March, 1992] © *1992 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***65***, *837—845 (1992)* 837

Photochemical Reactions of 4-Acylstyrenes. Effects of Acyl Substituents on Photocyclodimerization via an Excited Triplet State

Kyoji TSUBAKIYAMA,* Kohji MIYAGAWA, Kiyotaka KAIZAKI,
Masahide YAMAMOTO,*,† and Yasunori NISHIJIMA†
Research Institute for Material Science and Engineering,
Faculty of Engineering, Fukui University, Bunkyo, Fukui 910
† Department of Polymer Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

(Received August 25, 1991)

The photochemical reactions of 4-acylstyrenes (**1a**—**e**; acyl=acetyl, benzoyl, 1-naphthoyl, 2-naphthoyl, and 9-phenanthrylcarbonyl, respectively) were investigated, and their excited state behavior and photoreactivities are discussed in relation to the aryl ketone structures. Photoirradiation of **1a**—**e** in benzene gave two isomeric cyclodimers of *trans*- and *cis*-1,2-bis(4-acylphenyl)cyclobutanes (**2a**—**e** and **3a**—**e**) as main products, accompanied by the formation of some oligomers and polymers. The fractions of the *trans*-form in the cyclodimers were ca. 80%; this indicated that the cyclodimerization proceeded via the π,π^* triplet state. The quantum yields of the photodimerization for **la**—**e** were almost the same irrespective of the acyl substituents (Φ=0.03—0.04 at [**1a**—**e**]=0.1 mol dm^{-3}). Phosphorescence spectra of **1c** (τ=0.48 s) and **1d** (τ=0.91 s) observed in a rigid solution at 77 K, which coincided with those of the respective model aryl ketones, were ascribed to the low-lying excited π,π^* triplet states localized on the naphthalene moiety of the molecules. Phosphorescence emissions of **1a** and **1b** could not be detected. The transient absorption spectrum of **1d** (τ=23 ns) observed in a fluid solution at 293 K was tentatively assigned to the π,π^* triplet state mainly localized on the styrene moiety of the molecule. The photoreaction mechanism is discussed in terms of the intramolecular triplet energy transfer.

Direct and sensitized photopolymerizations of aromatic vinyl compounds such as styrenes and vinylnaphthalenes are frequently accompanied by photo[2+2] cycloaddition reactions.[1-5] Recently, the cycloaddition reactions have been extensively investigated from the standpoint of the photoinitiation of polymerization.[6] In our previous paper,[7] the photochemical reaction of 4-vinylbenzophenone (**1b**) was studied in connection with the photopolymerization of styrene derivatives from the excited triplet state. It was found that direct photoexcitation of **1b** in solution gave a *trans*-type cyclobutane dimer as a major product along with other oligomers and polymers; the photochemical reactivity was similar to that of styrene in the triplet state,[2,5] but not to that of benzophenone. This is because the lowest triplet state of **1b** is of the π,π^* configuration, in contrast to that of the ketone(n,π^*). The function of the benzoyl group is to bring the absorption of the compound into a readily accessible longer-wavelength region, and to promote intersystem crossing.

In the present study, the photocyclodimerization of acylstyrenes including 4-vinylacetophenone (**1a**), **1b**, 4-(1-naphthoyl)styrene (**1c**), 4-(2-naphthoyl)styrene (**1d**), and 4-(9-phenanthrylcarbonyl)styrene (**1e**) has been investigated to clarify the effects of acyl substituents on the photoreaction and excited triplet state. All the compounds studied in this work have been found to undergo photocyclodimerization to produce mainly *trans*-cyclodimers. They are expected to undergo efficient intersystem crossing into the triplet state in a manner similar to the corresponding aryl ketones: acetophenone,[8] phenyl naphthyl ketones,[8] and phenyl phenanthryl ketone.[9] However, acylstyrenes **1c**—**e** have two widespread π-chromophores, i.e., the aromatic fused-ring and styrene moieties, which are formally conjugated with the central carbonyl group,[10] and the photochemical and photophysical properties of acylstyrenes **1c**—**e** are considered to be appreciably different from those of **1a**,**b**. The photocyclodimerization process of such compounds will be discussed in terms of an intramolecular excitation transfer between conjugated chromophores.

Experimental

Measurements. NMR spectra were recorded on a JEOL FX-90Q spectrometer in CDCl$_3$ using tetramethylsilane as an internal standard. Mass spectra were taken with a JEOL JMS-01 SG-II spectrometer. Elemental analyses were performed in the Organic Analysis Center of Kyoto University. Melting points are uncorrected. UV absorption spectra were measured with a Shimadzu UV-200S spectrophotometer. Phosphorescence spectra were measured by a Hitachi MPF-4 fluorescence spectrophotometer using its attachment for phosphorescence. Phosphorescence lifetimes were obtained by a photon-counting phosphorimeter.[11] Transient absorption measurements were carried out with a nanosecond ruby laser photolysis apparatus:[12] Excitation wavelength, 347 nm; duration of pulse, 14 ns.

Materials. Methyl 1-naphthyl ketone (Tokyo Kasei) and phenyl 2-naphthyl ketone (Tokyo Kasei) were purified by distillation and recrystallization, respectively. Benzene was dried over calcium hydride and twice distilled. 2-Methyltetrahydrofuran (MTHF) was purified by passage through an alumina column, distillation over calcium hydride, and final vacuum distillation. Other solvents were distilled.

Acylstyrenes. 4-Vinylacetophenone (**1a**) was prepared by pyrolysis of poly(4-vinylacetophenone) according to the literature,[13] and purified by column chromatography on silca gel and recrystallization from hexane: Colorless crystals; mp 35—36 °C (lit,[13] 35.5—36 °C); ^{1}H NMR δ=2.57 (3H, s), 5.73 (1H, dd, J= 11 and 1 Hz), 5.84 (1H, dd, J=18 and 1 Hz), 6.75 (1H, dd, J=18 and 11 Hz), 7.45 (2H, br. d, J=9 Hz), and 7.90 (2H, br. d, J=9 Hz). Found: C, 82.09; H, 6.97%. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89%.

4-(1-Naphthoyl)styrene (**1c**) and 4-(9-phenanthrylcarbonyl)styrene (**1e**) were prepared from 4-chlorostyrene and the corresponding aromatic nitrile in the same manner as described previously for 4-vinylbenzophenone (**1b**)[7] and 4-(2-naphthoyl)styrene (**1d**).[14] These aroylstyrenes were purified by column chromatography on silica gel and recrystallized from hexane.

1c: Colorless crystals; mp 52—53.5 °C; ^{1}H NMR δ=5.37, (1H, dd, J=11 and 1 Hz), 5.84 (1H, dd, J=18 and 1 Hz), 6.74 (1H, dd, J=18 and 11 Hz), 7.38—7.61 (6H, m), and 7.76—8.15 (5H, m); ^{13}C NMR δ= 116.7 (CH=$\underline{C}H_2$), 135.9 ($\underline{C}H=CH_2$), and 197.1 (C=O). Found: C, 88.35; H, 5.56%. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46%.

1e: Colorless oil (could not be crystallized); ^{1}H NMR δ=5.41 (1H, dd, J=11 and 1 Hz), 5.88 (1H, dd, J=18 and 1 Hz), 6.79 (1H, dd, J=18 and 11 Hz), 7.42—8.16 (11H, m), and 8.75 (2H, br. d, J=8 Hz). Found: C, 89.48; H, 5.41%. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23%.

Photoreaction. A benzene solution of sample in a pyrex tube (ϕ=10 mm) was degassed by several freeze-pump-thaw cycles under high vacuum and the tube was sealed off. Photoirradiation was carried out by means of a 500 W high-pressure mercury lamp (Ushio USH-500D) fitted with a cutoff filter (Toshiba UV-35) at 293 K. After evaporation of the solvent, the photoproducts were analyzed by a gel-permeation chromatograph (GPC, JASCO TRIROTAR-S) fitted with a refractive index detector and a JASCO Megapak Gel-201 column eluting with chloroform. The reaction yields were determined from the chromatograms. Molecular weights of the polymeric products were estimated by the use of Shodex A-80M columns.

For the determination of quantum yield, the photoreaction was performed in a 1-cm quartz cell with irradiating light at 365 nm using two cutoff filters (Toshiba UV-D1A and Corning CS 0-52); the light intensity was found to be 3.6×10^{-8} einstein $cm^{-2}\,s^{-1}$ by iron (III) oxalate/phenanthroline actinometry.[15]

Identification of Cyclodimers. The isolation of the isomeric cyclodimers was made by means of a recycle GPC. The *cis* dimers generally had a larger elution volume than the *trans* dimers; several recyclings gave sufficient separation of the isomers. All the cyclodimers were obtained as a colorless oil or solid. The configurations of the two isomers were determined by ^{1}H NMR chemical shifts.[16] Analytical data for **2b** and **3b** were given in the previous report.[7]

***trans*-1,2-Bis(4-acetylphenyl)cyclobutane (2a):** ^{1}H NMR δ=2.07—2.40 (4H, m, CH_2), 2.53 (6H, s, CH_3), 3.54—3.71 (2H, m, CH), 7.28 (4H, br. d, J=8 Hz, phenyl-2), and 7.88 (4H, br. d, J=8 Hz, phenyl-3); ^{13}C NMR δ=25.3 (CH_2), 26.0 (CH_3), 47.5 (CH), 126.4 (phenyl-2), 128.2 (phenyl-3), 135.4 (phenyl-4), 149.0 (phenyl-1),and 196.5 (C=O); MS m/z (rel intensity) 292 (15%, M^+), 277 (3, M^+-CH_3), 264 (3, $M^+-C_2H_4$), 249 (7, M^+-CH_3CO), 146 (37, $M^+/2$), 131 (100, $M^+/2-CH_3$), and 103 (44, $M^+/2-CH_3CO$).

***cis*-1,2-Bis(4-acetylphenyl)cyclobutane (3a):** ^{1}H NMR δ=2.48 (6H, s, CH_3), 2.43—2.65 (4H, m, CH_2), 4.02—4.12 (2H, m, CH), 7.02 (4H, br. d, J=8 Hz, phenyl-2), and 7.68 (4H, br. d, J=8 Hz, phenyl-3); ^{13}C NMR δ=24.1 (CH_2), 26.2 (CH_3), 45.2 (CH), 127.8 (phenyl-2,3), 134.9 (phenyl-4), 146.8 (phenyl-1), and 197.4 (C=O); MS m/z (rel intensity) 292 (19%, M^+), 277 (3, M^+-CH_3), 264 (3, $M^+-C_2H_4$), 249 (7, M^+-CH_3CO), 146 (40, $M^+/2$), 131 (100, $M^+/2-CH_3$), and 103 (54, $M^+/2-CH_3CO$).

***trans*-1,2-Bis[4-(1-naphthoyl)phenyl]cyclobutane (2c):** ^{1}H NMR δ=2.06—2.44 (4H, m, CH_2), 3.52—3.76 (2H,m, CH), 7.26 (4H, br. d, J=8 Hz, phenyl-2), 7.35—7.58 (8H, m, aromatic), and 7.72—8.12 (10H, m, aromatic); ^{13}C NMR δ=25.7 (CH_2), 47.8 (CH), and 197.2 (C=O); MS m/z (rel intensity) 516 (18%, M^+), 488 (4, $M^+-C_2H_4$), 361 (3, $M^+-C_{10}H_7CO$), and 258 (100, $M^+/2$).

***cis*-1,2-Bis[4-(1-naphthoyl)phenyl]cyclobutane (3c):** ^{1}H NMR δ=2.45—2.62 (4H, m, CH_2), 4.04—4.24 (2H, m, CH), 7.01 (4H, br. d, J=8 Hz, phenyl-2), 6.36—6.70 (12H, m, aromatic), and 7.82—8.10 (6H, m, aromatic); ^{13}C NMR δ=23.9 (CH_2), 45.5 (CH), and 197.5 (C=O); MS m/z (rel intensity) 516 (24%, M^+), 488 (3, $M^+-C_2H_4$), 361 (2, $M^+-C_{10}H_7CO$), and 258 (100, $M^+/2$).

***trans*-1,2-Bis[4-(2-naphthoyl)phenyl]cyclobutane (2d):** ^{1}H NMR δ=2.14—2.58 (4H, m, CH_2), 3.62—3.86 (2H, m, CH), 7.37 (4H, br. d, J=8 Hz, phenyl-2), 7.48—7.68 (4H, m, aromatic), and 7.78—7.95 (12H, m, aromatic), and 8.25 (2H, br. s, naphthyl-1); ^{13}C NMR δ=25.8 (CH_2), 47.9 (CH), and 196.1 (C=O); MS m/z (rel intensity) 516 (16%, M^+), 488 (5, $M^+-C_2H_4$), 361 (11, $M^+-C_{10}H_7CO$), and 258 (100, $M^+/2$).

***cis*-1,2-Bis[4-(2-naphthoyl)phenyl]cyclobutane (3d):** ^{1}H NMR δ=2.48—2.68 (4H, m, CH_2), 4.08—4.32 (2H, m, CH), 7.10 (4H, br. d, J=8 Hz, phenyl-2), 7.37—7.93 (16H, m, aromatic), and 8.11 (2H, br. s, naphthyl-1); ^{13}C NMR δ=24.0 (CH_2), 45.5 (CH), and 196.2 (C=O); MS m/z (rel intensity) 516 (21%, M^+), 488 (2, $M^+-C_2H_4$), and 258 (100, $M^+/2$).

***trans*-1,2-Bis[4-(9-phenanthrylcarbonyl)phenyl]cyclobutane (2e):** ^{1}H NMR δ=2.08—2.50 (4H, m, CH_2), 3.56—3.80 (2H, m, CH), 7.28 (4H, br. d, J=8 Hz, phenyl-2), 7.42—8.15 (18H, m, aromatic), and 8.72 (4H, br. d, J=8 Hz, phenanthryl-4,5); ^{13}C NMR δ=25.8 (CH_2), 47.8 (CH), and 197.2 (C=O).

***cis*-1,2-Bis[4-(9-phenanthrylcarbonyl)phenyl]cyclobutane (3e):** ^{1}H NMR δ=2.48—2.62 (4H, m, CH_2), 4.08—4.27 (2H, m, CH), 7.04 (4H, br. d, J=8 Hz, phenyl-2), 7.34—8.02 (18H, m, aromatic), and 8.69 (4H, br. d, J=8 Hz, phenanthryl-4,5).

Results

Absorption Spectra. Figure 1 shows the UV absorption spectra of acylstyrenes **1a**—**d** in different solvents. In nonpolar hexane solvent, acetyl and benzoyl derivatives (**1a** and **1b**) exhibited some strong absorption bands ($\varepsilon\approx10^4$ $dm^3\,mol^{-1}\,cm^{-1}$) in the wavelength region from 240 to 300 nm due to $\pi\rightarrow\pi^*$ transitions of the styrene and/or benzene moieties and a weak band ($\varepsilon\approx10^2$) in the longer wavelength region of 320—400 nm due to an $n\rightarrow\pi^*$ transition of the carbonyl group. Changing from a nonpolar solvent (hexane) to a polar solvent (methanol) resulted in a shift of the π,π^* absorption band to longer wavelengths (red shift), and the n,π^* band to shorter wavelengths (blue shift). In the cases of the naphthoyl derivatives (**1c** and **1d**), the weak n,π^* absorption bands at 360—400 nm were somewhat

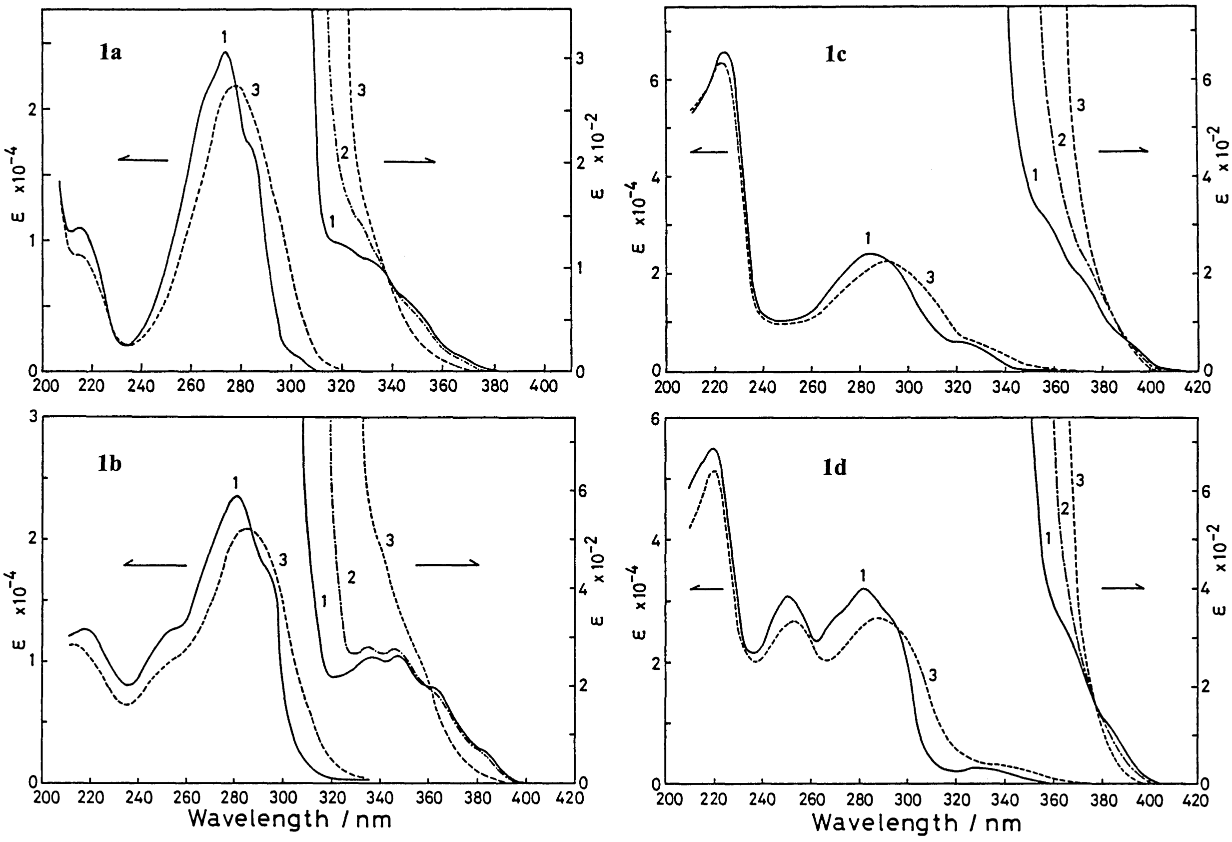


Fig. 1. UV absorption spectra of acylstyrenes **1a**—**1d** in (1) hexane, (2) benzene, and (3) methanol.

obscure even in nonpolar hexane owing to the existence of other π,π^* absorption bands ($\varepsilon \approx 10^3$) of the naphthalene moieties around 330 nm. The polar methanol solvent caused a blue shift of the n,π^* band and a red shift of the π,π^* band, resulting in complete masking of the $n \to \pi^*$ transition by the $\pi \to \pi^*$ transition. A similar absorption spectrum was also observed for the phenanthrylcarbonyl derivative (**1e**). These results indicated that the low-lying singlet states of acylstyrenes **1a**—**e** were of n,π^* character (mixed with π,π^*) similar to those of the corresponding aryl ketones such as acetophenone,[15] benzophenone,[15] naphthyl ketones,[15,17] and 9-phenanthrylcarbaldehyde.[17] Consequently, all the compounds **1a**—**e** were thought to undergo efficient intersystem crossing from the excited singlet states to the triplet states.[17,18]

Photoreaction. The photoirradiation ($\lambda > 320$ nm, UV-35 filter) of acylstyrenes **1a**—**e** (0.5 mol dm^{-3}) in degassed benzene solution gave two isomeric cyclodimers as main products, along with other oligomers and polymers. The cyclodimers were assigned to *trans*- and *cis*-1,2-bis(4-acylphenyl)cyclobutanes (**2a**—**e** and **3a**—**e**) from NMR and MS spectra of isolated compounds, as described in the experimental section. Dimers of the tetralin type could not be found in the reaction products of the acylstyrenes, although attempts to detect the dimers were performed by means of liquid chromatograpy with different packed columns. The photoproduct distribution was measured by gel-permeation chromatography (GPC). A typical GPC chromatogram for the photoproducts of **1e** is shown in Fig. 2. Here, the main peak (I) and the second one (II) are *trans*-

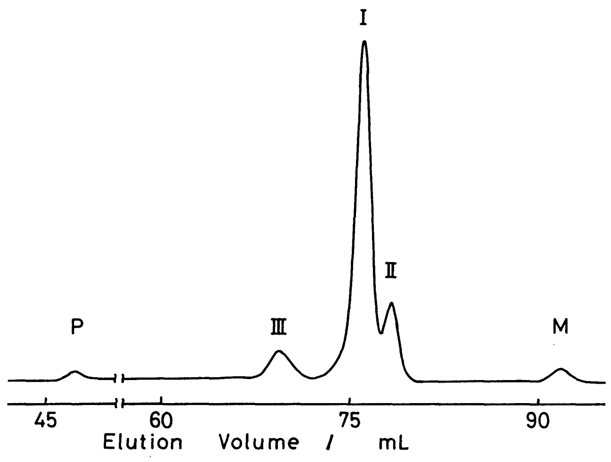


Fig. 2. GPC chromatogram of photoreaction products of **1e** (0.5 mol dm^{-3}) in benzene irradiated for 12 h.

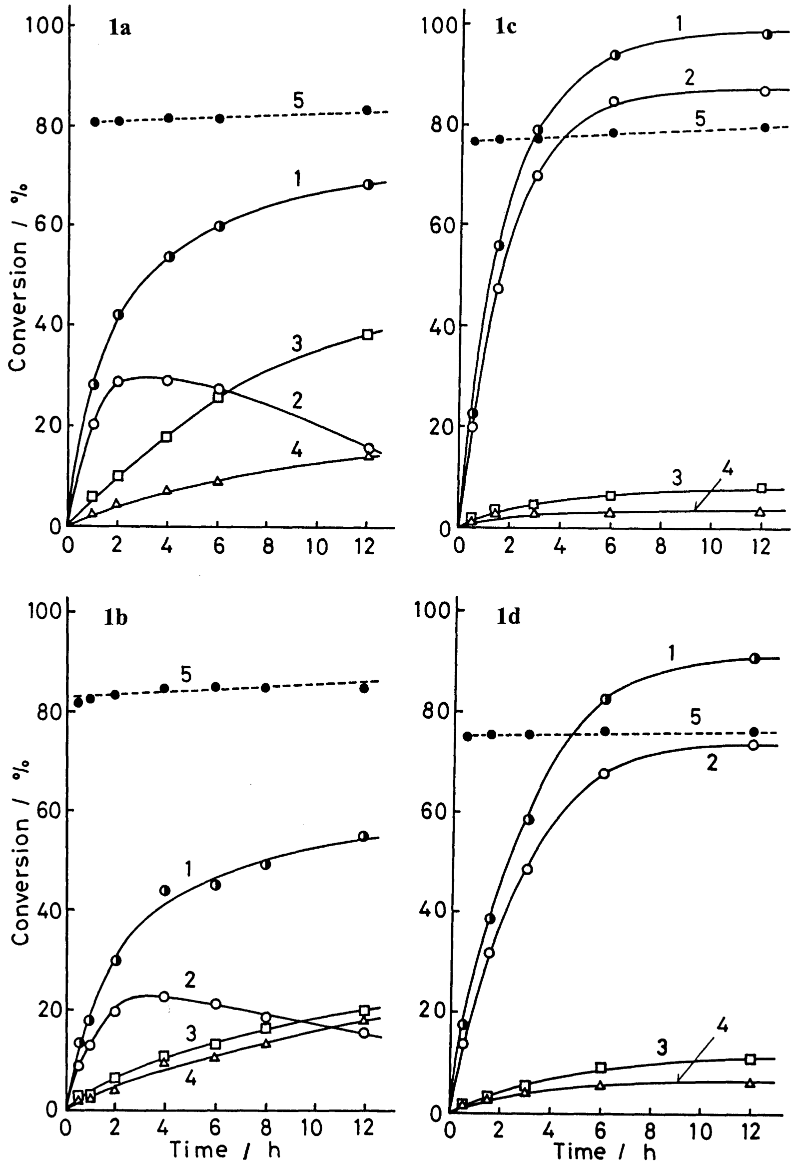


Fig. 3. Time-conversion plots of products in photoreactions of acylstyrenes **1a**—**1d** in benzene (0.5 mol dm^{-3}): (1) total products, (2) cyclodimers (**2**+**3**), (3) oligomers, (4) polymer, (5) fraction of *trans*-isomer in cyclodimers.

and *cis*-cyclobutane dimers (**2e** and **3e**), respectively. The third peak (III) is unidentified oligomers including trimers, and the last one (P) is the linear polymer ($MW\approx10^5$), and the peak (M) is the monomer (**1e**). Almost the same distribution pattern of photoproducts was observed for the reactions of the other acylstyrenes. In the subsequent analyses, therefore, the photoreaction was followed by GPC using the same procedure as that of the previous work;[7] that is, the chromatogram was divided into four areas: Dimers (I+II), oligomers (III), polymer (P), and monomer (M). The yield of the photoproducts was calculated on the basis of the total amount of products (I, II, III, and P) and monomer.

Figure 3 shows the time-conversion plots of photoproducts for **1a**—**1d**. In the cases of **1a** and **1b**, the cyclodimers are produced in preference to oligomers and polymer in the earlier stage of the photoreaction. However, the yield of cyclodimers reached a saturation point (20—30% at 2—3 h) and then it decreased with prolonged irradiation time, though the yields of oligomers and polymer increased. The reason for this decreasing was that the cyclodimers (**2a**,**b** and **3a**,**b**) were photochemically very unstable and underwent breakdown to the monomers($\Phi_M\approx0.5$).[19] The fraction of *trans*-form in the isomeric cyclodimers (100[**2**]/([**2**]+[**3**])) was 80—82% and it seemed to increase slightly with irradiation time. On the other hand, the photocyclodimerizations of **1c** and **1d** proceeded more preferentially, as can be seen from the figures. The yield finally reached about 80% of conversion. The fraction of *trans*-isomers in the cyclodimers seemed to be unchanged with irradiation time (ca. 77%). Almost the same result was obtained for the reaction of **1e**; after irradiation for 12 h, the yields of cyclodimers, oligomers, and polymer were 82% (*trans*-fraction, 78%), 11%, and 3%, respectively (Fig. 2). The selective formation of the cyclodimers observed in the reactions of **1c**—**1e** was attributable to the high photostability of the cyclodimers (**2c**—**e** and **3c**—**e**);[19] this was in contrast to the results obtained for **1a** and **1b**. The isomer ratios (trans : cis≈4 : 1) of the cyclodimers obtained here suggested that the photocyclodimerization of acylstyrenes **1a**—**e** proceeded via the triplet excited states.[2]

Quantum Yields of Photocyclodimerization. In order to determine the quantum yield of photocyclodimerization, the photoreaction (λ=365 nm, UV-D1A and CS0-52 filters) of acylstyrenes ([**1a**—**e**]=0.1 mol dm^{-3} in degassed benzene solution) was carried out under lower conversion (<6%) conditions. The time-conversion plots are shown in Fig. 4. Plots of the yields of cyclodimers for **1c**, **1d**, and **1e** are linear, whereas the plots for **1a** and **1b** are considerably curved even at low conversion below 3% because of the photocleavage reactions of the cyclodimers produced. The quantum yields (Φ_D) of the photodimerizations estimated from these results are summarized in Table 1. The values of Φ_D existed in a narrow range of 0.03—0.04; this suggested that the photoreactivities of acylstyrenes **1a**—**e** were not so largely affected by the acyl substituents.

The quantum yield of formation of initiating radicals for the polymerization of **1b** was estimated to be extremely low (ca. 2×10^{-4}) by considering the average molecular weight (ca. 10^5) of the polymer obtained under the same reaction conditions, as described previously.[7] The results of GPC analyses of the photoproducts (Figs. 2 and 3) suggested that the quantum yield for the production of oligomers was also very low (ca. 4×10^{-3}). Accordingly, the main reaction of the acylstyrenes by direct photoexcitation was cyclodimerization (Φ_D=3—4×10^{-2}). In the case of the photoreaction of styrene in bulk by direct singlet excitation, the quantum yields were reported to be 0.12 for the cyclobutane dimers and 5.6×10^{-4} for the initiating radicals of polymerization.[1] Photocyclodimerization is a bimolecular reaction involving attack of an excited molecule on a ground-state partner. Therefore, the rate of dimerization or the quantum yield depends on the concentration of the reactant. A plot of the reciprocal quantum yield of photocyclodimerization vs. the reciprocal concentration for **1c** was found to give a straight line, and a limiting quantum yield, Φ_D^∞=0.88, was obtained.[20] On the other hand, the plot for **1b** was somewhat curved because of the photocycloreversion of the dimers (**2b** and **3b**). Therefore, the exact value of Φ_D^∞ could not be determined. Detailed kinetic analysis including photocyclodimerization and photocycloreversion for **1b** is now under investigation.

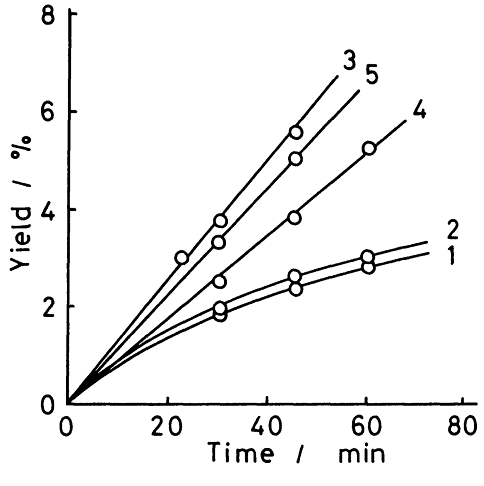


Fig. 4. Time-conversion plots for photocyclodimerization of acylstyrenes (0.1 mol dm^{-3}) in benzene: (1) **1a**, (2) **1b**, (3) **1c**, (4) **1d**, (5) **1e**.

Table 1. Quantum Yields of Photocyclodimerization[a)]

Acylstyrene	Φ_D
1a	ca. 0.03
1b	ca. 0.03
1c	0.042
1d	0.030
1e	0.037

a) [**1a**—**e**]=0.1 mol dm^{-3} in benzene, irradiated by 365 nm light at 297 K.

Emission Spectra. To elucidate the excited state of the acylstyrenes, measurements of the emission spectra were carried out in a rigid solution of MTHF at 77 K. For acetyl and benzoyl derivatives (**1a** and **1b**), neither fluorescence nor phosphorescence emission could be observed. It has been known that styrene gives no phosphorescence emission in spite of the considerable efficiency of intersystem crossing ($\Phi_{isc}\approx0.4$).[21] The lack of phosphorescence emission for **1a** and **1b** was thought to indicate that the lowest triplet state for the compounds was of the π,π^* configuration in contrast to that for acetophenone and benzophenone (n,π^*).[22] On the other hand, the naphthoyl derivatives (**1c** and **1d**) turned out to exhibit well-defined phosphorescence emission. The spectra and their decay curves are given in Figs. 5 and 6, respectively. Phosphorescene spectra of the model compounds, methyl 1-naphthyl ketone and phenyl 2-naphthyl ketone, were also measured for comparison, and the spectra are shown in Fig. 7.

As can be seen from Figs. 5 and 7, the spectra of **1c** and **1d** coincide in shape and position with those of their respective model compounds. The position of the maximum near the 0–0 band is at 503 nm (19900 cm^{-1}) for **1c** and at 482 nm (20700 cm^{-1}) for **1d** (Fig. 5), while it is at

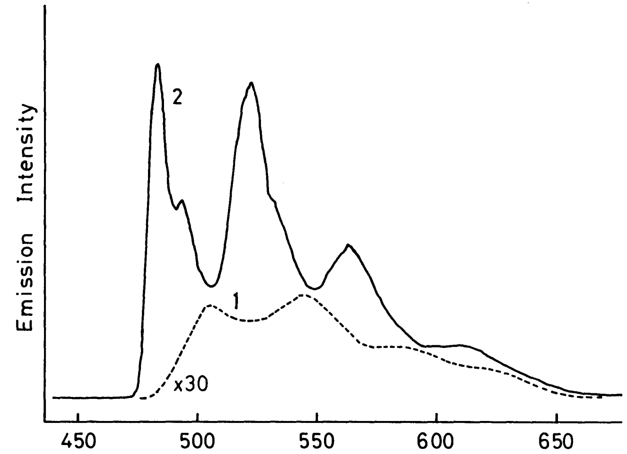


Fig. 5. Phosphorescence spectra of (1) **1c** and (2) **1d** in MTHF rigid solution at 77 K.

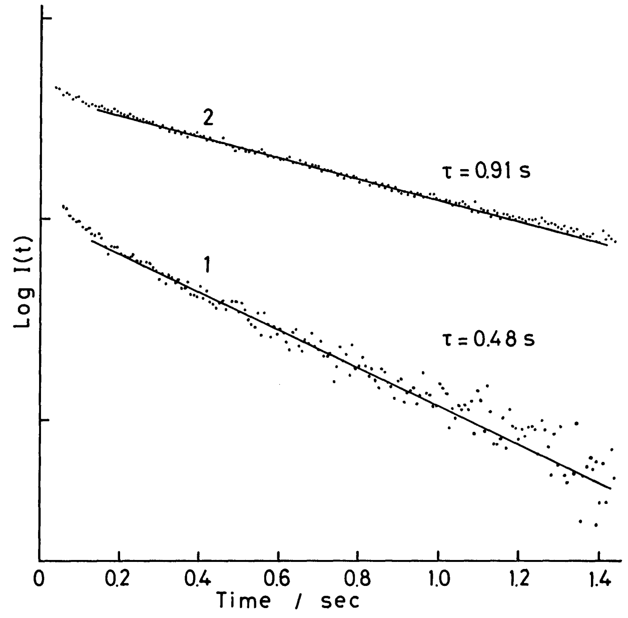


Fig. 6. Phosphorescence decay curves of (1) **1c** and (2) **1d** in MTHF rigid solution at 77 K.

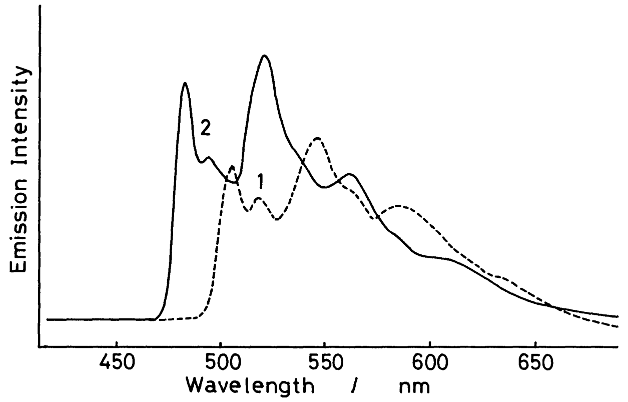


Fig. 7. Phosphorescence spectra of (1) methyl 1-naphthyl ketone and (2) phenyl 2-naphthyl ketone in MTHF rigid solution at 77 K.

505 nm for methyl 1-naphthyl ketone and at 482 nm for phenyl 2-naphthyl ketone (Fig. 7). It was reported by Yang et al.[23] that the positions of the 0–0 bands of 2-naphthaldehyde, methyl 2-naphthyl ketone, and phenyl 2-naphthyl ketone are at 480 nm within experimental error, while those of the 1-naphthyl series of ketones are at ca. 505 nm. This means that the lowest triplet state for a series of compounds bearing naphthoyl groups is almost unaffected by the substituents (–H, $-CH_3$, or $-C_6H_5$) on the opposite side of the carbonyl group from the naphthyl group; consequently, such a series of carbonyl compounds give almost the same phosphorescence spectra. It is also known that the lowest triplet state for naphthoyl compounds is π,π^* in nature.[24] From these considerations, it is thought that the phosphorescence spectra of **1c** and **1d** (Fig. 5) are attributable to the emission from the low-lying π,π^* triplet state in which the excitation energy (spin density) is localized on the naphthalene moiety of the molecules.[10] On the other hand, the emission intensity of **1c** was significantly weaker (about one eightieth) than that of **1d** as shown in Fig. 5, where the spectra were measured under the same experimental conditions. However, relatively long phosphorescence lifetimes (τ) of 0.48 s for **1c** and 0.91 s for **1d** were obtained (Fig. 6); these lifetimes are close to the reported values[15] of phenyl 1-naphthyl ketone (τ=0.74 s) and phenyl 2-naphthyl ketone (τ=1.16 s), respectively.

Transient Spectra. Measurements of the transient absorption spectra of **1b** and **1d** in a fluid solution of MTHF were carried out at 293 K by nanosecond laser photolysis. Although a reliable spectrum for **1b** failed to be obtained, the transient spectrum for 4-(2-naphthoyl)styrene **1d** was successfully measured. As shown in Fig. 8, the spectrum was characterized by a strong absorption below 400 nm and a weak absorption around 500 nm. The single exponential decay curve (λ=380 nm) in the figure gave a very short lifetime of ca. 23 ns. This spectrum of **1d** differs from the $T_1 \rightarrow T_n$ spectra of such naphthyl ketones as methyl 2-naphthyl ketone ($\lambda_{max}\approx 430$ nm, τ=94 μs in benzene)[25] and 4-ethylphenyl 2-naphthyl ketone ($\lambda_{max}\approx 430$ nm in MTHF).[14,19] Bonneau[21] has noted that styrene exhibits relatively strong transient absorption due to the short-lived "ethylenic" triplet state ($^3P^*$)[26] in the region of 320—345 nm; λ_{max} has been estimated to be shorter than 325 nm, though the spectrum has not been represented. The short lifetime observed here for **1d** is very close to those of the triplet states of styrene ($\tau\approx 25$ ns)[21] and 4-methoxystyrene ($\tau\approx 22$ ns).[27] From these facts, it seems that the transient spectrum of **1d** (Fig. 8) may be attributed to the π,π^* triplet state in which

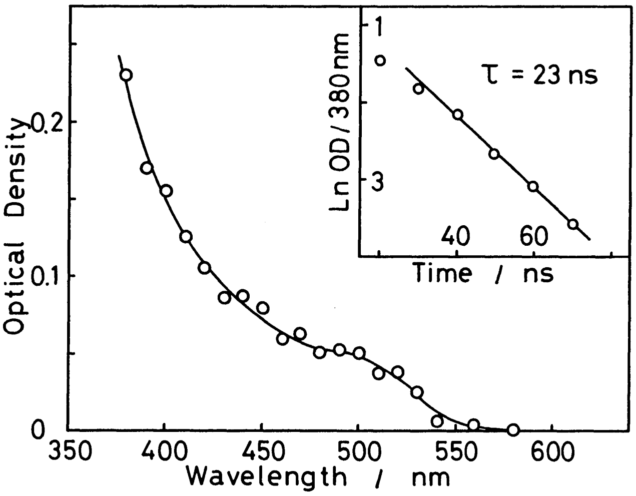
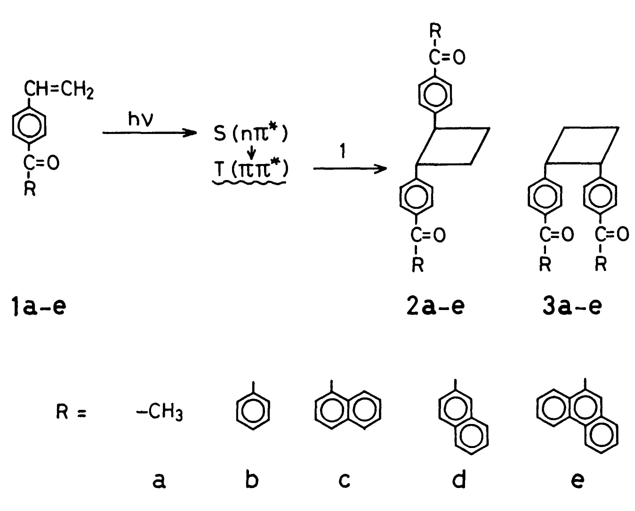


Fig. 8. Transient absorption spectrum of **1d** observed immediately after excitation and its decay plot in a fluid solution of MTHF at 293 K by nanosecond laser photolysis.

the excitation is mainly localized on the styrene moiety rather than on the naphthalene moiety in the molecule.

Discussion

As described above, direct photoirradiation of acylstyrenes (**1a**—**e**) having aryl ketone structures resulted in the formation of *trans*- and *cis*-cyclobutane dimers (**2a**—**e** and **3a**—**e**) as major products (Scheme 1). In these photocyclodimerizations, *trans*-cyclodimers were produced in preference to *cis*-cyclodimers (trans/cis≈4/1). It is well-known that the photocyclodimerization of aromatic olefins such as styrenes,[1-3] vinylnaphthalenes,[4] indene,[28] and acenaphthylene[29] obeys the excited spin-state mechanism; that is, the singlet excited state gives *cis*-cyclodimer via an excimer, whereas the triplet excited state produces predominantly *trans*-cyclodimer via a 1,4-biradical. The photocyclodimerization of **1a**—**e**, therefore, is thought to proceed stepwise through a 1,4-biradical produced by the addition of an excited π,π* triplet acylstyrene to another ground-state molecule; the ring-closure reaction of the 1,4-biradical preferentially produces thermodynamically more stable *trans*-cyclodidmers(**2a**—**e**) rather than *cis*-isomers (**3a**—**e**).



Scheme 1.

The excited singlet acylstyrenes (**1a**—**e**) are likely to undergo efficient intersystem crossing into the π,π* triplet state. The n,π* singlet energy on the carbonyl group for **1a** and **1b** directly flows into the π,π* triplet state on the styrene moiety, but this is not necessarily the case for other acylstyrenes (**1c**—**e**) which contain more widespread π-chromophores than a benzoyl group as an acyl substituent. The results of spectroscopic measurements suggest that two distinct low-lying π,π* triptet states are present for naphthoylstyrenes (**1c**, **d**); one is the triplet state $T_N(\pi,\pi^*)$ localized on the naphthalene (N) moiety and another is the triplet state $T_S(\pi,\pi^*)$ localized on the styrene (S) moiety. Naphthoylstyrenes have two different chromophores, the styrene and naphthalene moieties, which are formally conjugated with the central carbonyl group. In the first approximation for the excited triplet state of this type of molecule, the styrene and naphthalene moieties can be taken as independent chromophores.[10,24] The values of the lowest triplet energy (E_T) for styrene and naphthalene were reported to be 21600 and 21180 cm^{-1}, respectively; the difference is very small (ca. 400 cm^{-1}).[30] From the reported values of E_T and absorption data (Fig. 1), the relative energy levels of the excited states for naphthoylstyrenes can be estimated as shown in Fig. 9. The $T_N(\pi,\pi^*)$ state is the lowest triplet state, which corresponds to the emitting state observed in frozen media by phosphorescence spectrum (Figs. 5 and 6). The $T_S(\pi,\pi^*)$ state, which

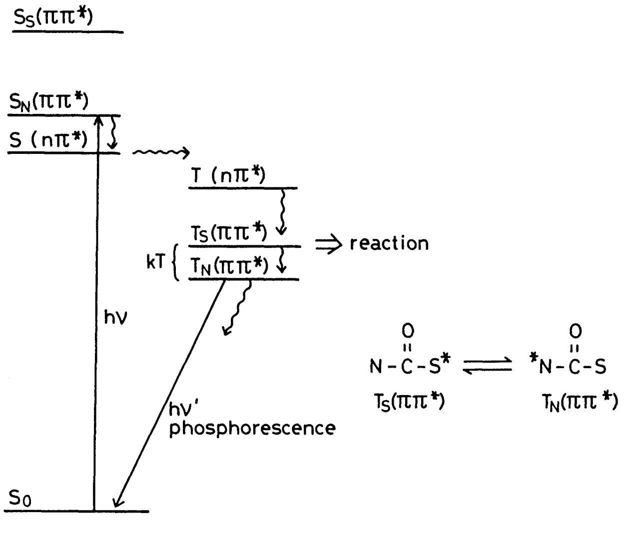
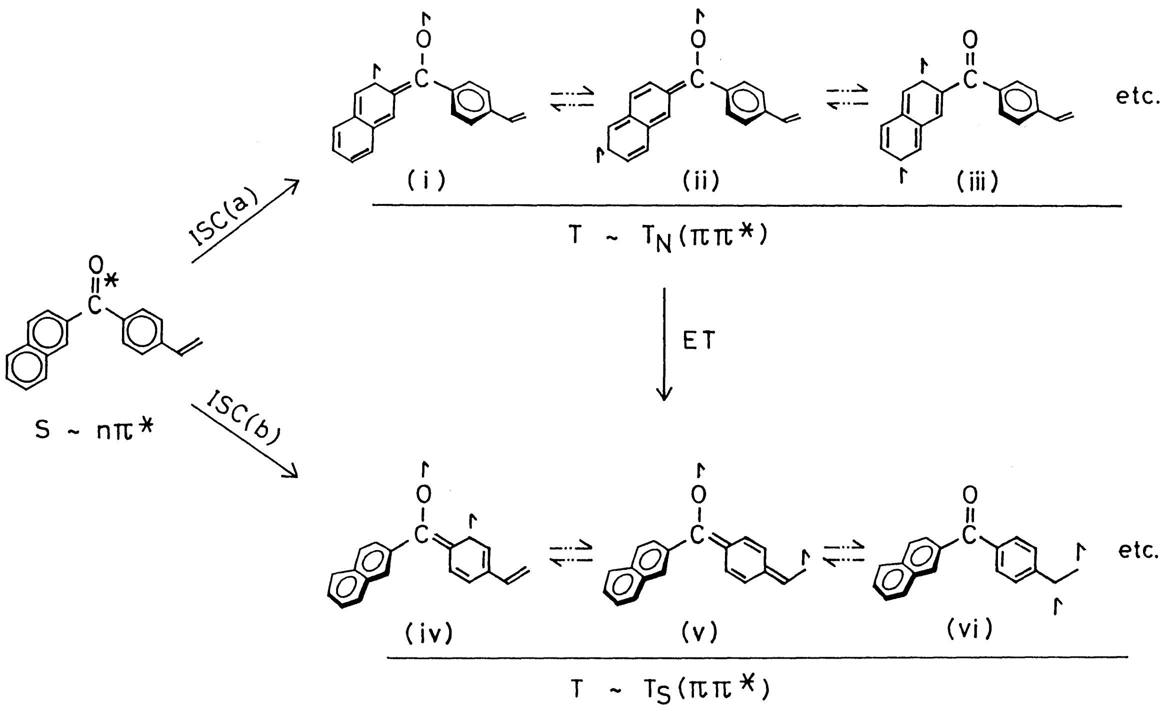


Fig. 9. Proposed state diagram and two possible low-lying π,π* triplet states for naphthoylstyrenes (**1c** and **1d**). $T_N(\pi,\pi^*)$ and $T_S(\pi,\pi^*)$ represent the triplet states localized on the naphthalene moiety (N) and on the styrene moiety (S) of the molecule, respectively.



Scheme 2.

corresponds to the reactive state for dimerization, is probably located on a level slightly higher than the $T_N(\pi,\pi^*)$ level.

In frozen media, the naphthoylstyrene (**1c**, **d**) molecules are caged in a rigid matrix and are expected to retain the same geometry in both the ground and excited states.[31] The excited triplet molecule of methyl 2-naphthyl ketone has been proposed to have a major contributing structure like the triplet species (**i**) shown in Scheme 2.[10] In frozen media, therefore, the naphthoyl moiety of **1d** has a coplanar structure where the carbonyl group is conjugated with the naphthyl group, so that the naphthoylstyrene readily undergoes intersystem crossing to produce the $T_N(\pi,\pi^*)$ state (ISC-**a** in Scheme 2). The presence of the absorption band around 330 nm due to the $\pi \rightarrow \pi^*$ transition of the naphthoyl moiety (Fig. 1) indicates that the carbonyl group is essentially conjugated with the naphthyl group in fluid media as well.[8] The carbonyl group in **1c**, **d** seems to be hardly cross-conjugated with the styrene moiety instead of the naphthalene moiety, considering the high singlet energy of styrene (ca. 34700 cm^{-1})[22] compared with that of naphthalene (ca. 31000 cm^{-1}).[30] Accordingly, the direct intersystem crossing into the $T_S(\pi,\pi^*)$ state (ISC-**b** in Scheme 2) may be ruled out. On the other hand, a triplet state like $T_N(\pi,\pi^*)$ would be normally expected to exhibit its characteristic transient spectrum with a relatively long lifetime ($\tau \approx 100\,\mu s$).[25] However, the transient spectrum observed for **1d** (Fig. 8) has been attributable to the very short-lived $T_S(\pi,\pi^*)$ state ($\tau \approx 25$ ns) rather than the $T_N(\pi,\pi^*)$ state, as described in the preceding section. It is, therefore, thought that in the triplet state, the fast intramolecular transfer of triplet energy takes place from the $T_N(\pi,\pi^*)$-naphthalene moiety to the $T_S(\pi,\pi^*)$-styrene moiety, and the cyclodimerization is initiated from the latter "ethylenic" triplet state (**v** and/or **vi** in Scheme 2).[21,26] Since the energy gap between the two states is estimated to be very small ($\Delta E \approx kT$), the intramolecular energy transfer to the "loose-bolt" reactive site would occur efficiently even with a little change in conformation.[10] This reflects the fact that the quantum yields of dimerization for **1c**,**d** are not lowered by the presence of the π-chromophores in the acyl moiety (Table 1); when such energy transfer fails to occur, the excitation energy is released within the π-chromophores, and consequently the dimerization reaction will not be induced.

In addition, the photophysical and photochemical properties for **1e** would be almost the same as those described above for **1c**,**d**, because E_T of phenanthrene (21600 cm^{-1}) is equal to that of styrene.[30] In the case of acylstyrene containing another acyl π-chromophore of much lower triplet energy such as anthracene (E_T= 14900 cm^{-1}) or pyrene (E_T=16900 cm^{-1}),[30] it can be presumed that the excitation energy on the π-chromophore is unable to transfer to the reactive $T_S(\pi,\pi^*)$ state located at a much higher energy level, and hence the efficiency of photodimerization will be extremely depressed.[19] Thus, the photocyclodimerization of aroylstyrenes **1c**—**e** is thought to be one of the typical photoreactions involving an intramolecular triplet energy transfer between conjugated chromophores.[10]

The authors wish to thank Professor Kimio Isa of Fukui University and Associate Professor Yoshio Wada of Kyoto Institute of Technology for their kind help in measuring the MS and phosphorescence spectra.

References

1) H. F. Kauffman, *Makromol. Chem.*, **180**, 2649, 2665, 2681, 2695 (1979).

2) W. G. Brown, *J. Am. Chem. Soc.*, **90**, 1916 (1968); F. R. Mayo, *ibid.*, **90**, 1289 (1968).

3) M. Yamamoto, T. Asanuma, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, **1975**, 53; T. Asanuma, M. Yamamoto, and Y. Nishijima, *ibid.*, **1975**, 56, 608; T. Gotoh, M. Yamamoto, and Y. Nishijima, *Polym. Bull.*, **2**, 357 (1980); A. Tsuchida, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 239; *Bull. Chem. Soc. Jpn.*, **60**, 2899 (1987).

4) Y. Shirota, A. Nishikata, T. Aoyama, J. Saimatsu, S.-C. Oh, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, **1986**, 64; K. Yamaguchi, S.-C. Oh, and Y. Shirota, *Chem. Lett.*, **1986**, 1445; S.-C. Oh, K. Yamaguchi, and Y. Shirota, *Polym. Bull.*, **18**, 99 (1987).

5) A. Ledwith, *Acc. Chem. Res.*, **5**, 133 (1972); S. Farid and S. E. Shealer, *J. Chem. Soc., Chem. Commun.*, **1973**, 677; Y. Yamamoto, M. Irie, Y. Yamamoto, and K. Hayashi, *J. Chem. Soc., Perkin Trans. 2*, **1979**, 1517; T.Majima, C. Pac, and H. Sakurai, *ibid*, **1980**, 2705; K. Mizuno, H. Ueda, and Y. Otsuji, *Chem. Lett.*, **1881**, 1237.

6) T. Li, A. B. Padias, and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **23**, 3899, 3904 (1990), and references cited therein.

7) K. Tsubakiyama, M. Yamamoto, and Y. Nishijima, *J. Polym. Sci. A: Polym. Chem.*, **26**, 1231 (1988).

8) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, New York (1966), p. 308; C. Parkanye, E. J. Baum, J. Wyatt, and J. N. Pitts, Jr., *J. Phys. Chem.*, **73**, 1132 (1969); D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).

9) D. K. Bredereck, T. Forster, and H. Oesterlin, "Luminescence of Organic and Inorganic Materials," ed by H. Kallman and G. Spruch, John Wiley & Sons, New York (1962), p. 161; A. P. Marchetti and D. R. Kearns, *J. Am. Chem. Soc.*, **89**, 769 (1967).

10) N. J. Turro, "Modern Molecular Photochemistry," Benjamin/Cummings Pub., Menlo Park, CA (1978), Chaps. 9 and 10.

11) S. Ito, H. Katayama, and M. Yamamoto, *Macromolecules*, **21**, 2456 (1988).

12) A.Tsuchida, M. Yamamoto, and Y. Nishijima, *J. Phys. Chem.*, **88**, 5062 (1984).

13) W. O. Kenyon and G. P. Waugh, *J. Polym. Sci.*, **32**, 83 (1958).

14) K. Tsubakiyama, M. Kuzuba, K. Yoshimura, M. Yamamoto, and Y. Nishijima, *Polym. J.*, **23**, 781 (1991).

15) S. L. Murov, "Handbook of Photochemistry," Mercel Dekker, New York (1973).

16) T. Nakano, A. Martin, C. Rivas, and C. Pérez, *J. Heterocycl. Chem.*, **14**, 921 (1977); H. Nozaki, I. Otani, R. Noyori, and M. Kawanisi, *Tetrahedron*, **24**, 2183 (1968).

17) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," John Wiley & Sons, New York (1969), Chap. 12; C. J. Seliskar, O. S. Khalil, and S. P. McGlynn, *Excited States*, **1**, 231 (1974).

18) M. A. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1958).

19) K. Tsubakiyama, K. Miyagawa, M. Yamamoto, and Y. Nishijima, Symposium on Photochemistry, Tsukuba, October 1983, Abstr., p. 393; to be published in this journal.

20) K.Tsubakiyama, M. Yabuno, and M. Yamamoto, The 37th Annual Meeting of Hokuriku Branch of the Society of Polymer Science Japan, Fukui, October 1988, Abstr., p. 7.

21) R. Bonneau, *J. Am. Chem. Soc.*, **104**, 2921 (1982); *J. Photochem.*, **10**, 439 (1979).

22) P. M. Crosby, J. M. Dyke, J. Metcalfe, A. T. Rest, K. Salisbury, and J. R.Sodeau, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 182; A. L. Lyons, Jr. and N. J. Turro, *J. Am. Chem. Soc.*, **100**, 3177 (1978); D. A. Condirston and J. D. Laposa, *Chem. Phys. Lett.*, **63**, 313 (1979).

23) N. C. Yang, M. Nussin, M. J. Jorgenson, and S. Murov, *Tetrahedron Lett.*, **1964**, 3657.

24) V. Ermolaev and A. Terenin, *J. Chim. Phys.*, **55**, 698 (1958); D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

25) M. Sumitani, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **51**, 2503 (1978); D. I. Schuster and M. D. Goldstein, *Mol. Photochem.*, **7**, 209 (1976).

26) M. C. Bruni, F. Momicchioli, I. Baraldi, and J. Langlet, *Chem. Phys. Lett.*, **36**, 484 (1975); J. Michl, *Photochem. Photobio.*, **25**, 141 (1977).

27) R. A. Caldwell and C. V. Cao, *J. Am. Chem. Soc.*, **104**, 6174 (1982); *ibid.*, **103**, 3594 (1981); R. A. Caldwell and C. Pac, *Chem. Phys. Lett.*, **64**, 303 (1979).

28) G. O. Schenck, W. Hartmann, S. P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962).

29) D. O. Kwan and J. C. Kozian, *J. Am. Chem. Soc.*, **97**, 249 (1975): R. Livingston and K. S. Wei, *J. Phys. Chem.*, **71**, 541 (1967).

30) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London (1970), p. 256.

31) D. Sen, B. K. Manna, and S. C. Bera, *J. Photochem. Photobiol. A: Chem.*, **60**, 101 (1991); R. Debnath and S. C. Bera, *J. Phys. Chem.*, **84**, 2623 (1980); K. Bhattacharyya, D. Roy, and M. Chodhury, *J. Lumin.*, **22**, 95 (1980).