Cycloreversion of 1-(1-Naphthyl)-5-phenylbicyclo[3.2.0]hept-6-ene to 1-(1-Naphthyl)-4-phenyl-1,3-cycloheptadiene by Triplet Sensitization and Direct Irradiation

Kenichi Nakabayashi,* Junichi Arimura,† Masahide Yasuda,† Kensuke Shima,† and Setsuo Takamuku††

Department of Chemistry, Faculty of Education, Miyazaki University, Gakuen-kibanadai, Miyazaki 889-21

†Department of Material Science, Faculty of Engineering, Miyazaki University, Gakuen-kibanadai, Miyazaki 889-21

††The Institute of Scientific and Industrial Research, Osaka University, 8-1, Mihogaoka, Ibaraki, Osaka 567

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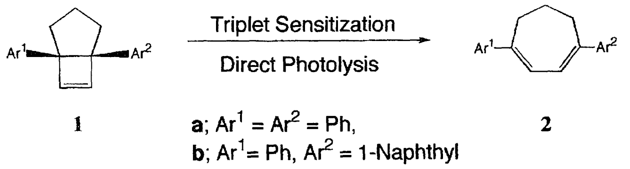
The cycloreversion of 1-(1-naphthyl)-5-phenylbicyclo[3.2.0]hept-6-ene (**1b**) to 1-(1-naphthyl)-4-phenyl-1,3-cycloheptadiene (**2b**) upon benzophenone (BP) sensitization and direct irradiation has been investigated. The triplet sensitization of **1b** in benzene gave **2b** quantitatively up to a stationary state where the quantum yield was 0.96. The triplet state of **2b** ($\lambda_{\max}=455$ nm, $\tau=4.6$ μs) was formed by the pulse radiolysis of **1b** in benzene. It has been found that cycloreversion proceeds by an adiabatic mechanism via a triplet state. The quantum yield for the formation of **2b** by the irradiation of **1b** at 313 nm was determined to be 0.17 in hexane. The fluorescence spectra of **1b** and **2b** indicated that diabatic cycloreversion occurred via a singlet state. The singlet and triplet energies of **1b**, as well as those of **2b**, were estimated to be 88, 60, 72, and 39 kcal mol^{-1}, respectively. The effect of a substitution of the naphthalene chromophore on bicyclo[3.2.0]hept-6-ene was estimated.

The photochemical cycloreversion of cyclobutenes has been extensively investigated by means of far-UV irradiation or laser-light irradiation,[1] and a photoreaction involving an electron donor–acceptor system.[2] We have been investigated in the cycloreversion of 1,5-diarylbicyclo[3.2.0]hept-6-ene (**1**) via excited singlet and triplet states as well as a photoinduced electron transfer reaction. Our previous studies using a pulse radiolysis technique demonstrated that the cycloreversion of 1,5-diphenylbicyclo[3.2.0]hept-6-ene (**1a**) to 1,4-diphenyl-1,3-cycloheptadiene (**2a**) in a triplet state occurs through an adiabatic mechanism (Scheme 1).[3,4] However, a typical triplet-sensitized reaction by benzophenone (BP) can not be applied to **1a**, since the triplet energy of **1a** ($E_T=78$ kcal mol^{-1}, 1 kcal = 4.18 kJ)[5] is higher than that of BP ($E_T=69$ kcal mol^{-1}).[5] In order to elucidate the cycloreversion of **1** in the triplet state, we report here on the BP-photosensitized cycloreversion of 1-(1-naphthyl)-5-phenylbicyclo[3.2.0]hept-6-ene (**1b**), which might have smaller E_T value than **1a**. Moreover, we carried out a direct photolysis of **1b** in a hexane solution in order to compare the reactivities of **1b** with those of **1a**.



Scheme 1.

Experimental

Instruments. The melting points were measured on a Yanaco melting-point apparatus. The ^{1}H NMR and ^{13}C NMR spectra were taken for $CDCl_3$ solutions on a Brucker AC-250P spectrometer. UV absorption spectra were recorded in hexane solutions using a Hitachi 150-20 spectrometer. HPLC analyses were performed on a Waters M-600 using a Wakosil AR as a column (eluent; $CH_3CN:H_2O=8:2$). The emission spectra were measured at 77 K in a deaerated EPA solution on a Hitachi F-4500 spectrophotometer equipped with phosphorescence accessories. A measurement involving a differential scanning calorimeter (DSC) was performed on a Seiko Electric DSC-200/SSC5000 at a scanning rate at 2—5 °C min^{-1}. T–T absorption spectra were measured using an L-band linear accelerator at Osaka University as the source of electron pulses. The energy was 28 MeV, the pulse width was selected to be 8 ns (single pulse), the dose was 0.7 kGy per pulse, and the diameter was approximately 0.4 cm. A transient-absorption measurement was carried out using a system comporising with the probe beam from a 450-W Xe-lamp, a monochromator, a PMT, and a transient digitizer.

The absorption spectra of the triplet states of **1b**—**3b** were measured by nanosecond pulse radiolysis of a degassed benzene solution. Initially, benzene molecules(B) are excited to form excited singlet and triplet states as well as excimers. These primary species transfer energy to a solute molecule (ArH). The formation of a small number of singlet-excited states (^{1}ArH*) and charged species of the solute cannot be excluded. However, it can be neglect, since the lifetimes of these species are generally short compared with those of the triplet states (^{3}ArH*). In order to distinguish the triplet species from other species, a triplet BP (^{3}BP*) is effectively formed by the addition of an excess amount of BP (20 mmol dm^{-3}) in this system ([BP]>[ArH]), since $\Phi_{\rm isc}$ of BP is very high ($\Phi_{\rm isc}=1$).[5] A triplet energy transfer from BP to a substrate, which was added at a rather low concentration (1—4 mmol dm^{-3}), was confirmed to proceed near to the diffusion-controlled rate for **2** by monitoring the T–T absorption band of BP ($\lambda_{\rm max}=530$ nm). By this technique, we could easily discriminate the triplet species of the solute from the other acitve species (Scheme 2).[6]

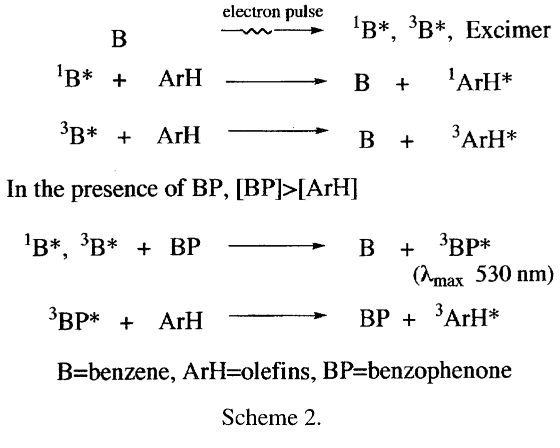
Materials. Commercially available BP and Azulene (AZ) were purified by recrystallization from ethanol or sublimation. Spectroscopic-grade benzene and hexane were used without further purification.

The preparation of **2b** was performed according to a modified method described in the literature,[7] as follows: Into an Et$_2$O solution (200 ml) of cycloheptan-1,4-dione (1.8 g)[7] with 1-naphtylbromide (6.8 g) was added *n*-BuLi/hexane solution (21 ml), which was then refluxed for 2 h. After the usual work-up, 1-(1-naphthyl)-8-oxabicyclo[3.2.0]heptan-1-ol (2.9 g) was obtained. 1-(1-naphthyl)-8-oxabicyclo[3.2.0]heptan-1-ol (2.9 g) was treated with *p*-toluenesulfonic acid (1.0 g) in benzene (250 ml) under reflux for 2 h to give a mixture of 1-(1-naphthyl)-3-cyclohepten-1-one and 1-(1-naphtyl)-4-cyclohepten-1-one (2.2 g). The reaction of the above-mentioned mixture (2.2 g) with a PhLi hexane solution (1.8 M, 16 ml) in Et$_2$O (100 ml) for 2 h gave a mixture of 4-(1-naphtyl)-1-phenyl-3-cyclohepten-1-ol and 4-(1-naphtyl)-1-phenyl-4-cyclohepten-1-ol (2.8 g). The above-mentioned mixture was heated in *p*-toluensulfonic acid at 135 °C for 5 min, immediately poured into ice-water and extracted with Et$_2$O after neutralization with a 10% NaOH aqueous solution to give **2b** (1.7 g).

1-(1-Naphthyl)-4-phenyl-1,3-cycloheptadiene (2b): Mp 99—100 °C (from EtOH); ^{1}H NMR $\delta=2.21$—2.31 (2H, m) 2.80 (2H, t, $J=5.8$ Hz), 2.92 (2H, t, $J=5.7$ Hz), 6.08 (1H, d, $J=3.64$ Hz), 6.27 (1H, d, $J=3.64$ Hz), 7.21—8.06 (12H, m); ^{13}C NMR $\delta=27.86$, 34.40, 37.38, 123.83, 125.00, 125.40, 125.63, 125.75, 125.98, 125.99, 126.45, 126.86, 127.05, 128.27, 128.35, 131.16, 133.85, 144.08, 144.47, 144.54, 145.15; UV (hexane) $\lambda_{\rm max}$ 304 nm (ε 25600). Calcd for C$_{23}$H$_{20}$: C, 93.24; H, 6.76%. Found; C, 93.03; H, 6.69%.

The preparation of **1b** was performed by the irradiation of a degassed Et$_2$O solution (100 ml) of **2b** (0.1 g) by a high-pressure mercury lamp (Eikosha PIH 300) for 20 min. After evaporation of the solvent, **2b** (0.08 g) was obtained.

1-(1-Naphtyl)-5-phenylbicyclo[3.2.0]hept-6-ene (1b): Mp 92—93 °C; ^{1}H NMR $\delta=1.73$—1.78 (1H, m), 2.08—2.32 (4H, m), 2.60—2.68 (1H, m), 6.13 (1H, d, $J=1.47$ Hz), 6.75 (1H, d, $J=1.47$ Hz), 6.75—7.63 (12H, m); ^{13}C NMR $\delta=24.19$, 29.66, 35.34, 65.37, 66.05, 123.81, 124.61, 124.90, 125.68, 126.13, 126.32, 126.49, 126.99, 127.00, 128.34, 130.04, 134.11, 137.50, 139.32, 140.04, 141.42; UV (hexane) $\lambda_{\rm max}$ 289 nm (ε 8400). Calcd for C$_{23}$H$_{20}$: C, 93.24; H, 6.76%. Found; C, 93.11; H, 6.81%.



Scheme 2.

The preparation of **3b** was carried out by the reaction of cinnamaldehyde with (1-naphtyl)methyltriphenylphosphonium chloride in the presence of MeONa in MeOH.[8]

1-(1-Naphthyl)-4-phenyl-1,3-butadiene (3b): Mp 106—107 °C; ^{13}C NMR $\delta=123.25$, 123.57, 125.64, 125.80, 126.08, 126.45, 127.65, 127.99, 128.64, 128.69, 129.42, 129.52, 131.13, 131.97, 133.12, 133.80, 134.64, 137.34; UV (hexane) $\lambda_{\rm max}$ 342 nm (ε 30000). Calcd for C$_{20}$H$_{16}$: C, 93.75; H, 6.25%. Found; C, 93.60; H, 6.10%.

Photoreactions and Determination of Quantum Yield. 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. A potassium chromate solution (0.2 g dm^{-3}, 10 mm path length) was used to isolate 313 nm light, whereas 366 nm light was obtained by passage through a glass filter (Corning CS7-37) and a 10% HCl aqueous solution of BiCl$_3$ (6.67 g dm^{-3}, 10 mm path length). A 2-hexanone actinometer and a tris(oxalato)ferrate(III) actinometer were used to determine for the quantum yield at 313 nm for direct photolysis in hexane and at 366 nm for the BP sensitization in benzene.

Results

BP-Photosensitized Cycloreversion of 1b. The irradiation of a degassed benzene solution (4 ml) containing BP (8.0×10^{-2} mol dm^{-3}) and **1b** (8.0×10^{-4} mol dm^{-3}) at 366 nm for 5 min quantitatively gave **2b**. However, no BP-photosensitized cycloreversion of **2b** to **1b** occurred at all. The quantum yield ($\Phi_{\rm T}$) for the formation of **2b** was determined at a given concentration of **1b** (1×10^{-3}—2×10^{-2} mol dm^{-3}) and BP (8.0×10^{-2} mol dm^{-3}). The usual double-reciprocal plots of Φ vs. [**1b**] showed a linear correlation, showing that the intercept and the intercept-to-slope ratio were 1.04 and 3700 mol^{-1} dm^3, respectively. From the intercept of the plots, the limiting quantum yields at a infinite concentration of **1b** was calculated to be 0.96 (Fig. 1).

Phosphorescence and Fluorescence Spectra. Measurements of the phosphorescence spectra were carried out in a rigid matrix of EPA at 77 K. The triplet energy of **1b** was estimated to be 60 kcal mol^{-1} from the 0–0 band (478 nm) of its phosphorescence spectrum. No phosphorescence spectrum of **2b** was observed in a rigid matrix of EPA at 77 K.

On the other hand, the fluorescence spectra of **1b** showed emission at $\lambda_{\rm max}$ 327 and 339 nm, showing that the shape of the fluorescence spectra is similar to that of a parent naphthalene. The fluorescence maximum of **2b** was observed at 415 nm with broad emission from 380 nm to 450 nm. Thus, the singlet energies ($E_{\rm S}$) of **1b** and **2b** were estimated to be 88 and 72 kcal mol^{-1}, respectively, from the 0–0 band (325 nm for **1b** and 396 nm for **2b**). No fluorescence spectra of **2b** by the excitation of **1b** was observed at room or low temperature.

T–T Absorption Spectra. The T–T absorption spectra

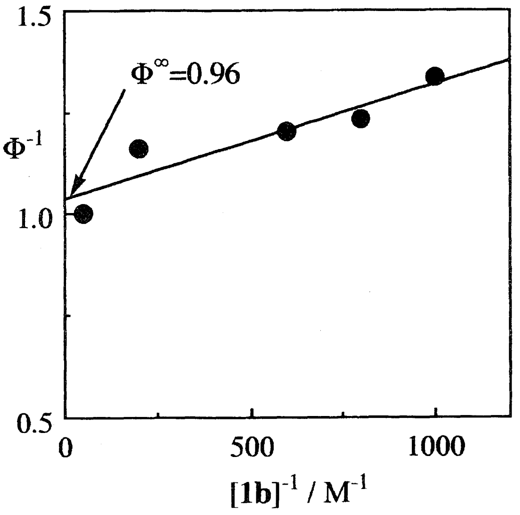


Fig. 1. Double-reciprocal plots of quantum yield for **2b** formation vs. concentration of **1b**.

of **1b** and **2b** 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 a solute.[9] The T–T absorption maxima of **2b** were observed at 455 nm, which decayed in first order with a decay constant of 2.1×10^5 s^{-1} (τ=4.8 µs). The 455 nm band was quenched by both oxygen ($E_T=22.5$ kcal mol^{-1}, [oxygen] = 1.8—7.8 mmol dm^{-3})[5] and azulene (AZ: $E_T=39.8$ kcal mol^{-1}, [AZ] = 1—10 mmol dm^{-3})[10] at $k_q=2.1\times10^9$ and 2.0×10^8 dm^3 mol^{-1} s^{-1}, respectively. Figure 2 shows the result for a pulse radiolysis of **2b** in the presence of BP (E_T=69 kcal mol^{-1}). The T–T absorption band of BP (λ_{max} = 530 nm) decayed according to pseudo-first-order kinetics, and the simultaneous formation of a new band (λ_{max} = 455 nm, τ = 4.6 µs: see Fig. 2B. inset) was formed. Thus, the absorption at 455 nm can be assigned to be the triplet state of **2b**. Moreover, the E_T value of **2b** was estimated to be less than 39 kcal mol^{-1} from the above quenching experiment.

The T–T absorption spectra of **1b** in the absence and presence of BP showed absorption at λ_{max} = 455 nm (τ = 4.6 µs), which was quenched by O_2 and AZ at $k_q=2.0\times10^9$ and 4.7×10^8 dm^3 mol^{-1} s^{-1}, respectively. Thus, the T–T absorption spectra of **1b** is the same to that of **2b**. Therefore, it is suggested that the triplet state of **1b** is readily converted into the triplet state of **2b** by an adiabatic process. The T–T absorption spectra of 1-(1-naphthyl)-4-phenyl-1,3-butadiene (**3b**) as an acyclic model compound of the **1b**-**2b** system is also shown in Fig. 2C.

Direct Photolysis of 1b. In order to compare the reactivities of BP-sensitization with those of the direct irradiation, we carried out direct photolysis of **1b** in hexane. The irradiation of **1b** (2.0×10^{-4} mol dm^{-3}) in a hexane solution (4 ml) with a 300 W high-pressure mercury lamp through a potassium chromate solution filter (313 nm) for 3 min at room temperature gave **2b** quantitatively without the formation of other products. The formation of **2b** increased linearly with the irradiation time up to 3% conversion. The quantum yield for the formation of **2b** from **1b** under direct irradiation at 313 nm in a hexane solution was determined to be 0.17 using a 2-hexanone as an actinometer. In this reaction, the value of the quantum yield did not change in the presence of oxygen.

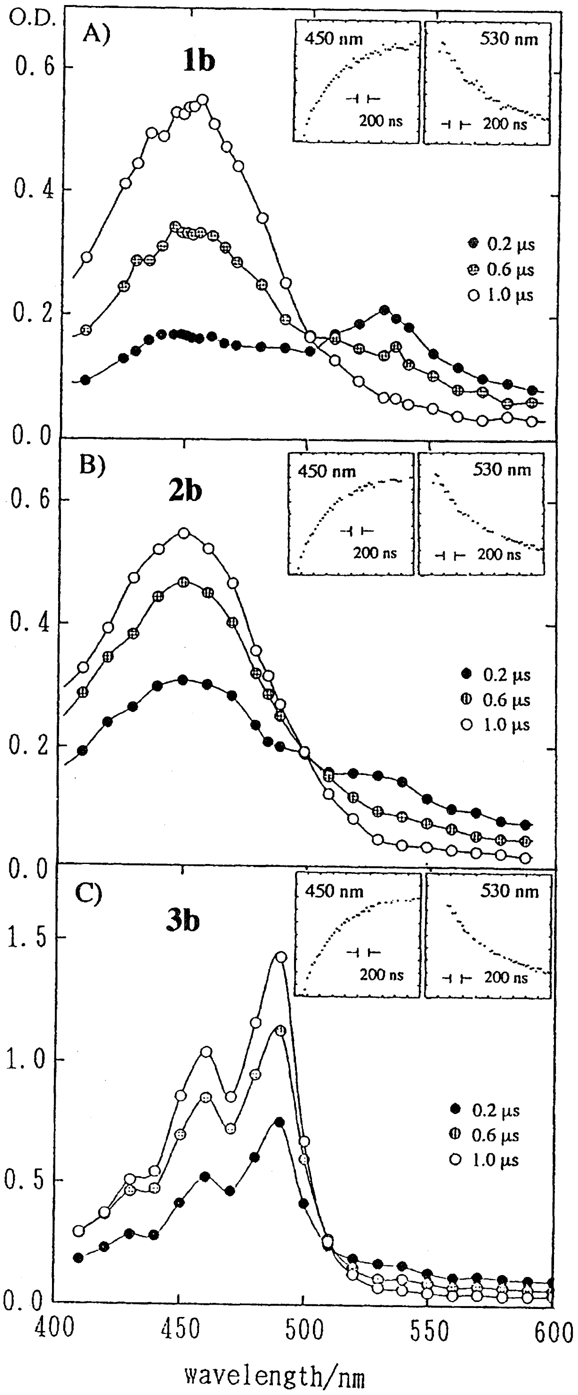


Fig. 2. Transient absorption spectra of **1b**—**3b** in the presence of BP in benzene at room temperature. A), [**1b**] = 4.0×10^{-3} mol dm^{-3}, [BP] = 2.3×10^{-2} mol dm^{-3}, B), [**2b**] = 4.2×10^{-3} mol dm^{-3}, [BP] = 2.0×10^{-2} mol dm^{-3}, C) [**3b**]=3.9×10^{-3} mol dm^{-3}, [BP]=2.1×10^{-2} mol dm^{-3}; insets are formation curve of **2b** and **3b** at 450 nm and decay curve of BP triplet at 530 nm.

Discussion

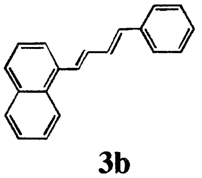
Mechanism via Triplet State. The spectral features of the transient species observed for **1b**—**3b** are summarized in Table 1. A common intermediate ($\lambda_{max}=455$ nm, $\tau=4.6$ μs) was observed in both compounds **1b** and **2b**, which was assigned to a triplet state of **2b** on the basis of the following observations: (i) The 455 nm band of this species is very close to that of 1-(1-naphthyl)-4-phenyl-1,3-butadiene (**3b**: $\lambda_{max}=460$ and 480 nm, $\tau=4.9$ μs) and its lifetime is long (on the μs order) (Chart 1). (ii) The 455 nm band is quenched not only by oxygen ($E_T=22.5$ kcal mol^{-1};[9] $k_q=2.0\times10^9$ dm^3 mol^{-1} s^{-1} for **1b** and 2.1×10^9 dm^3 mol^{-1} s^{-1} for **2b**) but also by azulene ($E_T=39.8$ kcal mol^{-1};[10] $k_q=4.7\times10^8$ dm^3 mol^{-1} s^{-1} for **1b** and 2.0×10^8 dm^3 mol^{-1} s^{-1} for **2b**). The triplet energy values of **1b** and **2b** were estimated to be 60 and 39 kcal mol^{-1} from the phosphorescence spectra in the EPA matrix at 77 K and the quenching of the T–T absorption spectra, respectively. The strain-energy difference between **1b** and **2b** in the ground state was estimated to be 13 kcal mol^{-1} by a measurement of the DSC of **1b**. From a calculation using these E_T values and the strain-energy difference, the conversion of ^{3}**1b*** into ^{3}**2b*** was found to be an exothermic process by ca. 34 kcal mol^{-1}. Since the quantum yield for the cycloreversion of **1b** via a triplet state is unity, there is no energy minimum in the triplet surface where crossing to the S_0 surface is possible. Therefore, the participation of other intermediates, such as 1,4-biradical, would be ruled out. From these results, one can conclude that an adiabatic cycloreversion took place in the triplet state of **1b** (Scheme 3). Schematic potential energy surfaces are shown in Fig. 3.

Substitution Effect of Cycloreversion Reaction. In view of these results, one can summarize the features of the cycloreversion of **1** to **2** (Table 2). The present study clearly demonstrated that an adiabatic cycloreversion of **1b** occurs via a triplet state ($\Phi_T=0.96$), whereas no adiabatic cycloreversion occurs via a singlet state ($\Phi_S=0.17$). Although these results are consistent with our previous result,[4] it should be noted that substitution with a naphthalene chromophore on bicyclo[3.2.0]hept-6-ene depresses the efficiency of cycloreversion via a singlet state. It is assume that the energy minimum lies in the singlet-state surface, since the quantum yield for the formation of **2b** from **1b** is very low, and photochemical cyclization from **2b** to **1b** can also occur ($\Phi=0.08$).[11] Moreover, no fluorescence spectra of **2b** by the excitation of **1b** was observed at room temperature. This indicated that no adiabatic cycloreversion of the singlet state of **1b** to the singlet state of **2b** by the excitation

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

Compounds	1b	2b	3b
λ_{max}/nm	455	455	460, 480
τ/μs	4.6	4.6	4.9
k_qO_2/dm^3 mol^{-1} s^{-1} a)	2.0×10^9	2.1×10^9	—c)
k_qAz/dm^3 mol^{-1} s^{-1} b)	4.7×10^8	2.0×10^8	—c)
Assignment	^{3}**2b***	^{3}**2b***	^{3}**3b***

a) The rate constant for the quenching by molecular oxygen. b) The rate constant for the quenching by azulene. c) Not determined.



3b

Chart 1.

$$\mathbf{1b} \xrightarrow{^3\mathrm{BP}^*} {}^3\mathbf{1b}^* \xrightarrow{\text{adiabatic}} {}^3\mathbf{2b}^* \longrightarrow \mathbf{2b}$$

E_T 60 kcal mol^{-1}

T-T λ_{max} 455 nm

τ_T 4.6 μs

$\Phi_{1\rightarrow2}=0.96$

E_T <39 kcal mol^{-1}

Scheme 3.

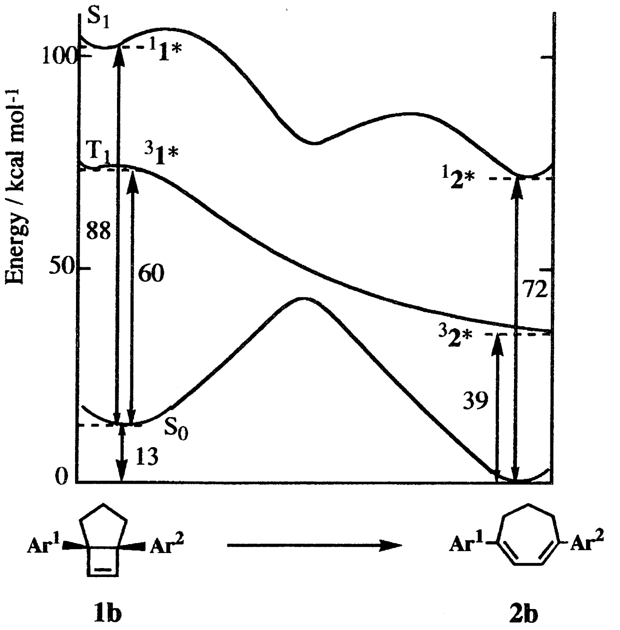


Fig. 3. Schematic potential energy surfaces between **1b** and **2b**.

Table 2. Substitution Effects for the Cycloreversion of **1** to **2**

	1a	→	2a	1a	→	2b
Φ_S		0.64			0.17	
Φ_T		0/100c)			0.96	
τ/μs		2.8			4.6	
E_S/kcal mol^{-1}	102		75	88		72
E_T/kcal mol^{-1}	78		39	60		39
ST/kcal mol^{-1} a)		20			13	
ΔG/kcal mol^{-1} b)		59			34	

a) Strain energy of **1** was determined by DSC. b) Energy difference between triplet state of **1** and **2**. c) The isomer ratio at stationary state.

of **1b** occurs, and that only a diabatic cycloreversion occurs in the case of direct irradiation. It is assume that a jump from the excited singlet-state surface to the ground-state surface occurs at the minimum point, i.e., a diabatic process from ^{1}**1*** to the ground state of **1** or **2** (Fig. 3). The present study demonstrates that the efficiency of the cycloreversion of these system (**1**–**2**) can be controlled by an aromatic substituent. In a direct photolysis of the naphthyl derivative (**1b**–**2b**), it is possible for the cycloreversion to occur after an intersystem crossing (isc) from the excited singlet state of **1b** to the excited triplet state of **1b** ($^1\mathbf{1b}^*\rightarrow{}^3\mathbf{1b}^*\rightarrow{}^3\mathbf{2b}^*\rightarrow\mathbf{2b}$), because efficiency of isc of naphthalene, itself, is normally high.[5)] However, we could not clearify such a mechanism based on our spectroscopic and products analyses.

It should be noted that **1a** and **1b** have a bicyclic structure with cyclobutene, cyclopentate rings, and aromatic substituents on the C1- and C5-positions with a face to face arrangement. In other words, two types of arylsubstituents exist as a cis-configuration. Although additional studies are needed to understand the reasons why the efficiency of the cycloreversion changes depending upon the aromatic substituent, the electronic interaction between aromatic substituent and cyclobutene ring seems to be one of the important factors.

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