Photoisomerization and Photocyclization Reactions of 1-Styrylanthracene

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On triplet sensitization, 1-styrylanthracene (**1SA**) undergoes adiabatic cis→trans one-way isomerization ($^3c^* \rightarrow {}^3t^*$) similarly to 2-anthrylethylenes. However, upon direct irradiation, *cis*-**1SA** in the singlet excited state mostly undergoes cyclization to a dihydrophenanthrene-type product (**DHP**), 4a,4b-dihydrobenzo[*b*]-chrysene, competing with an inefficient intersystem crossing to $^3c^*$ followed by one-way isomerization. The produced **DHP**, in deaerated benzene, is reverted to *cis*-**1SA** by a thermal ($E_a = 14.9$ kcal mol^{-1}) or a photochemical pathway; however, under an oxygenated atmosphere **DHP** gives benzo[*b*]chrysene. A failure in the production of a cyclized product upon the excitation of *trans*-**1SA** shows that the isomerization really takes place in a one-way fashion.

The photochemistry of arylethylenes has attracted much attention, and their photophysical and photochemical processes have been extensively elucidated. Especially, cis–trans isomerization,[1—9] rotational isomerization (rotamerism),[10—13] cyclization,[14—20] and oxidation reactions[21] have been widely investigated.

We found a cis→trans one-way photoisomerization of 2-anthrylethylenes proceeding through an adiabatic mechanism on the triplet potential-energy surface.[1,22—28] The isomerization starts from the cis triplet ($^3c^*$) resulting from either direct irradiation (then after an intersystem cross to a triplet) or a triplet sensitization of the cis isomer, by an adiabatic rotation of the double bond to the trans triplet ($^3t^*$) passing through the twisted triplet ($^3p^*$), but not accompanying an intersystem crossing at $^3p^*$ to the twisted ground state (p).

The effects of the substitution position of a styryl group on the photochemistry of styrylanthracenes have been examined and discussed in terms of the difference in the mechanism of the isomerization proposed for anthrylethylenes.[5—9,23—31] This paper reports on the photochemical behavior of *cis*- and *trans*-1-styrylanthracene (**1SA**), particularly on the photochemistry of the cis isomer. *cis*-**1SA** undergoes a cis→trans one-way isomerization in the triplet excited state in a similar manner as *cis*-2-styrylanthracene (*cis*-**2SA**), whereas the singlet excited *cis*-**1SA** efficiently undergoes a photocyclization reaction, giving a dihydrophenanthrene derivative (**DHP**) in a similar way as some diarylethylenes,[14—16] in competition with an inefficient intersystem crossing leading to a one-way isomerization (Scheme 1). Such a cyclization was not detected in *cis*-**2SA**. The thermal and photochemical behavior of **DHP** is also described.

Experimental

1-(Bromomethyl)anthracene. 1-(Bromomethyl)anthracene was prepared by a reported method.[32—34] Benzanthrone (20 g, 0.083 mol) dissolved in concd sulfuric acid (240 ml) was added to hot water (1200 ml) with stirring. Then, after the addition of chromium trioxide (80 g, 0.80 mol), the solution was refluxed for 6-h and anthraquinone-1-carboxylic acid was precipitated. The precipitate was collected by filtration, washed with hot water, and then dissolved in aqueous ammonia. Acidification of the solution with hydrochloric acid afforded a precipitate, which was further recrystallized from acetic acid.

Subsequently, this compound was treated in essentially the same way as that for 2-substituted anthracene derivatives previously reported.[28] Anthraquinone-1-carboxylic acid was reduced by zinc and aqueous ammonia to 1-anthracenecarboxylic acid, which was treated with thionyl chloride in benzene to give the acid chloride, and subsequently esterified with methanol. The resulting methyl 1-anthracenecarboxylate was reduced by lithium aluminum hydride in dry ether to give 1-(hydroxymethyl)anthracene. 1-(Bromomethyl)anthracene was obtained by the reaction of 1-(hydroxymethyl)anthracene with phosphorus tribromide in $CHCl_3$.

1-Styrylanthracene (1SA). Benzaldehyde (0.74 g, 7.0 mmol) and 1-anthrylmethyltriphenylphosphonium bromide (1.25 g, 2.3 mmol) prepared from 1-(bromomethyl)anthra-

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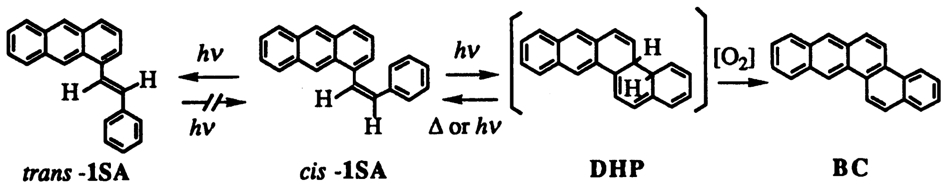

Scheme 1.

cene and triphenylphosphine were placed in absolute ethanol (200 ml) under nitrogen. Sodium ethoxide (1.6 g, 23 mmol) in ethanol (50 ml) was added dropwise to this solution. The solution was kept under stirring in a dark room for 17-h, and then refluxed for 3-h. To this solution benzene (30 ml) was added; the resulting precipitate was collected by filtration, washed with benzene, and recrystallized from hexane to give *trans*-**1SA**. To the filtrate was added benzene (100 ml), and the solution was washed with water. The organic layer was dried by anhydrous sodium sulfate, concentrated by evaporation, and chromatographed over SiO_2 eluted with a hexane–benzene (9:1) mixture to separate *cis*- and *trans*-**1SA**. Each isomer was purified by recrystallization from ethanol.

***cis*-1SA:** Mp 66—68 °C; ^1H NMR ($CDCl_3$) δ=6.93 (d, 1H, J=12.1 Hz, C=CH), 7.07 (s, 5H, ArH), 7.23—7.53 (m, 5H, C=CH and ArH), 7.86—8.08 (m, 3H, ArH), 8.38 (s, 1H, ArH), 8.55 (s, 1H, ArH); UV (PhH) λ_{max} 386 nm (ε 6400), 368 (6400), 295 (6500). Found: C, 93.95; H, 5.97%. Calcd for $C_{22}H_{16}$: C, 94.24; H, 5.76%.

***trans*-1SA:** Mp 138—140 °C; ^1H NMR ($CDCl_3$) δ= 7.06—7.59 (m, 7H, C=CH and ArH), 7.63—7.79 (m, 3H, ArH), 7.96—8.12 (m, 4H, ArH), 8.46 (s, 1H, ArH), 8.76 (s, 1H, ArH); UV (PhH) λ_{max} 391 nm (ε 11400), 308 (13400). Found: C, 94.17; H, 5.74%. Calcd for $C_{22}H_{16}$: C, 94.24; H, 5.76%.

Other Chemicals. 9,10-Diphenylanthracene was crystallized three times from ethanol and sublimed under a vacuum. 9*H*-Fluoren-9-one was twice recrystallized from ethanol. Spectroscopic grade benzene (Dotite) was used as a solvent.

Absorption and Fluorescence Spectra. The absorption spectra were recorded on a JASCO UVIDEC-660 or a Hitachi U-3000 spectrophotometer. Corrected fluorescence spectra were measured in benzene under argon or nitrogen on a Hitachi F-4000 or F-4010 spectrofluorimeter; the correction was performed using a Rhodamine B solution. 9,10-Diphenylanthracene and anthracene were used as standards for the determination of the fluorescence quantum yields. The fluorescence spectrum of *cis*-**1SA** at a low concentration in argon-purged benzene changed during the measurement; it was therefore subsequently measured with a faster scanning rate (120 $nm\,s^{-1}$) and the sample was replaced by a fresh one every two scannings.

Fluorescene Lifetime Measurements. A Horiba NAES 1100 single-photon counting instrument was used to determine the fluorescence lifetimes. A hydrogen arc lamp was used as an excitation light source (with a band path filter UV-340) and a monochromator was placed before the detector. The samples were purged with argon. The signals were collected up to 1×10^4 or 4×10^4 counts.

Transient Absorption Measurements. The transient absorption spectra were measured by a conventional laser-flash photolysis system. Excitation was performed by an XeCl excimer laser (Lamda Physik EMG 101, 308 nm, 150 mJ/pulse, 10 ns fwhm), an XeF excimer laser (351 nm, 100 mJ/pulse, 14 ns fwhm) or an XeCl-excimer-laser-pumped dye laser (Lamda physik FL3002, stilbene 3 dye, 425 nm, 3.5 mJ/pulse, 5 ns fwhm). The monitoring light of a pulsed xenon arc (Wacom KXL-151, 150 W) through a monochromator (JASCO CT-25C) was amplified by a photomultiplier (Hamamatsu Photonics R928) and stored in a storage scope (Iwatsu TS-8123). The signals were transferred to a computer (NEC PC-9801VX21) and accumulated for 2—4 times to be averaged, and then computer analyzed.

The molar extinction coefficient (ε_T) of triplet **1SA** (λ_{max}=570 nm) was determined by a comparison with that of 9*H*-fluoren-9-one (λ_{max}=430 nm, ε_T=5900 $M^{-1}\,cm^{-1}$)[35] (M≡mol dm^{-3}) used as a triplet sensitizer. The quantum yield for the intersystem crossing (Φ_{isc}) of **1SA** was determined by a comparison with that of anthracene used as a standard (Φ_{isc}=0.73 for anthracene)[36] in the same manner as previously described in detail.[26]

Photochemistry. Stationary irradiation was performed by a 400-W high-pressure mercury lamp using a UV-D36B glass filter (366 nm light, for direct excitation) or a $CuSO_4$ and $NaNO_2$ solution filter (405 and 435 nm light, for sensitized excitation).[37] Samples were prepared in benzene and purged with argon or nitrogen, or degassed by three freeze-pump-thaw cycles. The cis and trans isomers of **1SA** were analyzed by GPC (Shimadzu GC-14A) with an OV-1 column (25 m) and HPLC systems (Waters 600 or JASCO 880-PU) using a Zorbax ODS column (25 cm) with a methanol–water (98:2) mixture or a Senshu Pak. Silica-1251-R column (25 cm) with a hexane–ethyl acetate (99:1) mixture. The absorption spectra were also measured using an HPLC-UV detector (Shimadzu SPD-M6A) fitted with a JASCO 880-PU system.

The mass spectra were measured with a Shimadzu QP-2000 GC-MS spectrometer.

The reaction rates of **DHP** for a thermal reversion and reaction with oxygen were measured by a Hitachi U-3000 spectrophotometer using a Neslab RTE-110 temperature-controlled bath after irradiation of 355-nm light from a Continuum Surelight I-10.

Isomerization quantum yields were measured using potassium tris(oxalato)ferrate(III) actinometry.[38]

Results

Absorption and Fluorescence Spectra. Figure 1 shows the absorption spectra of *cis*- and *trans*-**1SA** in benzene. The trans isomer exhibited a much higher ε_{max} than the cis isomer, but no anthracene-like vibrational structure bands. Figure 1 also shows the fluorescence and fluorescence excitation spectra of *cis*- and *trans*-**1SA** in argon-purged benzene. The fluorescence

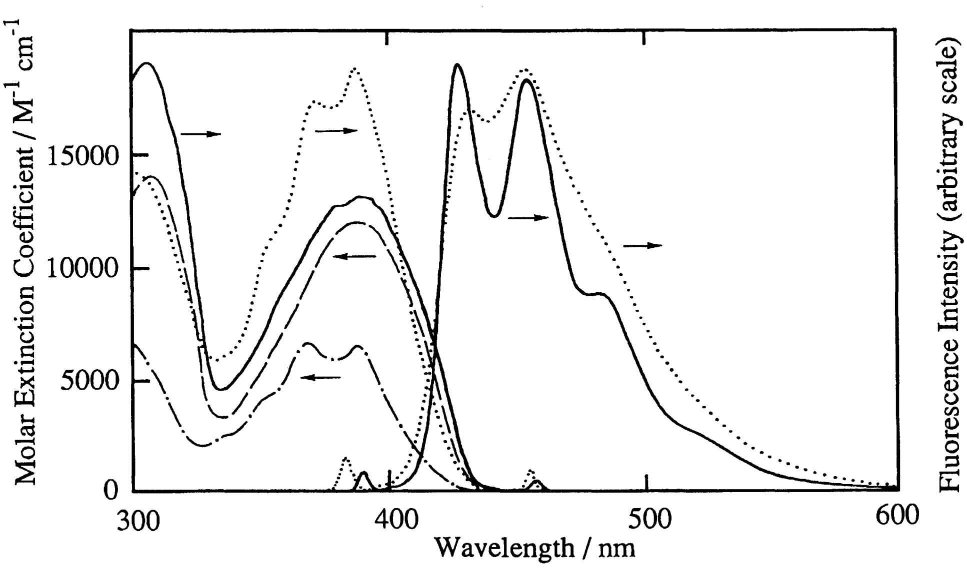

Fig. 1. Absorption spectra of *cis*-**1SA** (-·-·-) and *trans*-**1SA** (- - -), and fluorescence and fluorescence excitation spectra of *cis*-**1SA** (····) and *trans*-**1SA** (——) in argon purged benzene. Fluorescence spectra were recorded on excitation at 380 and 390 nm, and the excitation spectra were recorded by monitoring at 453 and 456 nm for *cis*-**1SA** and *trans*-**1SA** respectively.

spectrum of the cis isomer had a less-defined structure than that of the trans isomer. The fluorescence excitation spectra of the cis and trans isomers agree very well with the corresponding absorption spectra. No spectral change was observed upon changing of the excitation wavelengths (300—420 nm for fluorescence spectrum) or the monitoring wavelengths (420—480 nm for excitation spectrum).

The fluorescence quantum yields (Φ_f) were determined to be 0.70 and 0.07 for *trans*- and *cis*-**1SA**, respectively. The Φ_f did not depend on the excitation wavelength within the experimental uncertainty. The singlet excitation energies (E_s) were estimated from the mean values of the absorption and the fluorescence maxima as being 69.8 and 69.7 kcal mol^{-1} for *trans*- and *cis*-**1SA**, respectively, since they show large Stokes shifts of 2900 and 2300 cm^{-1}, respectively, which may arise from structural change accompanied by excitation.

Fluorescence Lifetimes. The fluorescence of *trans*-**1SA** decayed single exponentially with a lifetime (τ_f) of 4.69 ns with a reasonable χ^2 value: 1.45. However, the decay of the fluorescence lifetime of *cis*-**1SA** was not single-exponential, but fitted considerably well a two-component analysis with lifetimes of 0.85 (50.1%) and 4.58 ns (49.9%) with $\chi^2=1.38$. Since the longer lifetime component was close to the lifetime of the trans isomer, this component might arise from the accumulated trans isomer, though in a small amount, in the sample during the measurement due to exposure to light in the spectrofluorometer. According to a GC analysis, the amount of the trans isomer was increased from less than 2% to less than 5% during the measurement. A ten-times larger Φ_f for the trans (0.70) than the cis isomer (0.07) resulted in the observed high population of the fluorescence. The rates of fluorescence emission (k_f) were obtained as 0.8×10^8 and 1.5×10^8 s^{-1} for *cis*- and *trans*-**1SA**, respectively, by using $k_f=\Phi_f/\tau_f$.

Transient Absorption Spectra. Figure 2 shows the transient absorption spectra **1SA** (1.0×10^{-4} M) observed upon the excitation of 9*H*-fluoren-9-one (1.0×10^{-2} M) as a triplet sensitizer with a 425-nm laser in argon-purged benzene. Both *cis*- and *trans*-**1SA** efficiently quenched the triplet 9*H*-fluoren-9-one; with a decrease in the $T_n \leftarrow T_1$ absorption of 9*H*-fluoren-9-one (430 nm) in intensity, the $T_n \leftarrow T_1$ absorption of **1SA** at around 570 nm increased in intensity with an isosbestic point (490 nm) (Fig. 2-a,b). The transient absorption spectra of the *cis*- and *trans*-**1SA** showed essentially the same spectra, and the resulting absorptions decayed according to first-order kinetics with a lifetime of 21 μs. The triplet state of **1SA** exhibited an absorption maximum at 570 nm (Fig. 2-a), which was at a much longer wavelength than those of anthracene and **2SA**.[24,26] The spectra were broad and had a less-defined structure.

Direct excitation of *trans*-**1SA** (1.0×10^{-4} M) afforded the same $T_n \leftarrow T_1$ absorption (Fig. 2-c) as that observed upon triplet sensitization (Fig. 2-a) after the decay of strong fluorescence. However, the excitation of *cis*-**1SA** gave a very different transient absorption from the trans-isomer. *cis*-**1SA** showed, in addition to the weak $T_n \leftarrow T_1$ absorption around 570 nm, a broad strong absorption due to **DHP** at around 420 nm (Fig. 2-d), which did not decay on the microsecond time scale.

Intersystem Crossing Yield. The Φ_{isc} was estimated from the $T_n \leftarrow T_1$ absorption spectra. The extinction coefficient (ε) at the absorption maximum (570 nm) of the triplet state of **1SA** was determined to be 29000 M^{-1} cm^{-1} by a comparison with that of a triplet sensitizer 9*H*-fluoren-9-one ($\varepsilon_T=5900$ M^{-1} cm^{-1} at 430

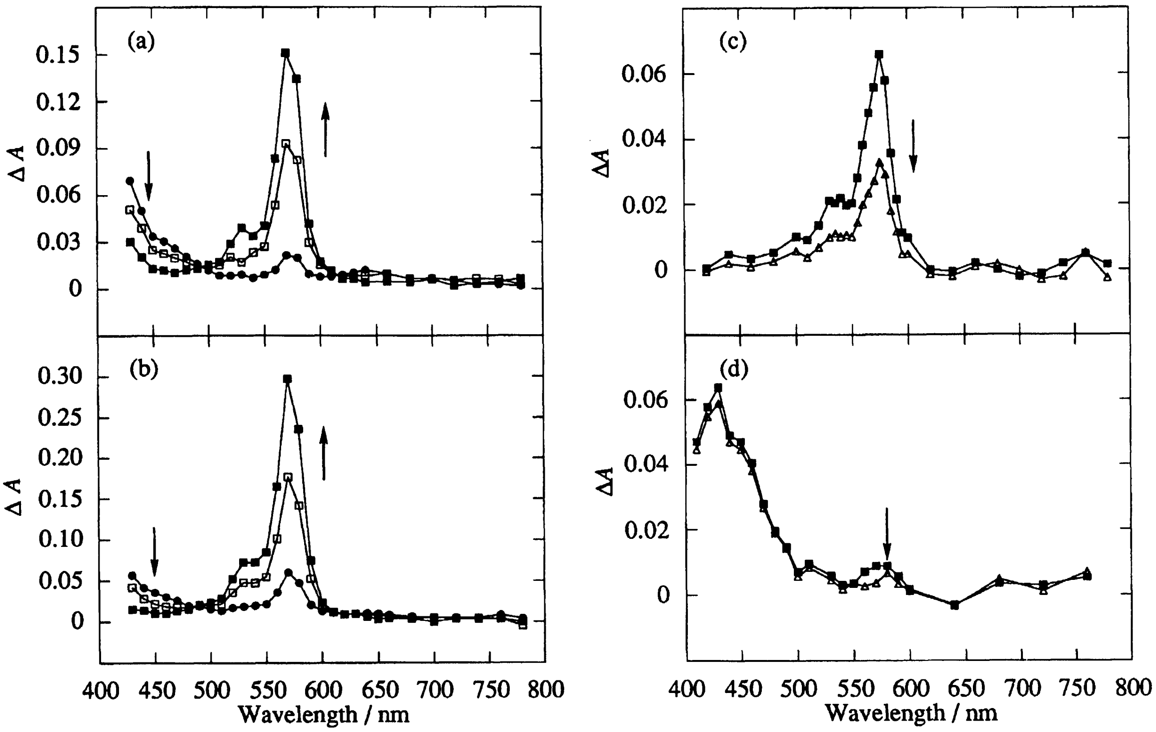

Fig. 2. Transient absorption spectra of *trans*-**1SA** and *cis*-**1SA** obtained on excitation at 425 nm in the presence of 9*H*-fluoren-9-one as a triplet sensitizer (a and b, respectively) and at 308 nm in the absence of a triplet sensitizer (c and d, respectively) in argon purged benzene. The spectra were obtained at 160 (●), 630 ns (□), 1.6 (■), and 16 μs (△) after the laser pulse.

nm).[35] It was assumed that the observed absorption could be attributed to the planar trans triplet, even upon excitation of the cis isomer with no deactivation at the cis or twisted triplet, and that a perfect energy transfer was accomplished from the sensitizer to *cis*- and *trans*-**1SA** (the same number of olefin triplets as those of sensitizer triplets were generated). The Φ_{isc} values estimated were 0.05 and 0.20 for *cis*- and *trans*-**1SA**, respectively.

Photochemical Behavior. The direct irradiation of *cis*-**1SA** with 366-nm light led to cyclization to a dihydrophenanthrene-type product (**DHP**) accompanying inefficient isomerization to the trans isomer. On the other hand, *trans*-**1SA** gave neither *cis*-**1SA** nor **DHP** (therefore no benzo[*b*]chrysene: **BC**) upon similar irradiation. In addition, no **DHP** or **BC** was observed upon triplet sensitization.

Upon irradiation of a solution of *cis*-**1SA** (1×10^{-3} M) in benzene (4 ml) under an argon atmosphere with 366-nm light from a 1-kW medium-pressure mercury lamp, the solution immediately turned to yellow; the absorption spectrum increased in intensity at wavelengths shorter than 550 nm without showing any maximum. When the solution was kept in the dark after 1-min irradiation, a yellow color gradually bleached, as shown in Fig. 3. The color quickly disappeared when the solution was further irradiated or kept in the dark at high temperature (56.8 °C). The yellow color was ascribed to the production of **DHP** and the bleaching to a reversion of **DHP** to *cis*-**1SA**.

The intermediacy of **DHP** was confirmed by the production of **BC** under an oxygen atmosphere. Upon the irradiation of a benzene solution of *cis*-**1SA** for 1 min under oxygen under otherwise the same condition, the yellow color disappeared quite rapidly. This might have been due to the oxidation of **DHP** by molecular oxygen to **BC**. The GC-MS spectrum of the reaction mixture indicated that **BC** was among the products, and that the absorption spectrum of a peak separated on HPLC was in good agreement with the spectrum reported for **BC**.[39] The similarity of the absorption spectrum and the primitive ^{1}H NMR spectrum of **DHP** to those reported to **DHP**-derivatives[16,40,41] also supported the intermediacy of **DHP**. Weak, but distinct and characteristic, signals were observed at $\delta=3.35$, 3.43, 5.90, 5.99, 6.23, and 6.50 after the irradiation of *cis*-**1SA** in deaerated benzene-d_6 in an NMR tube, although most aromatic signals were not clearly identified.

The reversion of **DHP** to *cis*-**1SA** was observed by absorption spectroscopy. Upon irradiation of a solution of *cis*-**1SA** (2×10^{-5} M) in benzene (4 ml) under an argon atmosphere by a 355-nm laser pulse, the absorption band due to the **DHP** increased in intensity, similar to that described above. However, the spectrum returned to be almost identical with *cis*-**1SA** with a small contribution of the trans isomer when the solution was photolized at 460±10 nm by a 150 W Xe-lamp for 10 min or when the solution was kept in the dark for 4-h.

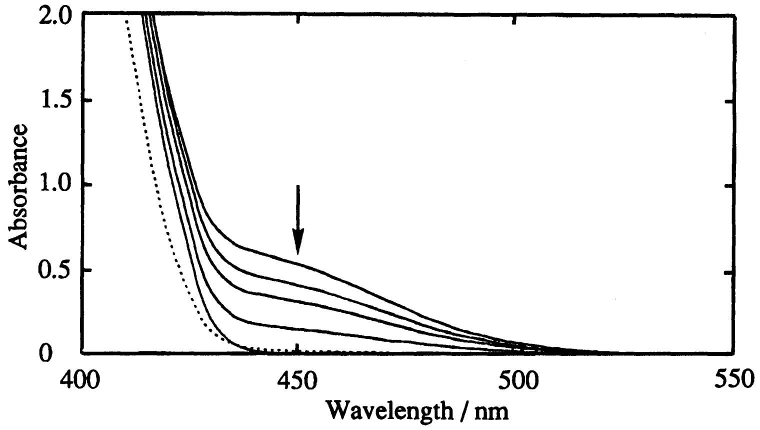

Fig. 3. Absorption spectra obtained on 366 nm direct excitation of *cis*-**1SA** in argon purged benzene. The spectra were recorded for a sample before irradiation (dotted line) and irradiated (1 min) samples kept in the dark after irradiation for 2, 50, 110, 230 min, and 24 h from top to bottom (solid line).

The first-order rate constant for the reaction of **DHP** with oxygen ($k_{ox}[O_2]$) was more than 30-times faster than that of the thermal reversion (k_{rev}) of **DHP** in benzene under oxygen. Therefore, the molar extinction coefficient of **DHP** at 450 nm ($\varepsilon_{DHP}{}^{450}$) was determined to be 14000 $M^{-1}\,cm^{-1}$ based on the absorbance measured immediately after the photolysis (irradiation with 355-nm laser pulse) and the amount of **DHP** formed, which was estimated from the amount of **BC** determined with GC by assuming that all **DHP** was converted to **BC** under oxygen. The rate constants were actually determined to be 3.9×10^{-5} s^{-1} for k_{rev} and 1.4×10^{-3} s^{-1} for $k_{ox}[O_2]$ at 20 °C by monitoring the spectral change ($[O_2]=9.02\times10^{-3}$ M).(42) The second-order rate constant of **DHP** with oxygen was determined to be 0.15 $M^{-1}\,s^{-1}$ by plotting the disappearance rates of **DHP** against the oxygen concentrations in benzene (under degassed, air- and oxygen-saturated conditions).

The quantum yield of the formation of **DHP** (Φ_{DHP}) was estimated to be 0.65 by a comparison of the absorbances in the transient spectra. The changes in the absorbance just after laser excitation (ΔA_0) due to the formation of **DHP** and **1SA** triplets ($^3t^*$) were 0.05 and 0.008 at 450 nm and 570 nm, respectively. These values were divided by $\varepsilon_{DHP}{}^{450}$ (14000 $M^{-1}\,cm^{-1}$) and ε_T^{570} (29000 $M^{-1}\,cm^{-1}$), respectively, to give the concentrations of **DHP** and $^3t^*$. Then, Φ_{DHP} was obtained by using Φ_{isc} of 0.05 for *cis*-**1SA**, as described above.

The rates of thermal reversion of **DHP** to *cis*-**1SA** were measured to be 1.29×10^{-5} to 7.91×10^{-4} s^{-1} in deaerated benzene at various temperatures of between 6.7 to 56.8 °C; the Arrhenius plot (Fig. 4) gave the activation energy (E_a) and the pre-exponential factor (A) as 14.9 kcal mol^{-1} and 5.1×10^6 s^{-1}, respectively.

The excitation of **DHP** at 460 nm gave no fluorescence, but led to a photochemical reversion to *cis*-**1SA**. The quantum yield (Φ_{rev}) for this process was determined to be 0.33.

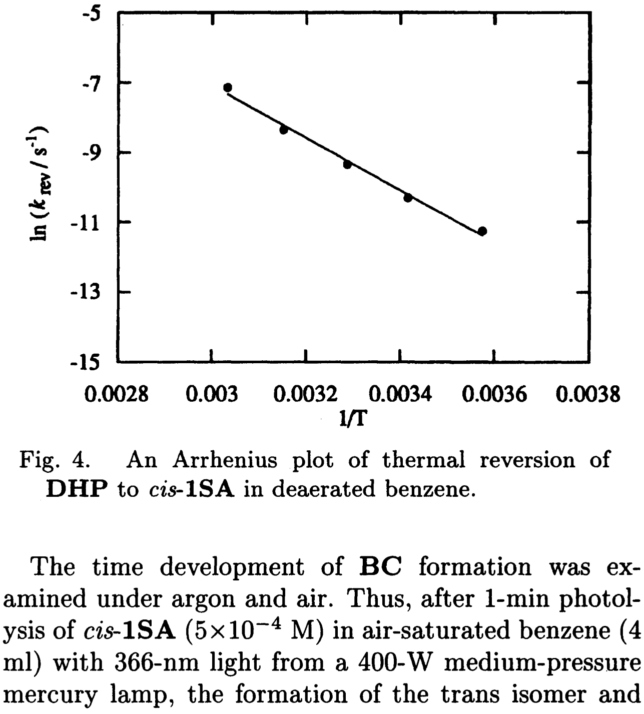

Fig. 4. An Arrhenius plot of thermal reversion of **DHP** to *cis*-**1SA** in deaerated benzene.

The time development of **BC** formation was examined under argon and air. Thus, after 1-min photolysis of *cis*-**1SA** (5×10^{-4} M) in air-saturated benzene (4 ml) with 366-nm light from a 400-W medium-pressure mercury lamp, the formation of the trans isomer and **BC** was detected by HPLC or GC. After 2.5-h, the cis-isomer completely disappeared, and was converted to the trans isomer and a significant amount of **BC**. Figure 5 shows the absorption spectra of the **BC** obtained with HPLC fitted with a multi-channel detector. The quantum yields for the production of **BC** (Φ_{BC}) were measured to be 0.066 and 0.13 under argon and air, respectively, by a comparison with the isomerization quantum yields ($\Phi_{c\rightarrow t}$), which were 0.10 and 0.045 under argon and air, respectively, in an initial cis concentration of 5.7×10^{-4} M. It should be noted that no **BC** was detected at all upon the irradiation of carefully degassed samples (5 freeze-pump-thaw cycles); also the yield of **BC** depended on the oxygen concentration. Although an increase in the oxygen concentration reduced $\Phi_{c\rightarrow t}$, it increased Φ_{BC}.

Cis-Trans Isomerization and Isomerization

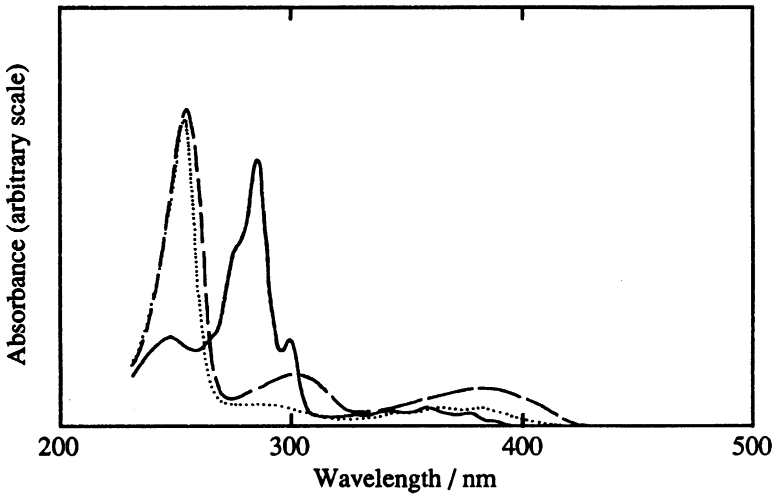

Fig. 5. Absorption spectra of *cis*-**1SA** (dotted line), *trans*-**1SA** (dashed line), and **BC** (solid line) measured by a multi-channel diode array detector fitted to HPLC.

Quantum Yields. Photostationary state isomer ratios were determined for **1SA** in deaerated benzene in both the presence and absence of a triplet sensitizer. Under 9*H*-fluoren-9-one-sensitized irradiation at 405 and 435 nm, although the cis isomer isomerized to the trans isomer, the trans isomer did not isomerize to the cis isomer at all. Therefore, **1SA** underwent a cis-to-trans one-way isomerization. In addition, the isomerization quantum yields ($\Phi_{c\rightarrow t}$) increased linearly with increasing concentration of the cis isomer, as shown in Fig. 6. The slopes ($S = k_q\tau_T$) and intercepts (I) of the plots were 1700 M^{-1} and 0.45, respectively, for 9*H*-fluoren-9-one sensitization and 63 M^{-1} and 0.02, respectively, for direct excitation. Then, the S/I values were obtained as being 3800 and 3200 M^{-1} for sensitized and direct excitation, respectively.

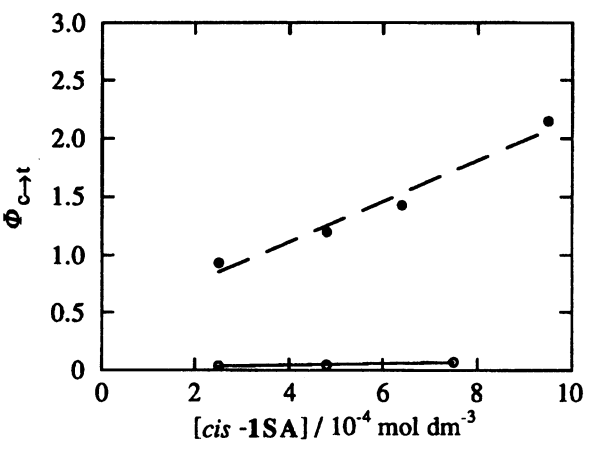

Fig. 6. Plots of the quantum yields for cis→trans isomerization ($\Phi_{c\rightarrow t}$) of **1SA** on direct irradiation (366 nm, open circles) and on 9*H*-fluoren-9-one sensitization (405 nm, solid circles) against the cis isomer concentration.

Discussion

Mechanism for Triplet Sensitized Isomerization. Upon 9*H*-fluoren-9-one sensitization, **1SA** undergoes a cis-to-trans "one-way" isomerization. The quantum yield ($\Phi_{c\rightarrow t}$) linearly increased far exceeding unity with increasing cis isomer concentration. These results clearly show that the isomerization proceeds in an adiabatic way through a quantum chain process, similarly to 2-anthrylethylenes, according to the following mechanism (Eqs. 1, 2, 3, 4, and 5):[1,22—25,28]

$$S \xrightarrow{h\nu} {}^1S^* \rightarrow {}^3S^*, \quad (1)$$

$$^3S^* + c \rightarrow S + {}^3c^*, \quad (2)$$

$$^3c^* \rightarrow ({}^3p^*) \rightarrow {}^3t^*, \quad (3)$$

$$^3t^* \rightarrow t, \quad (4)$$

$$\text{and } {}^3t^* + c \rightarrow t + {}^3c^*. \quad (5)$$

In the above, S is a sensitizer. The cis triplet ($^3c^*$) resulting from excitation of the cis isomer (c) (Eq. 2) converts to the trans triplet ($^3t^*$) adiabatically (Eq. 3) by passing through the perpendicular triplet ($^3p^*$), which is not situated as an energy minimum. The resulting $^3t^*$ undergoes either a unimolecular deactivation to the ground-state trans isomer (t) (Eq. 4) or an energy transfer to c to regenerate $^3c^*$ (Eq. 5).

Upon laser excitation of 9*H*-fluoren-9-one as a sensitizer, both *cis*- and *trans*-**1SA** afforded the same $T_n \leftarrow T_1$ absorption, assigned to $^3t^*$. Under the present experimental conditions, *cis*-**1SA** did not give any absorption attributable to $^3c^*$, which was supposed to be detected at a slightly shorter wavelength than that of $^3t^*$.[22,24] This means that during the laser pulse, the initially resulting $^3c^*$ quickly converts to $^3t^*$ in a way similar to the triplet states of **2SA**.[24,28]

According to Eqs. 1, 2, 3, 4, and 5, the isomerization quantum yield is expressed by

$$\Phi_{\mathrm{c}\to\mathrm{t}} = \Phi^{\mathrm{s}}_{\mathrm{isc}} \times \frac{k^{\mathrm{s}}_{\mathrm{q}}[\mathrm{cis}]}{k^{\mathrm{s}}_{\mathrm{d}} + k^{\mathrm{s}}_{\mathrm{q}}[\mathrm{cis}]} \times (1 + k_{\mathrm{q}}\tau_{\mathrm{T}}[\mathrm{cis}]), \tag{6}$$

where $\Phi^{\mathrm{s}}_{\mathrm{isc}}$ represents the quantum yield for an intersystem crossing of the sensitizer, $k^{\mathrm{s}}_{\mathrm{d}}$ and $k^{\mathrm{s}}_{\mathrm{q}}$ represent the decay rate constant of the triplet sensitizer and the quenching rate constant of the triplet sensitizer by *cis*-**1SA**, respectively; τ_{T} and k_{q} represent the lifetime of $^3\mathrm{t}^*$ and the quenching rate constant of $^3\mathrm{t}^*$ by c, respectively. Accordingly, the quantum yield of isomerization depends on the efficiencies for the formation of the sensitizer triplets ($\Phi^{\mathrm{s}}_{\mathrm{isc}}$) for energy transfer from the sensitizer triplet state to *cis*-**1SA** $[k^{\mathrm{s}}_{\mathrm{q}}[\mathrm{cis}]/(k^{\mathrm{s}}_{\mathrm{d}}+k^{\mathrm{s}}_{\mathrm{q}}[\mathrm{cis}])]$, and for the subsequent quantum chain process $(k_{\mathrm{q}}\tau_{\mathrm{T}}[\mathrm{cis}])$, that is, the efficiency for energy transfer from $^3\mathrm{t}^*$ to the cis isomer. The efficiency of the energy transfer from the triplet excited sensitizer to *cis*-**1SA** is taken to be unity for simplicity because of the high concentration of the cis-isomer under the experimental conditions.

The $\Phi_{\mathrm{c}\to\mathrm{t}}$ value increases linearly with increasing cis isomer concentration, as expected from Eq. 6. The *S*/*I* ratio (=3800 M^{-1}) of Fig. 6 corresponds to $k_{\mathrm{q}}\tau_{\mathrm{T}}$, which gives $k_{\mathrm{q}}=1.8\times10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ when divided by the $^3\mathrm{t}^*$ lifetime (21 μs). The energy transfer from $^3\mathrm{t}^*$ to cis proceeds with a slightly lower rate constant than the diffusion-controlled one, reflecting that the energy-transfer process is slightly endothermic. However, the quantum chain process proceeds very efficiently. This is attributed to the long lifetime of $^3\mathrm{t}^*$, which allows the energy transfer to take place with high efficiency in competition with the slow deactivation of $^3\mathrm{t}^*$.

Chemistry on Direct Irradiation. Exhibition of the characteristic fluorescence of *cis*-**1SA** indicates that the singlet energy surface around $^1\mathrm{c}^*$ is stabilized by the substitution of an anthryl group, and that $^1\mathrm{c}^*$ has a sufficient lifetime to emit fluorescence or to intersystem cross to the triplet surface, similar to the case of **2SA**.[24,28]

The destinations of $^1\mathrm{c}^*$ are expressed as follows (Eqs. 7, 8, 9, 10, 11, and 12):

$$\mathrm{c} \xrightarrow{h\nu} {}^1\mathrm{c}^*, \tag{7}$$

$${}^1\mathrm{c}^* \to \mathrm{c} + h\nu_{\mathrm{f}}, \tag{8}$$

$${}^1\mathrm{c}^* \to \mathrm{c}, \tag{9}$$

$${}^1\mathrm{c}^* \to \mathbf{DHP} \xrightarrow{\mathrm{O_2}} \mathbf{BC}, \tag{10}$$

$${}^1\mathrm{c}^* \to {}^3\mathrm{c}^*, \tag{11}$$

$$\text{and } \mathbf{DHP} \to \mathrm{c}. \tag{12}$$

After excitation of the cis isomer (Eq. 7), $^1\mathrm{c}^*$ undergoes the emission of fluorescence (Eq. 8), an internal conversion to the ground state (Eq. 9), photocyclization to **DHP** (Eq. 10), and an intersystem crossing to the triplet state (Eq. 11). **DHP** thermally reverts to the *cis*-**1SA** (Fig. 7). The sum of the efficiencies of each process is to be unity, as expressed in

$$\Phi_{\mathrm{f}} + \Phi_{\mathrm{ic}} + \Phi_{\mathrm{isc}} + \Phi_{\mathrm{DHP}} = 1, \tag{13}$$

where Φ_{f}, Φ_{ic}, Φ_{isc}, and Φ_{DHP} represent the quantum efficiencies of the fluorescence, internal conversion, intersystem crossing, and photocyclization, respectively.

For *trans*-**1SA**, Φ_{DHP} is zero and $\Phi_{\mathrm{f}}+\Phi_{\mathrm{isc}}$ is 0.90, close to unity. On the other hand, for *cis*-**1SA**, Φ_{DHP} is as large as 0.65, which is quite large among the many reports on the photocyclization of diarylethenes.[16] However, $\Phi_{\mathrm{DHP}}+\Phi_{\mathrm{f}}+\Phi_{\mathrm{isc}}$ remains at 0.77, which is slightly smaller than unity. This may be attributed to a diabatic deactivation to *cis*-**1SA** (Fig. 7) or an internal conversion.[17] Upon direct excitation by laser, *trans*-**1SA** gave the same transient absorption due to the $\mathrm{T}_n\leftarrow\mathrm{T}_1$ transition as that on the triplet sensitization; however, *cis*-**1SA** afforded an absorption mostly due to **DHP** in addition to that of a small amount of the triplet state. Figure 7 summarizes the schematic potential energy surfaces and the efficiencies of each reaction path.

As for the cis→trans isomerization, Fig. 6 is a plot of the isomerization quantum yields versus [cis] to give a linear relation with 63 M^{-1} as the slope. When the isomerization on direct excitation proceeds in the triplet manifold after an intersystem crossing from the singlet to the triplet state of $^3\mathrm{c}^*$ as in **2SA**, the quantum yield for cis-to-trans isomerization is expressed by

$$\Phi_{\mathrm{c}\to\mathrm{t}} = \Phi_{\mathrm{isc}} \times \Phi^{\mathrm{T}}_{\mathrm{c}\to\mathrm{t}} = \Phi_{\mathrm{isc}}(1 + k_{\mathrm{q}}\tau_{\mathrm{T}}[\mathrm{cis}]), \tag{14}$$

where $\Phi^{\mathrm{T}}_{\mathrm{c}\to\mathrm{t}}$ denotes the quantum yield for isomerization in the triplet state.

The slope obtained upon direct irradiation (Fig. 6) is smaller than that obtained upon triplet-sensitized irradiation, reflecting that Φ_{isc} is less than unity. The intercept corresponds to Φ_{isc}. The $k_{\mathrm{q}}\tau_{\mathrm{T}}$ value is obtained as 3200 M^{-1} from the ratio of the slope/intercept. Accordingly, the k_{q} value, the energy-transfer rate constant from $^3\mathrm{t}^*$ to c, is estimated as $1.5\times10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ by using τ_{T}, 21 μs. This value well agrees with that obtained from the triplet sensitization, $1.8\times10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$.

As for photocyclization, the direct excitation of *cis*-**1SA** gives **DHP**, which is easily oxidized to **BC**; however, excitation of the trans-isomer does not yield **DHP** at all. **DHP** shows an absorption with $\lambda_{\mathrm{max}}=450$ nm and a molar extinction coefficient, $\varepsilon=14000\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, which are very similar to those of a dihydrophenanthrene-type intermediate previously reported.[16] **DHP** undergoes a cycloreversion reaction to *cis*-**1SA** photochemically or thermally. The excitation of **DHP** at 480 nm in deaerated benzene at ambient temperature does not give fluorescence, but leads to a reversion to *cis*-**1SA** with $\Phi_{\mathrm{rev}}=0.33$. The thermal reversion in deaerated benzene takes place with an activation energy (E_{a}) of 14.9 kcal mol^{-1}, which is slightly smaller than that of stilbene.[16] The pre-exponential factor ($A=5.1\times10^6$ s^{-1}) is comparable to those of cycloreversion of the **DHP**-derivatives, as previously reported.[16] Those rel-

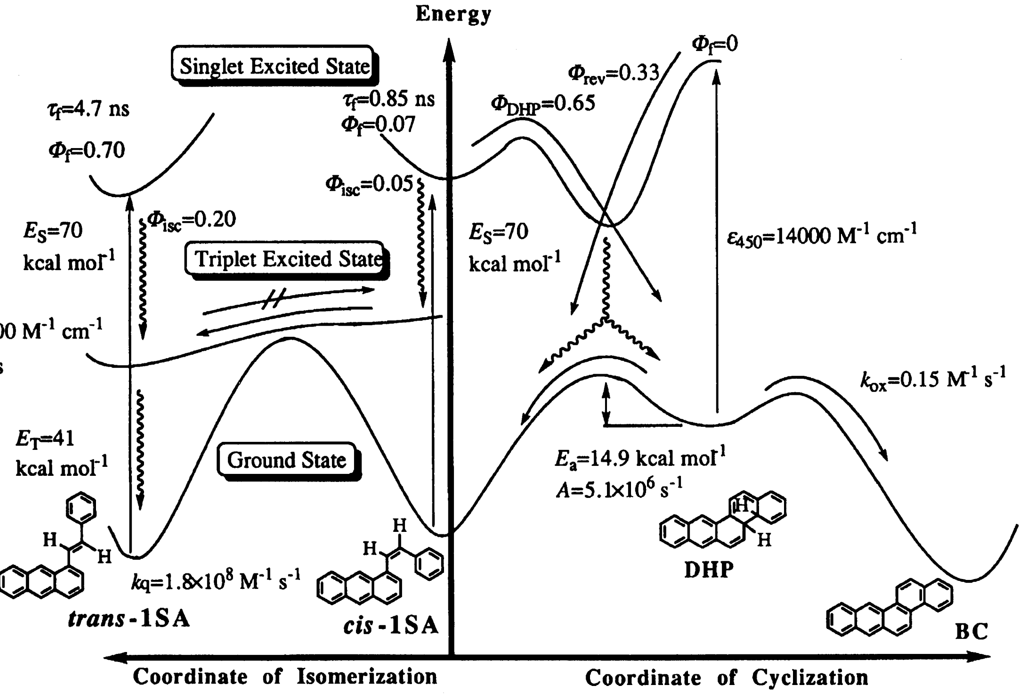

Fig. 7. Schematic potential energy surfaces of the isomerization and cyclization of **1SA** including the efficiencies.

atively small A show that the cycloreversion might proceed through a transition state with a more rigid conformation than that of **DHP**. Those values correspond to the activation parameters as $\Delta H^{\ddagger}=14.3$ kcal mol^{-1}, $\Delta S^{\ddagger}=-38.1$ cal K^{-1}mol^{-1} and $\Delta G^{\ddagger}=25.7$ kcal mol^{-1}. **DHP** is easily oxidized to **BC** with molecular oxygen with a rate constant of 0.15 M^{-1} s^{-1}.

$\Phi_{c\rightarrow t}$ depends on the concentration of *cis*-**1SA**; however Φ_{BC} is independent of the concentration of *cis*-**1SA**. In addition, although the introduction of air decreases $\Phi_{c\rightarrow t}$ from 0.10 to 0.045, Φ_{BC} increases from 0.066 to 0.13 when [cis]=5.7×10^{-4} M. The irradiation of a sample prepared with very careful degassing does not give **BC** at all. Thus, although oxygen quenches the quantum chain process of the isomerization, it promotes the aromatization of **DHP**. The Φ_{BC} obtained upon irradiation with a 1-kW medium-pressure mercury lamp at 366 nm was much smaller than that expected from Φ_{DHP} and k_{ox} estimated from the irradiation of an Nd-YAG laser (at 355 nm). This finding shows that upon stationary irradiation (366 nm) the resulting **DHP** is continuously excited and more facilely reverts to *cis*-**1SA** before it reacts with oxygen than upon Nd-YAG laser excitation (355 nm).

No cyclized product was detected upon the irradiation of *trans*-**1SA** in benzene under either degassed, air saturated, or oxygen saturated conditions. If the isomerization proceeded in the mutual way between the two isomers, the cyclization product should have been efficiently produced, even upon irradiation of the trans isomer. The above results are consistent with the fact that direct irradiation as well as triplet sensitization leads to one-way isomerization.

Conclusion

In the triplet state of **1SA**, the isomerization proceeds through an adiabatic cis-to-trans one-way pathway, similarly to **2SA**. However, in the singlet excited state, *cis*-**1SA** undergoes very efficient photocyclization to give **BC** through **DHP** in the presence of oxygen. This is characteristic to *cis*-**1SA**, since no production of a photocyclization product was observed in the case of *cis*-**2SA**. Failure in the formation of the cyclization product upon excitation of *trans*-**1SA** shows that the isomerization is really one-way, because the generation of the cis isomer would give **BC** through **DHP**. **BC** is produced by the oxidation of **DHP** with oxygen with a rate constant of 0.15 M^{-1} s^{-1}. **DHP** gives *cis*-**1SA** thermally with $E_a=14.9$ kcal mol^{-1} or photochemically.

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References

1) T. Arai and K. Tokumaru, *Chem. Rev.*, **93**, 23 (1993), and references cited therein.

2) J. Saltiel and Y.-P. Sun, in "Photochromism. Molecules and Systems," ed by H. Dürr and H. Bonas-Laurent, Elsevier, Amsterdam (1990), p. 64, and references cited therein.

3) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

4) R. A. Caldwell and L. Zhou, *J. Am. Chem. Soc.*, **116**, 2271 (1994).

5) H. Görner, *J. Photochem. Photobiol. A: Chem.*, **43**, 263 (1988).

6) L. Sun and H. Görner, *Chem. Phys. Lett.*, **208**, 43 (1993).

7) L. Sun and H. Görner, *J. Phys. Chem.*, **97**, 11186 (1993).

8) K. Sandros and H-D. Becker, *J. Photochem. Photobiol.*, **39**, 301 (1987).

9) K. Sandros and H-D. Becker, *J. Photochem. Photobiol. A: Chem.*, **43**, 291 (1988).

10) T. Karatsu, N. Yoshikawa, A. Kitamura, and T. Tokumaru, *Chem. Lett.*, **1994**, 381, and references cited therein.

11) U. Mazzucato and F. Momicciolі, *Chem. Rev.*, **91**, 1679 (1991), and references cited therein.

12) S. R. Flom, V. Nagarajan, and P. F. Barbara, *J. Phys. Chem.*, **90**, 2085 (1986).

13) A. M. Brearley, S. R. Flom, V. Nagarajan, and P. F. Barbara, *J. Phys. Chem.*, **90**, 2092 (1986).

14) F. B. Mallory and C. W. Mallory, *Org. Reac.* (*N. Y.*), **30**, 1 (1984).

15) W. H. Laarhoven, in "Organic Photochemistry," ed by A. Padwa, Mercel Dekker, New York (1989), Vol. 10, p. 163, and cited therein.

16) K. A. Muszkat, *Top. Curr. Chem.*, **88**, 89 (1980), and references cited therein.

17) J. H. Frederick, Y. Fujiwara, J. H. Penn, K. Yoshihara, and H. Petek, *J. Phys. Chem.*, **95**, 2845 (1991).

18) J-M. Rodier and A. B. Myers, *J. Am. Chem. Soc.*, **115**, 10791 (1993).

19) M. Irie, *Yuki Gosei Kagaku Kyokaishi* (*J. Synth. Org. Chem., Jpn.*), **49**, 373 (1991).

20) M. Irie, O. Miyatake, and K. Uchida, *J. Am. Chem. Soc.*, **114**, 8715 (1992).

21) A. P. Scaap and K. A. Zaklika, in "Singlet Oxygen," ed by H. H. Wasserman and R. W. Murrray, Academic Press, New York (1979), and references cited therein.

22) T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, T. Hiresaki, H. Furuuchi, H. Zeng, H. Sakuragi, and K. Tokumaru, *Pure Appl. Chem.*, **60**, 989 (1989), and references cited therein.

23) T. Arai, T. Karatsu, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **1983**, 2873.

24) T. Karatsu, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **115**, 9 (1985).

25) T. Karatsu, M. Tsuchiya, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **169**, 36 (1990).

26) T. Karatsu, T. Arai, H. Sakuragi, K. Tokumaru, and J. Wirz, *Bull. Chem. Soc. Jpn.*, **67**, 891 (1994).

27) T. Karatsu, A. Kitamura, H. Zeng, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1992**, 2193.

28) T. Karatsu, M. Tsuchiya, T. Arai, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **67**, 3030 (1994).

29) G. Galiazzo, A. Spalletti, F. Elisei, and G. Gennari, *Gazz. Chim. Ital.*, **119**, 277 (1989).

30) U. Mazzucato, A. Spalletti, and G. Bartocci, *Coord. Chem. Rev.*, **125**, 251 (1993).

31) K. Bhattacharyya, S. K. Chattopadhyay, S. Baral-Tosh, and P. K. Das, *J. Pys. Chem.*, **90**, 2646 (1986).

32) E. B. Barnett, J. W. Cook, and H. H. Grainger, *Chem. Ber.*, **57**, 1775 (1927).

33) A. Sonoda, F. Ogura, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **35**, 853 (1962).

34) S. Akiyama, S. Misumi, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **35**, 1826 (1962).

35) R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, **67**, 1904 (1971).

36) B. Amand and R. Bensasson, *Chem. Phys. Lett.*, **34**, 44 (1975).

37) S. L. Murov, I. Carmichael, and G. L. Hug, "Handbook of Photochemistry," Marcel Dekker, New York (1993), p. 322.

38) Ref. 37, p. 299.

39) E. Clar and L. Lombardi, *Chem. Ber.*, **65**, 1411 (1932).

40) T. Knittel, G. Fischer, and E. Fischer, *J. Chem. Soc., Chem. Commun.*, **1972**, 84.

41) T. Wismonski-Knittel, G. Fischer, and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 1930.

42) Ref. 37, p. 289.