{-3} mol dm^{-3}) on a Hitachi F-4500 spectrometer. Oxidation potentials of **1a** and **1b** were determined by Yanagimoto V10-PG cyclic voltammeter vs. Ag/AgNO$_3$ in acetonitrile using tetramethylammonium tetrafluoroborate as the supporting electrolyte. The L-band linear accelerator at Osaka Univ. was used as the source of electron pulse. The energy was 28 MeV and the pulse width was selected as an 8 ns. The dose was 0.74 kGy per pulse and the beam diameter was ca. 4 mm. γ-Radiolysis in dichloromethane was carried out in Pyrex cells using a ^{60}Co source up to a dose of 0.49 kGy at room temperature.

Photoreactions and Determination of Quantum Yields. Photoirradiation was carried out with an Eikosha PIH-300 high-pressure Hg lamp under cooling with water using appropriate light filters and a "merry-go-round" turntable. An aqueous CuSO$_4$-NH$_3$ filter solution was used to isolate the >405-nm light.

Results and Discussion

Irradiation of a degassed acetonitrile solution containing DCA (5×10^{-4} mol dm^{-3}) and **1a** (1×10^{-2} mol dm^{-3}) with a 300 W high pressure Hg lamp through an aqueous CuSO$_4$-NH$_3$ filter solution (>405 nm) for 20 min gave **2a** in 27 % yield without formation of other products. The products were detected by HPLC. No products was detected by irradiation of DCA with **1a** or **2a** in degassed acetonitrile solution. The photosensitized reaction of **1a** with DCA in benzene also proceeded.

The formation of **2a** increased linearly with irradiation time up 5% conversion. Limiting quantum yields (Φ) were determined for the formation of **2a** by usual double-reciprocal plots of quantum yields (Φ^{-1}) vs. concentration of **1a**. Figure 1 shows linear plots for the formation of **2** from DCA-photosensitized reaction of **1** in acetonitrile and benzene solution, respectively.
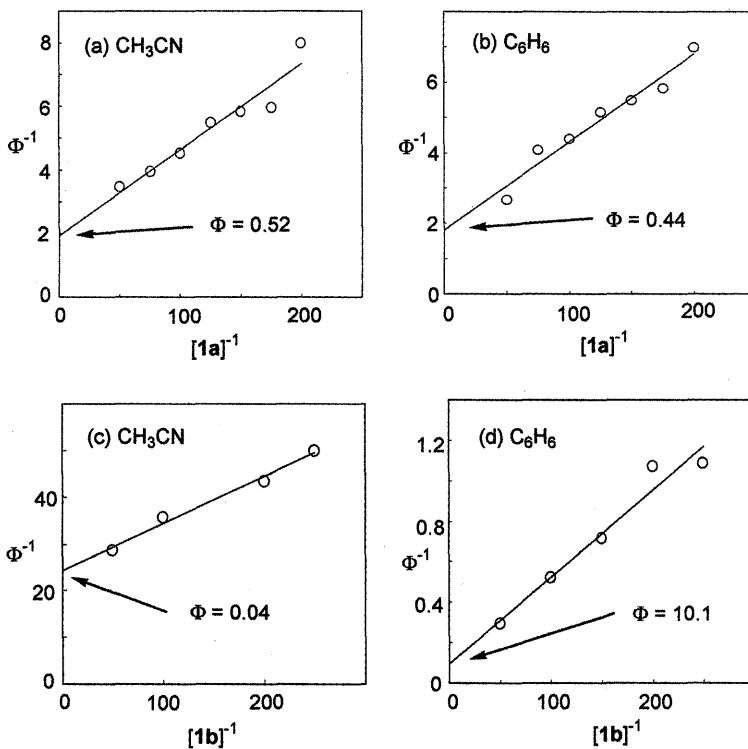
Fig. 1. Plots of Φ^{-1} vs. $[1]^{-1}$ in DCA-photosensitized reaction of **1** in CH$_3$CN and C$_6$H$_6$

From these intercept, in the case of **1a**, the values of Φ determined to be 0.52 and 0.44 in acetonitrile and benzene, respectively. Table 1 lists the intercept-to-slope ratios (I/S) of the plots together with the Φ for the formation of **2**.

Table 1. Limiting Quantum Yields (ϕ) for the Formation of **2**, Fluorescence Quenching Rate Constant (k_q) and Oxidation Potential.

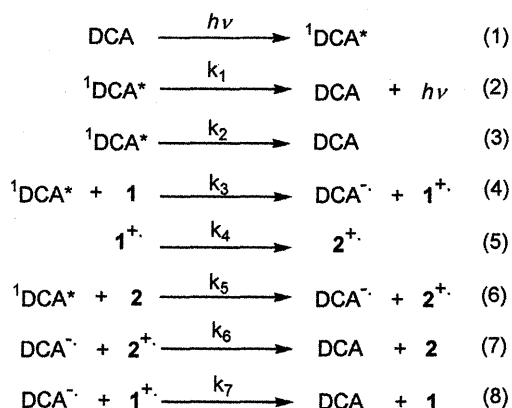| Comp.	Solv.	K_{sv} /dm^{3}mol^{-1}	k_q[a] /dm^{3}mol^{-1}s^{-1}	I/S[b]	Φ	$E^{ox}_{1/2}$ /V
1a	CH$_3$CN	166	1.1×10^{10}	71	0.52	1.61
1a	C$_6$H$_6$	106	8.5×10^9	103	0.44	
2a	CH$_3$CN	396	2.6×10^{10}			0.85
2a	C$_6$H$_6$	197	1.6×10^{10}			
1b	CH$_3$CN	329	2.2×10^{10}	240	0.04	1.02
1b	C$_6$H$_6$	162	1.3×10^{10}	23	10.1	
2b	CH$_3$CN	494	3.2×10^{10}			0.85
2b	C$_6$H$_6$	274	2.2×10^{10}			

[a] Calculation using τ_F = 15.3 ns (in CH$_3$CN) and 12.4 ns (in C$_6$H$_6$) for DCA.
[b] The intercept(I) and the intercept-to-slope ratio (I/S) of the plots for the formation of **2** in figure 1. [c] Half-wave oxidation potential vs. Ag/AgNO$_3$ in CH$_3$CN.

The fluorescence of DCA was effectively quenched by the **1** and **2** in degassed acetonitrile and benzene. The rate constants, k_q for the fluorescence quenching are shown in Table 1. The values of k_q were calculated from the slope of Stern-Volmer plots. They showed nearly diffusion controlled rates. No exciplex emission was observed in either solvent.

The oxidation potentials are also shown in Table 1. From these data, the free energy changes(ΔG) for a one-electron-transfer from the electron donating compoupnds to the excited singlet state DCA (^{1}DCA*) were estimated by use of the Rehm-Weller equation.[7] Negative ΔG values were obtained in all cases (-2.9 kcal mol^{-1} for **1a** and -16.6 kcal mol^{-1} for **1b**).

It is shown that the fluorescence of DCA is quenched by the **1** almost at a diffusion controlled rate and a one-electron-transfer from **1** to ^{1}DCA* in acetonitrile is estimated to be exothermic. These results strongly suggest that, in the DCA-sensitized photoreactions of **1**, the cycloreversion of **1** is suggested to proceed via the cation radical of **1** formed by the complete electron transfer from **1** to ^{1}DCA* rather than via exciplex formation. Moreover, the intercept-to-slope ratio (I/S) obtained from quantum yield measurements shows reasonable agreement with Ksv values for the fluorescence quenching (Scheme 2).

$$DCA \xrightarrow{\ h\nu\ } {}^{1}DCA^{*} \qquad (1)$$

$${}^{1}DCA^{*} \xrightarrow{\ k_1\ } DCA + h\nu \qquad (2)$$

$${}^{1}DCA^{*} \xrightarrow{\ k_2\ } DCA \qquad (3)$$

$${}^{1}DCA^{*} + 1 \xrightarrow{\ k_3\ } DCA^{-\cdot} + 1^{+\cdot} \qquad (4)$$

$$1^{+\cdot} \xrightarrow{\ k_4\ } 2^{+\cdot} \qquad (5)$$

$${}^{1}DCA^{*} + 2 \xrightarrow{\ k_5\ } DCA^{-\cdot} + 2^{+\cdot} \qquad (6)$$

$$DCA^{-\cdot} + 2^{+\cdot} \xrightarrow{\ k_6\ } DCA + 2 \qquad (7)$$

$$DCA^{-\cdot} + 1^{+\cdot} \xrightarrow{\ k_7\ } DCA + 1 \qquad (8)$$

Scheme 2

In order to clear the reactive intermediates of cycloreversion of **1** to **2**, the transient absorption spectra were measured at room temperature and 77K in dichloroethane(DCE) and buthyl chloride, respectively. In these halogenated solvents, it is well-known that radical cations of the solute molecule which possesses a lower ionization potential than that of the solvent used are mainly produced by the irradiation.[8] The pulse radiolysis of **1a** in DCE was carried out under argon at room temperature (Fig. 2).
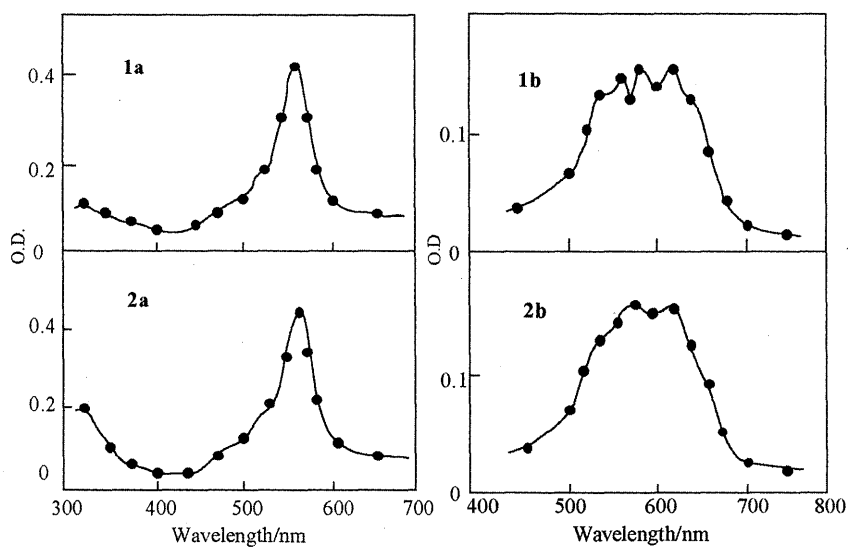

Fig. 2. Transient absorption spectra recorded immediately after an electron pulse in the pulse radiolysis of an argon-saturated DCE solution of **1a**, **2a**, **1b**, and **2b** (5×10^{-3} mol dm^{-3}) at room temperature.

The spectral changes were observed when the γ-radiolysis of **1** was carried out in a buthyl chloride matrix (1.0 x 10^{-2} mol dm^{-3}) at 77K. These results suggest that the spectral changes in the pulse radiolysis and γ-radiolysis are caused by a successive convesion: radical cation **1** to radical cation **2**. In the cases of **1a** and **2a**, a sharp absorption band were obtained at 560 nm in both case. This band was assigned to a radical cation of **2a** on the results obtained by 77K matrix γ-irradiation. We have not been successful for monitor directly the absorption of **1$^{+\cdot}$** . From these results, we assume the following mechanism (Scheme 3).

a ; λ_{max} = 560 nm

b ; λ_{max} = 560-650 nm
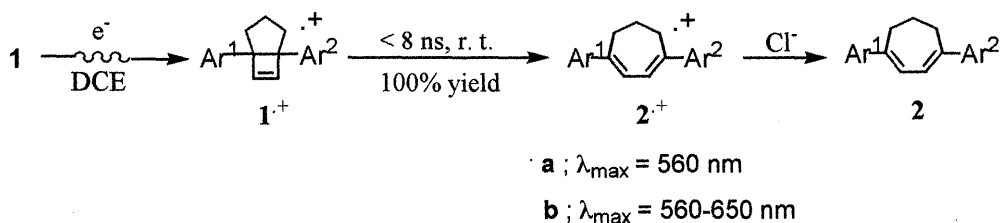
Scheme 3

The activation energy for the disrotatory cycloreversion of **1$^{+\cdot}$** to**2$^{+\cdot}$** roughly estimated to be less than 7-13 kcal mol^{-1} if the cycloreversion of 3-phenylcyclobutene radical cation in the gas phase is taken into account, which is significantly lower than that estimated for the cycloreversion of 1,2-diphenylcyclobutene.

In conclusion, the cycloreversion of **1** was occurred via cation radical intermediate (Scheme 4).

1a; $E^{ox}_{1/2}$=1.68 V

1b; $E^{ox}_{1/2}$=1.02 V
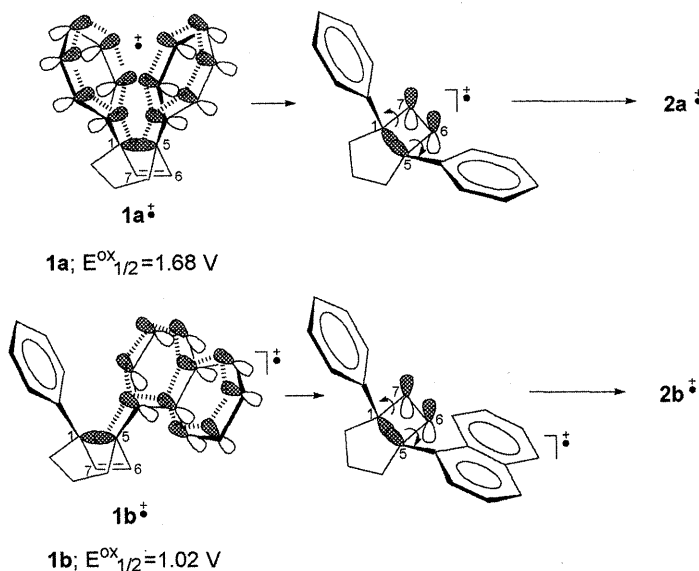
Scheme 4

The cycloreversion of **1** involve C_6-C_7 π-orbitals and C_1-C_5 σ-orbitals of the cyclobutene rings. The positive charge is distributed mainly or localized an π-orbitals of aryl-substituents because of the lower oxidation potential of aryl-substituents. However, the positive charge must develop in the cyclobutene ring enough to decrease C_1-C_5 σ-bond strength through the interaction between π-orbitals of aryl-substituents and C_1-C_5 σ-orbitals for the occurrence of the fast and quantitative cycloreversion. Because of lower ionization potential of naphthalene (IP = 8.12 eV) than that of benzene (IP = 9.23 eV), the positive charge is more localized in the naphthyl group of **1b**$^{+\cdot}$ than in the phenyl group in **1a**$^{+\cdot}$. This would lead to less efficient π-σ interaction between π-orbitals of naphthl group and C_1-C_5 σ-orbitals and to less decrease of the C_1-C_5 bond strength of **1b**$^{+\cdot}$ than that of **1a**$^{+\cdot}$. Cleavage of C_1-C_5 σ-bond of **1**$^{+\cdot}$ is followed by electrocyclic reaction of C_1-C_5 σ-orbitals and C_6-C_7 π-orbitals in a disrotatory manner giving **2**$^{+\cdot}$. The detailed studies for the whole mechanism and efficiency for the radical cation of these system are in progress and will be described elsewhere in near future.

References and Notes

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5 Compounds **1** and **2** were synthesized by litereture's method; P. Courtot, *Ann. Chim.,* **8**, 197 (1963); K. Nakabayashi, Y. Tahara, M. Yasuda, K. Shima, and S. Takamuku, *Bull. Chem. Soc. Jpn.,* **66**, 698 (1993); K. Nakabayashi, J. Arimura, M. Yasuda, K. Shima, and S. Takamuku, *Bull. Chem. Soc. Jpn.,* **69**, 1313 (1996).

6 Buthyl chloride was used as solvent. The sample solutions were irradiated at 77K with γ-rays from a 370 TBq ^{60}Co source. The transient absorption spectra were measured at 77K and also during annealing by a multichannel photodetector.

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