Cycloreversion of Aryl-Substituted Cyclobutene by Direct Photolysis and Pulse Radiolysis

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The cycloreversion of 1,5-diphenylbicyclo[3.2.0]hept-6-ene (**1**) to 1,4-diphenyl-1,3-cycloheptadiene (**2**) has been studied by direct photolysis and radiolysis. The γ-radiolysis of **1** in benzene gave **2** quantitatively up to a stationary state where the ratio of **1** to **2** is 0 : 100. However, no isomerization of **2** to **1** occurred. The triplet state of **2** ($\lambda_{\max}$=380—385 nm; τ=2.7—2.8µs) was formed by pulse radiolysis of **1** in benzene. It has been found that cycloreversion proceeds by an adiabatic mechanism via the triplet state. On the other hand, the quantum yield for the formation of **2** by the irradiation of 254 nm light to **1** was determined to be 0.64 in hexane. The fluorescence spectra of **1** and **2** also indicated that diabatic cycloreversion occurred. The singlet and triplet energy values of **1**, as well as those of **2**, were estimated to be 102, 78, 75, and 40 kcal mol^{-1}, respectively. The energy difference between the ground states of **1** and **2** was determined to be 20 kcal mol^{-1} from DSC measurements.

The cycloreversion of cyclobutenes has received much attention as a fundamental organic reaction. Therefore, the cycloreversion process has been extensively investigated by pyrolysis,[1] direct photolysis by far UV irradiation or laser-light irradiation,[2] and photoreaction involving an electron donor–acceptor system.[3] However, little is known about the cycloreversion of cyclobutenes via the triplet state, since they have a triplet energy that is too high to be sensitized by such typical triplet sensitizers as benzophenone. γ-Radiolysis and pulse radiolysis techniques applied to benzene solutions can efficiently provide the triplet state of benzene (E_T=84.3 kcal mol^{-1}),[4] which can be used as a sensitizer to generate the excited triplet state of substrates having a high triplet energy.[5] As a part of our investigation concerning the excited triplet state by the radiolysis technique, we have found that a triplet sensitized cycloreversion of 1,5-diphenylbicyclo[3.2.0]hept-6-ene (**1**) to 1,4-diphenyl-1,3-cycloheptadiene (**2**) proceeds through an adiabatic mechanism.[6] In order to elucidate more details concerning the mechanism for the cycloreversion of **1** to **2**, we investigated the cycloreversion by the spectroscopic studies and measurements of the quantum yields under benzene-triplet sensitization as well as direct photolysis (Chart 1).

Experimental

Instruments. UV absorption spectra were recorded in hexane solutions using a Hitachi 150-20 spectrometer. Product analysis was carried out by HPLC on a Waters M-600 HPLC using a Wakosil AR as a column (eluent; hexane and ether). The emission spectra were measured at 77 K in a deaerated EPA (ether : isopentane : ethanol =5 : 5 : 2) solution on a Shimadzu RF-501 spectrophotometer. For phosphorescence measurements, phosphorescence accessories were equipped. Measurements involving differential scanning calorimetry (DSC) were performed using a Seiko Electric DSC-200/SSC5000 with a scanning rate at 2—5°C min^{-1} at the laboratory of Research Institute for Polymers and Textiles.

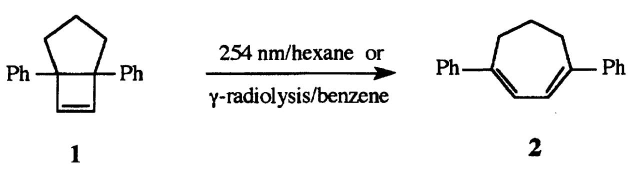

Chart 1.

Materials. Syntheses of **1** and **2** were performed according to a method described in the literature.[7] The products were purified by repeated recrystallizations from ethanol. *r*-1,*t*-2,*t*-3,*c*-4-Tetraphenylcyclobutane (TPCB) was prepared by the photodimerization of *trans*-stilbene in benzene.[8] TPCB was purified by column chromatography on silica gel using a mixture of benzene and cyclohexane as an eluent. The structures of these compounds, **1**, **2** and TPCB were satisfactorily confirmed based on the spectral data. Commercially available 1,4-diphenyl-1,3-butadiene (**3**), benzophenone (BP) and azulene (Az) were purified by recrystallization from ethanol or sublimation. Spectroscopic-grade benzene and hexane were used without further purification.

Photoreactions and Determination of Quantum Yields. The concentration of **1** was set in 1.0×10^{-2} mol dm^{-3}. Aliquot portions (4 cm^3) of reactant solutions and actinometer solutions were introduced into quartz tubes (8 mm, i.d.) and degassed by four freeze-pump-thaw cycles under a high vacuum. Irradiation was carried out with an Eikosha ELA 10 low-pressure Hg lamp using a merry-go-round turntable. The quantum yield was determined using a photocleavage reaction of TPCB to *trans*-stilbene as an actinometer.[9]

γ-Radiolysis. γ-Radiolysis in benzene was carried out in Pyrex cells (8 mm i.d.) using a ^{60}Co source up to a dose of 0.49 kGy at room temperature.

Pulse Radiolysis. In order to measure the T–T absorption spectra of compounds **1**—**3**, we used an L-band linear accelerator at Osaka university as the source of electron pulses. The energy was 28 MeV and the pulse width was selected to be 8 ns. The dose was 0.74 kGy per pulse and the beam diameter was ca. 4 mm. A 450 W xenon pulse lamp (OPG-450, Osram), a monochrometer (Nikon G-250), a photomultiplier tube (R-928), and a programmable digitizer (Tektronix 7912 AD) were used. The system was controlled by computer.

The absorption spectra of the triplet states of **1**—**3** were measured by nanosecond pulse radiolysis of the degassed benzene solution. Initially, benzene molecules are excited to form the excited singlet and triplet states and also excimers. These primary species transfer the energy to solute molecules. Although the formation of small amounts of the singlet excited state and charged species of the solute can not be excluded, the lifetimes of these species are generally short compared with those of triplet states. In the case of the addition of an excess amount of BP (2.0×10^{-2} mol dm^{-3}) to this system, a triplet BP is effectively formed, since the ϕ_{isc} of BP is very high ($\phi_{isc}=1$).[4] A triplet energy transfer from BP to a solute which was added in rather low concentration (1—4×10^{-3} mol dm^{-3}) was confirmed to proceed at a nearly diffusion-controlled rate by monitoring the T–T absorption band of BP ($\lambda_{max}=530$ nm).[10] We can thus selectively generate the triplet species of the solute in both the presence and absence of BP.

Results

Absorption, Fluorescence, and Phosphorescence Spectra. The UV absorption spectrum of **2** in hexane exhibited a broad absorption band over a wavelength region from 250 to 370 nm ($\lambda_{max}=316$ nm, $\varepsilon=2.0\times10^4$ mol^{-1} cm^{-1}). On the other hand, **1** has no absorption at longer wavelengths than 300 nm ($\lambda_{max}=262$ nm, $\varepsilon=6.0\times10^2$ mol^{-1} cm^{-1}).

Measurements of the fluorescence and phosphorescence spectra were carried out in a rigid solution of EPA at 77 K. The singlet energy of **2** was estimated to be 75 kcal mol^{-1} from the 0–0 band (380 nm) of the fluorescence spectrum of **2**. The singlet energy of **1** was estimated to be 102 kcal mol^{-1} from both the UV absorption spectrum and fluorescence spectrum. No fluorescence spectra of **2** by the excitation of **1** was observed. The triplet energy (E_T) of **1** was estimated to be 78 kcal mol^{-1} from the 0–0 band (367 nm) of the phosphorescence spectrum of **1**. Since no phosphorescence spectrum of **2** was observed, the E_T of **2** was estimated to be ca. 40 kcal mol^{-1} from the results that the transient absorption at 385 nm (see below) was quenched by azulene ($E_T=39.8$ kcal mol^{-1})[11] with a rate constant of 4.9×10^8 dm^3 mol^{-1} s^{-1}.

γ-Radiolysis in Benzene. The γ-radiolysis of a benzene solution can produce the excited triplet state of benzene with a relatively high energy ($E_T=84.3$ kcal mol^{-1}) in a good yield ($G=4.7$),[12] which transfers the energy to solute molecules.[5] The γ-radiolysis of **1** (4.1×10^{-3} mol dm^{-3}) in benzene gave **2** quantitatively up to a stationary state where the ratio of **1** to **2** is 0 : 100. No isomerization from **2** to **1** occurred (Fig. 1).[13]

Direct Photolysis in Hexane. Figure 2 shows the spectral changes resulting from the photolysis of **1** (5.1×10^{-4} mol dm^{-3}) under 254 nm light irradiation in hexane. The irradiation of **1** gave **2** quantitatively without the formation of other products. The formation of **2** increased linearly with the irradiation time up to 3% conversion. The quantum yield (ϕ) for the formation of **2** from **1** under direct irradiation at 254 nm light in hexane was determined to be 0.64 using TPCB as an actinometer.[9]

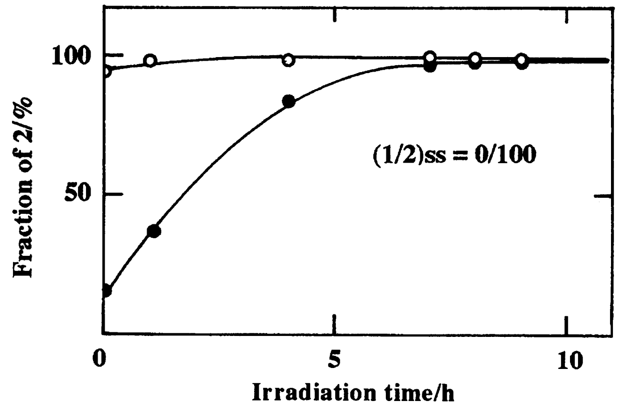

Fig. 1. γ-Radiolysis of **1** (●) and **2** (○) in benzene at room temperature; [**1**]=[**2**]=4.1×10^{-3} mol dm^{-3}.

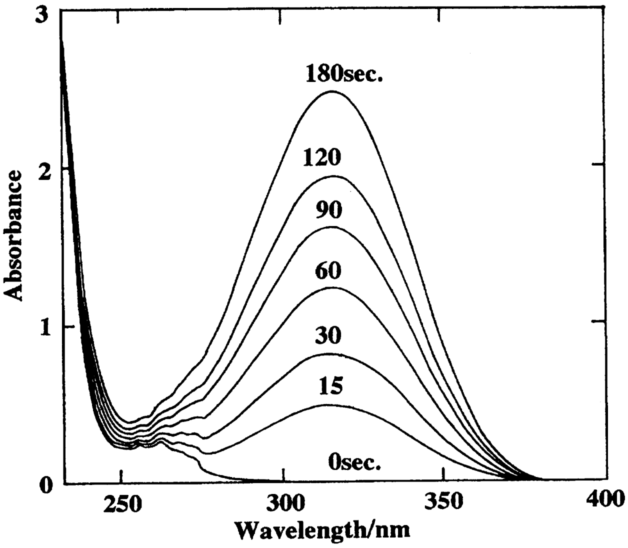

Fig. 2. UV absorption changes after 254-nm irradiation in hexane at room temperature; [**1**]=5.1×10^{-4} mol dm^{-3}.

T–T Absorption Spectra of 1—3 by Pulse Radiolysis in Benzene. For mechanistic analysis, the T–T absorption spectra were measured by nanosecond pulse radiolysis for a degassed benzene solution. It is well known that pulse radiolysis in benzene is an excellent method to produce the triplet state of the solute,[14] similarly to γ-radiolysis. The transient absorption spectra for **1**—**3** are shown in Fig. 3. The acyclic diene, 1,4-diphenyl-1,3-butadiene (**3**), was used as a criterion for assigning the other transient species (Chart 2).

In the case of **1**, absorption maxima were observed at

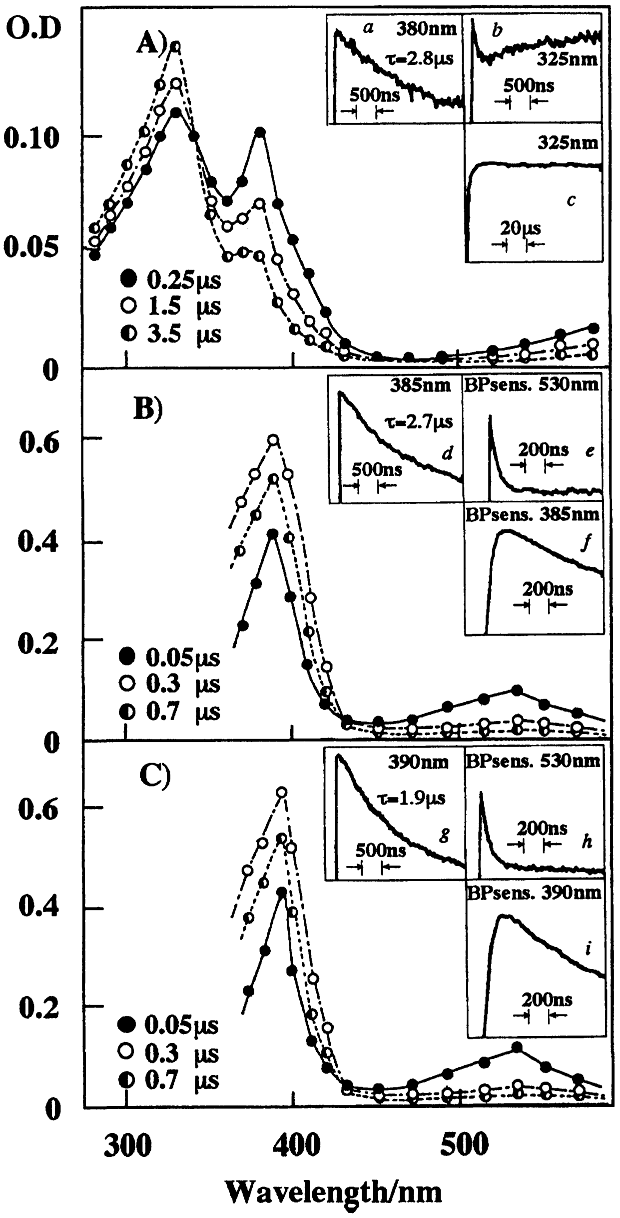

Fig. 3. Transient absorption spectra of **1**—**3** in the presence or absence of BP in benzene at room temperature. A, [**1**]$=4.3\times10^{-3}$ mol dm^{-3}, B, [**2**]$=4.5\times10^{-3}$ mol dm^{-3}, [BP]$=2.3\times10^{-2}$ mol dm^{-3}, C, [**3**]$=4.2\times10^{-3}$ mol dm^{-3}, [BP]$=2.0\times10^{-2}$ mol dm^{-3}; insets *d* and *g* are in the absence of BP.

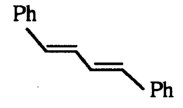

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Chart 2.

325 and 380 nm. The transient absorption at 380 nm increased immediately after irradiation, and then decayed at a rate of 3.6×10^5 s^{-1} (see inset *a* in Fig. 3A). A transient absorption band at 325 nm decayed rapidly, and then gradually increased (inset *b*). The rapidly decaying species could not be assigned because its lifetime is very short (<10 ns). The slow formation band (inset *c*) was assigned to **2** in the ground state, since the band agreed with the UV absorption spectra of **2** shown in Fig. 2, and was not affected by the addition of molecular oxygen. The T–T absorption of the triplet state of **1** was not observed in the transient absorption spectra of **1** in Fig. 3A.

In the case of **2**, the transient species was detected at $\lambda_{max}=385$ nm immediately after the pulse in the absence of BP (see inset *d* in Fig. 3B). This band decayed by first-order kinetics (3.8×10^5 s^{-1}). In order to confirm the formation of the triplet **2**, the pulse radiolysis of **2** was carried out in the presence of BP ($E_T=69$ kcal mol^{-1}).[4] The T–T absorption band of BP (λ_{max} 530 nm) decayed rapidly (inset *e*), and the simultaneous formation of a new absorption band due to **2** triplets was observed at 385 nm (inset *f*). The ε_{max} value of triplet **2** was estimated to be 3.0×10^5 dm^2 mol^{-1} on the basis of the ε_{max} value of triplet BP.[10]

In the case of **3**, the absorption maximum (λ_{max}) was observed at 390 nm. The lifetime is shorter than those of **1** and **2**, since the relaxation can occur by bond rotation at the excited triplet state. This band decayed by first-order kinetics (5.3×10^5 s^{-1}; see inset *g* in Fig. 3C). The pulse radiolysis of **3** in the presence of BP shows that the T–T absorption band of BP (λ_{max} 530 nm) decayed rapidly (inset *h*), and that the simultaneous formation of a new absorption band due to **3** triplets was observed at 390 nm (inset *i*).

Discussion

Cycloreversion Mechanism of 1 via the Triplet State. The spectral features of the transient species observed for **1**—**3** are summarized in Table 1. In the transient absorption spectra of **1** and **2**, a common intermediate ($\lambda_{max}=380$—385 nm, $\tau=2.7$—2.8 μs) was observed. The absorption band was assigned to a triplet state with a structure of **2** on the basis of the following observations: (i) The 380—385 nm band is very close to that of **3** ($\lambda_{max}=390$ nm, $\tau=1.9$ μs)[15] and its lifetime is rather long (μs order). (ii) The 380—385 nm band observed for the cases of **1** and **2** was quenched not only by oxygen ($E_T=22.5$ kcal mol^{-1};[5] $k_q=1.8\times10^9$

Table 1. Spectral Features of the Transient Species for **1**—**3** in Benzene

Compounds	**1**	**2**	**3**
λ_{max}/nm	380	385	390
τ/μs	2.8	2.7	1.9
k_{qO_2}/dm^3 mol^{-1} s^{-1} [a]	1.8×10^9	1.7×10^9	2.0×10^9
k_{qAz}/dm^3 mol^{-1} s^{-1} [b]	5.8×10^8	4.9×10^8	9.5×10^8
Assignment	^{3}**2***	^{3}**2***	^{3}**3***

a) The rate constant for the quenching by molecular oxygen. b) The rate constant for the quenching by azulene.

$dm^3\ mol^{-1}\ s^{-1}$ for **1** and $1.7\times10^9\ dm^3\ mol^{-1}\ s^{-1}$ for **2**) but also by azulene (E_T=39.8 kcal mol^{-1};[11] $k_q=5.8\times10^8$ $dm^3\ mol^{-1}\ s^{-1}$ for **1** and $4.9\times10^8\ dm^3\ mol^{-1}\ s^{-1}$ for **2**). Since the quenching was not efficient when azulene was used, the available triplet energy of the transient species, that is, the energy gap between the T_1 and S_0 surfaces of **2**, was estimated to be around 40 kcal mol^{-1}.

As has been discussed,[6] the cycloreversion of **1** to **2** by γ-radiolysis in benzene was initiated by the formation of the excited triplet state of **1** ($^{3}\mathbf{1}^{*}$) by an energy transfer from the excited triplet state of benzene generated by γ-radiolysis. According to the above mentioned results, $^{3}\mathbf{1}^{*}$ isomerized to $^{3}\mathbf{2}^{*}$ with an adiabatic process along the triplet energy surface, as shown in Scheme 1. The participation of ionic species from **1** can be ruled out due to the fact that the formation of **2** was not affected by the addition of an electron scavenger, such as butyl chloride.

Schematic Potential Energy Surfaces between 1 and 2. The schematic potential energy surfaces between **1** and **2** are shown in Fig. 4. The energy difference between **1** and **2** in the ground state was determined to be 20 kcal mol^{-1} from the DSC thermogram at different rising rates of temperature (2—5°C min^{-1}). We assumed that the activation energy for the reaction path from **1** to **2** in the ground state surface was about 45 kcal mol^{-1} based on a comparison with other cycloreversion reactions.[16] From the quenching experiment, the E_T value of **2** was estimated to be ca. 40 kcal mol^{-1}. This E_T value is similar to the E_T value of **3** (42.3 kcal mol^{-1}) reported by Hug et al.[17] The triplet energies of **1** and **2** are, therefore, 78 and 40 kcal mol^{-1}, respectively. From a calculation using these E_T values and the strain energy difference, the conversion of $^{3}\mathbf{1}^{*}$ into $^{3}\mathbf{2}^{*}$ was found to be an exothermic process by ca. 58 kcal mol^{-1}. Since the ratio of **1** to **2** in the stationary state is 0 : 100, there is no energy minimum in the triplet surface where crossing to the S_0 surface is possible. It is thus suggested that $^{3}\mathbf{1}^{*}$ is readily converted into $^{3}\mathbf{2}^{*}$ by an adiabatic process along a downhill energy surface. Therefore, the participation of other intermediates, such as 1,4-biradical, would be ruled out.

On the other hand, the energy minimum lies in the singlet-state surface, since the quantum yield for the formation of **2** from **1** ($\phi_{1\rightarrow2}=0.64$) is less than unity and the photochemical cyclization from **2** to **1** can also take place. A jump from the excited state surface to the ground-state surface occurs at the minimum point, i.e. a diabatic process from $^{1}\mathbf{1}^{*}$ to the ground state of **1** or **2**. The fact that the fluorescence emission of **2** by direct excitation of **1** could not be observed, supports the above conclusion. Since the fluorescence and phosphorescence spectra of **1** can be observed, the presence of the same energy barriers exist for the isomerization of **1** to **2** via both S_1 and T_1 surfaces. Schematic energy surfaces for the cycloreversion of **1** to **2** are shown in Fig. 4 based on the above observation.

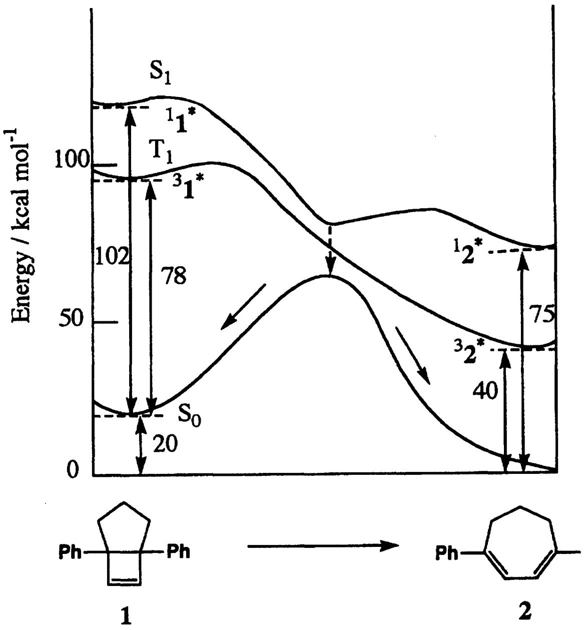
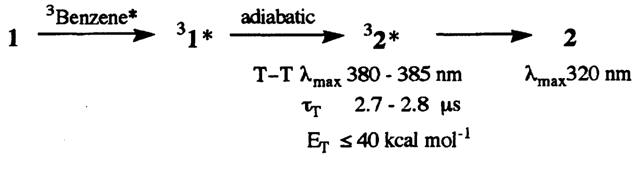


Fig. 4. Schematic potential energy surfaces between **1** and **2**.



Scheme 1.

Several examples of an adiabatic photochemical process via the triplet state have been reported.[18] Especially, an adiabatic cycloreversion has been found in the aromatic "Dewar" compounds.[19] For examples, the Dewar naphthalene[20] and Dewar anthracene[21] undergo a photochemical adiabatic cycloreversion on S_1 and T_1 surfaces. Also, an adiabatic cycloreversion of Dewar benzene[22] occurs via the triplet state by a quantum chain process, whereas no adiabatic cycloreversion occurs via the singlet excited state. Except for the Dewar systems, however, no adiabatic cycloreversion of cyclobutene derivatives on the triplet surface has been reported. Therefore, our present work may contribute to the excited-state chemistry of cyclobutenes in which a novel adiabatic cycloreversion can be observed via the triplet state.

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