methylcyclooct-4-en-1-ol (**3**): IR (thin film) 3370 (m br), 3040 (w), 2960 (s), 2920 (s), 2850 (s), 1470 (m), 1440 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 3 H), 1.5–1.9 (m, 6 H), 1.72 (br s, 3 H), 2.0–2.5 (m, 4 H), 2.08 (s, 1 H), 5.5 (m, 1 H); ^{13}C NMR (C_6D_6) δ 23.0, 24.3, 24.5, 30.4, 31.5, 37.5, 43.7, 73.4, 125.5, 135.7; high resolution mass spectrum ($^-$OH neg. ion), calcd for (m − 1) $C_{10}H_{17}O$ 153.12794, found 153.1266.

***exo*-2,6-Dimethyl-9-oxabicyclo[4.2.1]nonan-2-ol (4a).** A solution of 138 mg (0.895 mmol) of 1,5-dimethylcyclooct-4-en-1-ol in 15 mL of methylene chloride containing 700 mg of Celite was charged with 386 mg (1.79 mmol) of pyridinium chlorochromate and 0.16 mL (2.69 mmol) of acetic acid, and this mixture was heated to reflux under argon for 2 days. The reaction mixture was diluted with 20 mL of a mixture of ether and petroleum ether (1:1), and this was passed through a column containing 10 g of alumina. The column was rinsed with an additional 50 mL of the mixture of ether and petroleum ether, and the eluate was concentrated. The crude product was purified by flash chromatography (5 g of silica; ether/petroleum ether (1:1)) to yield 72 mg (47%) of *exo*-2,6-dimethyl-9-oxabicyclo[4.2.1]nonan-2-ol (**4a**) as a pale yellow oil: IR (thin film) 3550 (w), 3450 (m br), 2960 (s), 2920 (s), 2860 (s), 1470 (w), 1450 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 3 H), 1.34 (s, 3 H), 1.4–2.2 (m, 10 H), 2.92 (br s, 1 H), 4.05 (br dd, 1 H, J = 5.1, 9.7 Hz); ^{13}C NMR (C_6D_6) δ 19.6, 24.5, 26.9, 29.1, 39.4, 41.9, 42.5, 73.8, 81.4, 87.5; high resolution mass spectrum (EI), calcd for $C_{10}H_{18}O_2$ 170.13068, found 170.1308.

***endo*-2,6-Dimethyl-9-oxabicyclo[4.2.1]nonan-2-ol (4b).** A solution of tetramethylzirconium[12] was prepared by slowly adding 6.3 mL (8.84 mmol) of 1.4 M methyllithium in ether to a flame-dried flask containing 515 mg (2.21 mmol) of zirconium tetrachloride at −20 °C under argon. The mixture was stirred for 20 min at −20 °C, at which time a solution of 155 mg (1.01 mmol) of 1-methyl-9-oxabicyclo[4.2.1]nonan-5-one (**2**) in a total of 3 mL of freshly distilled tetrahydrofuran was added. The reaction mixture was stirred for 1.5 h at −20 °C and was poured into 25 mL of 5% aqueous HCl. This mixture was extracted with 30 mL of ether, and the organic portion was extracted with 25 mL each of saturated aqueous sodium bicarbonate and brine. The ether solution was dried over sodium sulfate and concentrated to yield 155 mg (91%) of *endo*-2,6-dimethyl-9-oxabicyclo[4.2.1]nonan-2-ol (**4b**) as a pale yellow oil: IR (thin film) 3400 (m br), 2960 (s), 2920 (s), 2870 (m), 1475 (w), 1450 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 3 H), 1.35 (s, 3 H), 1.5–2.3 (m, 10 H), 2.4 (br s, 1 H), 4.05 (dd, 1 H, J = 3.8, 9 Hz); ^{13}C NMR (C_6D_6) δ 20.6, 26.8, 29.5, 30.2, 39.9, 40.3, 43.2, 73.8, 82.8, 86.4; high resolution mass spectrum (EI), calcd for $C_{10}H_{18}O_2$ 170.13068, found 170.1324.

***endo*-1,5-Dimethyl-9-oxabicyclo[6.1.0]nonan-5-ol (5) and *endo*-1,5-Dimethyl-9-oxabicyclo[3.3.1]nonan-2-ol (6).** A solution of 204 mg (1.32 mmol) of 1,5-dimethylcyclooct-4-en-1-ol (**3**) in 20 mL of methylene chloride containing 278 mg (3.31 mmol) of sodium bicarbonate at 0 °C was charged portionwise with 274 mg (3.31 mmol) of 85% *m*-chloroperoxybenzoic acid over 30 min and stirring was continued for 6 h at 0–15 °C. The reaction mixture was decanted and was extracted twice with 20 mL of saturated sodium bicarbonate and twice with 20 mL of brine. The organic solution was dried over magnesium sulfate and was concentrated to give 291 mg of crude product, which was purified (9 g of silica; ether/petroleum ether, 1:1) to yield 91 mg (40%) of *endo*-1,5-dimethyl-9-oxabicyclo[6.1.0]nonan-5-ol (**5**) as a pale yellow oil and 65 mg (29%) of *endo*-1,5-dimethyl-9-oxabicyclo[3.3.1]nonan-2-ol (**6**) as a pale yellow oil. Spectral data for **5**: IR (thin film) 3430 (s br), 2960 (s), 2920 (s), 2870 (s), 1470 (s), 1450 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6 H), 1.4–2.2 (m, 10 H), 2.33 (s, 1 H), 2.75 (m, 1 H); ^{13}C NMR (C_6D_6) δ 21.1, 21.5, 24.9, 30.6, 35.4, 36.4, 39.1, 59.7, 63.0, 70.9. Spectral data for **6**: IR (thin film) 3400 (s br), 2980 (s), 2940 (s), 1455 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 1.21 (s, 3 H), 1.4–2.3 (m, 10 H), 2.52 (s, 1 H), 3.59 (t, 1 H, J = 9 Hz); ^{13}C NMR (C_6D_6) δ 20.1, 28.6, 29.4, 30.0, 31.9, 35.1, 36.7, 69.6, 73.1, 74.5.

1,5-Dimethyl-9-oxabicyclo[3.3.1]nonan-2-one (7). A solution of 36 mg (0.211 mmol) of *endo*-1,5-dimethyl-9-oxabicyclo[3.3.1]nonan-2-ol (**6**) in 15 mL of methylene chloride containing 180 mg of Celite was charged with 91 mg (0.423 mmol) of PCC and stirred at room temperature for 1 day. The reaction mixture was diluted with 10 mL of a mixture of ether and petroleum ether (1:1), and this was passed through a column of 4 g of alumina. The column was eluted with a further 30 mL of the mixture of ether and petroleum ether, and the eluate was concentrated to yield 32 mg (89%) of 1,5-dimethyl-9-oxabicyclo[3.3.1]nonan-2-one (**7**) as a pale yellow oil: IR (thin film) 2960 (s), 2930 (s), 2860 (s), 1720 (s), 1450 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 3 H), 1.35 (s, 3 H), 1.3–2.3 (m, 8 H), 2.8 (m, 2 H); ^{13}C NMR (C_6D_6) δ 18.5, 24.9, 31.5, 31.7, 33.6, 34.8, 37.1, 70.3, 80.7, 217.0; high resolution mass spectrum ($^-$OH neg. ion), calcd for (m − 1) $C_{10}H_{15}O_2$ 167.10720, found 167.1048.

Acknowledgment. We thank J. P. Huang and B. Muñoz for their help in obtaining the ^{13}C NMR spectra. The high resolution mass spectra were provided by the Rockfeller University Mass Spectrometric Research Resource, Prof. F. H. Field, Director (supported by NIH grant #RR00862). We also acknowledge the support of our research by the NIH through grants #GM35652 and #RR07231.

Registry No. 1, 114969-42-5; 2, 108462-73-3; 3, 67103-48-4; 4a, 117711-93-0; 4b, 117734-16-4; 5, 117711-95-2; 6, 117711-94-1; 7, 117711-96-3; cyclooct-4-en-1-one, 6925-14-0; 1,5-dimethylcycloocta-1,5-diene, 3760-14-3; 1,5-dimethyl-9-oxabicyclo[6.1.0]non-4-ene, 56031-79-9.

Accelerated Photodimerization of Stilbenes in Methanol and Water

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Received June 10, 1988

Photodimerization of stilbenes **1a–f**, especially that of 4- and 3-acetylstilbenes (**1c** and **1d**, respectively), is more efficient when a hydroxylic solvent (methanol or water) is employed as the reaction medium than when a nonhydroxylic solvent (hexane, benzene, or acetonitrile) is employed. The stilbenes **1a–f** are more strongly fluorescent in methanol than in benzene. It is proposed that this accelerated photodimerization in the hydroxylic solvent originates from formation of a fluorescent solute–solute aggregate.

Strategies for application of hydrophobic interactions to organic syntheses have practical, mechanistic, and biological interests. As a result of the hydrophobic association of organic solutes in water, rates and selectivities of certain bimolecular reactions are profoundly changed by doing the reactions in aqueous medium. For example,

0022-3263/89/1954-0587$01.50/0

Table I. Photolyses of Stilbenes 1 and 2 in Different Solvents at Different Concentrations[a]

				percentage of products, %			
				cyclobutane dimers[c]		geometrical isomers	
run	Ar of 1 or 2	concn × 10^2, M	solvent[b] (v/v)	3 + 4	5 + 6	1	2
1	**a**, Ph	5.8	Hex–Bz (1:1)	4	2	48	46
2		5.9	MeOH–Bz(7:3)	6	3	53	38
3	**b**, *p*-MeC_6H_4	5.9	Bz	8	trace	47	45
4		5.8	MeOH–Bz(7:3)	9	trace	43	48
5	**c**, *p*-$MeCOC_6H_4$	5.8	Hex–Bz (1:1)	0	0	35	65
6		5.0	Bz	0	0	22	78
7		5.9	MeCN–Bz(1:1)	trace	0	20	80
8		5.8	MeOH–Bz(7:3)	31 (16 + 15)	0	16	53
9		0.66	Hex–Bz (1:1)	0	0	32	68
10		0.60	MeCN	0	0	22	78
11		0.63	MeOH	13	trace	16	71
12		0.01[d]	Bz	0	0	*e*	*e*
13		0.01[d]	MeCN	0	0	*e*	*e*
14		0.01[d]	MeOH	trace	0	*e*	*e*
15		0.01[d]	water	11 (5 + 6)	trace	*e*	*e*
16		–	solid	no reaction			
17	**d**, *m*-$MeCOC_6H_4$	5.8	Bz	0	0	18	73[f]
18		5.8	MeOH–Bz(7:3)	13	0	21	57[g]
19	**e**, *p*-NCC_6H_4	5.1	Bz	13 (9 + 4)	4 (2 + 2)	49	34
20		5.0	MeCN	5	1	37	57
21		5.1	MeOH	34 (22 + 12)	7 (4 + 3)	25	34
22		0.49	Bz	7	2	46	45
23		0.49	MeOH	19	4	32	45
24		0.02[d]	Bz	0	0	*e*	*e*
25		0.02[d]	MeOH	4	0	*e*	*e*
26		0.02[d]	water	57 (36 + 21)	23 (12 + 11)	*e*	*e*
27	**f**, *m*-NCC_6H_4	4.9	Bz	8	trace	47	45
28		4.9	MeOH	20	trace	32	48

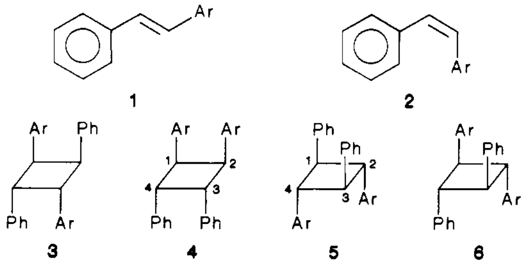
[a] Unless otherwise specified, a trans isomer **1** was employed as the starting compound. Irradiations were carried out with a 400-W high-pressure mercury lamp (Pyrex) for 8 h under bubbling nitrogen. [b] Hex, hexane; Bz, benzene; MeCN, acetonitrile. [c] Yields of the respective regioisomers are in parentheses. [d] A cis isomer **2** was used as the starting compound. [e] Not determined. [f] 2-Acetylphenanthrene (**7**) (2%) and 4-acetylphenanthrene (**8**) (7%) were formed.[21] [g] **7** (3%) and **8** (6%) were formed.[21]

several Diels–Alder reactions,[1] the benzoin condensation,[2] and photodimerizations of coumarins,[3] stilbenes,[4] alkyl cinnamates,[5] and thymines[6] have been found to proceed in water with a dramatically increased rate as compared with that in common organic solvents. In the area of photophysical studies, enhanced excimer (or exciplex) formation in aqueous media is frequently observed.[7]

In their brief paper, Ramamurthy et al. reported that stilbenes underwent photodimerization in water at very low concentrations (~10^{-4} M), whereas irradiation in benzene at such low concentrations gave no dimer.[4] We have now found that this photodimerization is prompted not only when water is the solvent but also when methanol is the solvent.

Results and Discussion

Product Distributions of Photolyses. A series of *trans*-stilbenes **1a–f** and *cis*-stilbenes **2c** and **2e** were dissolved in various organic solvents (5 × 10^{-2}–10^{-4} M) or water (~10^{-4} M) and irradiated with a 400-W high-pressure mercury lamp (Pyrex) for 8 h under bubbling nitrogen. Owing to the virtual insolubility of the trans isomers in water, only the cis isomers, which are usually more easily soluble than the trans counterparts,[8] were subjected to the irradiation in water. After photolyses, product mixtures were analyzed by HPLC and NMR. Along with the trans–cis isomerization (**1** ⇄ **2**), formation of the cyclobutane dimers (**3–6**) was found to occur, depending upon the reaction conditions. Compositions of the photoproducts are summarized in Table I.



cis-anti-cis all-trans

a, Ar = Ph; **b**, Ar = *p*-MeC_6H_4; **c**, Ar = *p*-$MeCOC_6H_4$; **d**, Ar = *m*-$MeCOC_6H_4$; **e**, Ar = *p*-NCC_6H_4; **f**, Ar = *m*-NCC_6H_4

In general, the yield for the cis-anti-cis dimers **3** and **4** is much higher than that for the all-trans dimers **5** and **6**. Particularly noteworthy is a contrasting result between the hydroxylic solvent (methanol and water) and the nonhydroxylic solvent (hexane, benzene, and acetonitrile). Thus in the hydroxylic media, dimers **3–6** are produced with reasonable efficiencies (runs 2, 4, 8, 11, 15, 18, 21, 23, 26, and 28). In particular, the photodimerizations of *cis*-4-acetylstilbene (**2c**) and *cis*-4-cyanostilbene (**2e**) proceed

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Table II. Absorption and Fluorescence Spectra of *trans*-Stilbenes 1a–f in Methanol and Benzene[a]

	absorptn max, nm (ε)		fluorescence max, nm (rel int)[b]		% of dimers (**3–6**)[c]	
compd	MeOH	Bz	MeOH	Bz	MeOH or MeOH–Bz	Bz or Bz–Hex
1a	295 (28 200) 307 (26 700)	299 (25 300) 311 (24 800)	349 (1.4)	351 (1.0)	9	6
1b	299 (24 700) 311 (24 100)	302 (22 100) 315 (22 200)	352 (1.4)	357 (1.0)	9	8
1c	326 (33 900)	328 (32 800)	432 (5.0)	*d*	31	0
1d	295 (30 200)	298 (26 200)	470 (0.7)	*d*	13	0
1e	319 (39 500)	324 (34 500)	379 (0.5)	375 (0.3)	41	17
1f	295 (29 800)	300 (25 300)	375 (8.1)	368 (0.7)	20	8

[a] Concentration 3–7 × 10^{-5} M at room temperature. [b] Relative intensity 1.0 for *trans*-stilbene (**1a**) in benzene. [c] From the data in Table I. [d] No fluorescence.

smoothly in water even at very low concentrations (~10^{-4} M) (runs 15 and 26), in line with the previous report.[4] In the nonhydroxylic media, however, the photodimerization is not efficient. Especially, the efficiencies for the acetyl derivatives **1c** and **1d** are essentially 0 in these solvents even under the high stilbene concentrations (~5 × 10^{-2} M) (runs 5–7 and 17).

Since *trans*-4-acetylstilbene (**1c**) is completely photostable as crystals (run 16), it is unlikely that the dimers **3c–6c** are formed through light absorption by the undissolved microcrystalline particle. Since the photodimerization is inefficient in polar acetonitrile (runs 7, 10, 13, and 20), the high polarity of the hydroxylic solvents (water and methanol) does not seem to be directly relevant to the reaction. As was previously proposed,[4] the efficient photodimerization in water may be attributed to the hydrophobic association of the stilbene molecules in aqueous solution. Probably a similar aggregative interaction of the solutes in methanol is also true to a certain extent.

It is known that the degree of a solute–solute interaction in solution (i.e., a hydrophobic interaction for aqueous solution) is related to an entropy of solution of the solute ΔS. A large negative value of ΔS is considered to reflect a strong solute–solute interaction.[9] Values of ΔS (cal K^{-1} mol^{-1}) when gaseous cyclohexane is dissolved in various solvents at 298 K are as follows: −21.5 (hexane), −20.5 (benzene), −21.5 (acetonitrile), −29.3 (methanol), −45.0 (water).[10] These data seem to indicate that the solute aggregation occurs not only in water but also in methanol to some extent, resulting in the enhanced photodimerization in the hydroxylic solvents.

Mechanistic Studies of Photodimerizations. Sensitized irradiation of 4-acetylstilbene (**1c**) in methanol in the presence of Michler's ketone, a triplet sensitizer, afforded no cyclobutane dimers. Only the trans–cis isomerization (**1c** ⇄ **2c**) was observable. Alternatively, added 2,5-dimethyl-2,4-hexadiene, a triplet quencher, had no effect on both the dimerization and trans–cis isomerization of **1c** in methanol. Similar results were obtained from sensitization and quenching experiments for 4-cyanostilbene (**1e**). Therefore, it appears that the photodimerization of **1c** and **1e** occurs from their excited singlet states, as is usually the case with stilbene derivatives.[11] The trans–cis isomerization of stilbenes is known to occur from either their excited singlet or triplet states.[12]

Absorption and fluorescence spectra of **1a–f** were measured in methanol and in benzene. The absorption and fluorescence maxima are somewhat solvent-dependent (Table II), and the spectra in methanol are slightly less structured than those in benzene (e.g., Figures 1 and 2). The relative fluorescence intensity and the total yield of the cyclobutane dimers are also listed in Table II. It is interesting to note here that for each compound both the fluorescence and the dimerization are more efficient in methanol than in benzene and, in benzene, nonfluorescent **1c** and **1d** give no dimers.

Since the photodimerization is even more efficient in water, the effect of addition of water on the fluorescence spectrum of **1c** in methanol was examined (Table III).

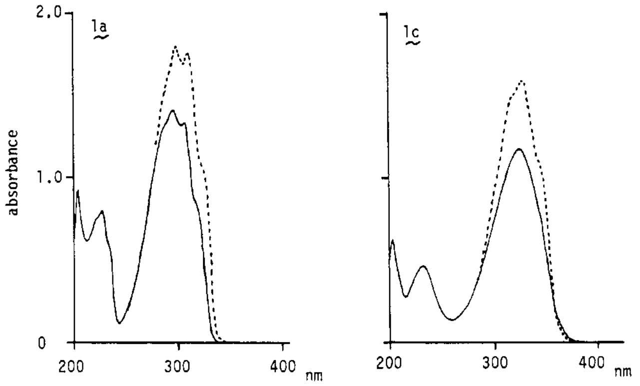

Figure 1. Absorption spectra of *trans*-stilbene (**1a**) and *trans*-4-acetylstilbene (**1c**) in methanol (—) and benzene (---); [**1a**] = 4.75 × 10^{-5} M in methanol and 7.10 × 10^{-5} M in benzene; [**1c**] = 3.44 × 10^{-5} M in methanol and 5.22 × 10^{-5} M in benzene.

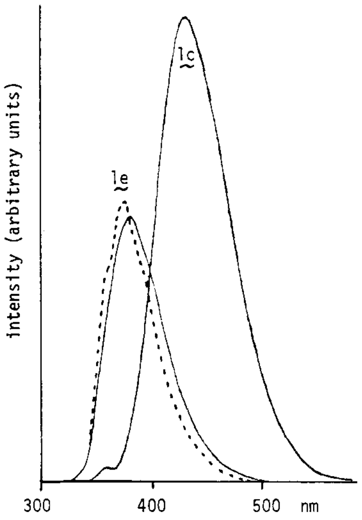

Figure 2. Fluorescence spectra of *trans*-4-acetylstilbene (**1c**) and *trans*-4-cyanostilbene (**1e**) in methanol (—) and benzene (---); concentration, ca. 5 × 10^{-5} M; excitation wavelength, 360 nm for **1c** and 340 nm for **1e**; **1c** is nonfluorescent in benzene.

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Table III. Effect of Addition of Water on the Fluorescence of *trans*-4-Acetylstilbene (1c) in Methanol (5.0 × 10^{-5} M)

solvent, vol %		fluorescence	
MeOH	water	maximum, nm	relative intensity
100	0	433	1.00
90	10	435	1.37
70	30	440	1.91
50	50	443	2.40
40	60	448	2.40
30	70	454	1.86

Besides a red shift in the fluorescence maximum, an increase in the fluorescence intensity was observed upon addition of water (up to 50 vol %). However, further addition of water led to a decrease in the intensity, possibly because of precipitation of a part of **1c**. The red shift with increasing solvent polarity (Table III) and the large apparent Stokes shift of the fluorescence for **1c** and **1d** in methanol (Table II) may indicate the possibility that the emission monitored in these cases is due to excimers[7] or, more likely, excited aggregates.

From the above results, it may be proposed that the observed acceleration in the photodimerization of **1a–f** in the hydroxylic solvents (methanol and water) (Table I) originates from formation of a fluorescent solute–solute aggregate.[13] The magnitude of the acceleration depends on the molecular structure: an especially remarkable promotion is observed for **1c** and **1d**.

Time Course for Photolyses. The time course for the photolysis of *trans*-4-cyanostilbene (**1e**) or *cis*-4-cyanostilbene (**2e**) in methanol was monitored by HPLC. When the reaction was started by irradiation of the trans isomer **1e**, the dimers **3e–6e** were formed immediately after irradiation (Figure 3a). By contrast, in the case of the photolysis of the cis isomer **2e** as the initial reactant, there was a time lag in the formation of the dimers (Figure 3b). This result suggests that the dimers **3e–6e** are formed from excitation of the trans isomer **1e** rather than from excitation of the cis isomer **2e**.

Structures of Cyclobutane Dimers. The dimers **3a** (=**4a**) and **5a** (=**6a**) are known.[15a] The dimes **3c**, **4c**, **3d**, **4d**, **3e**, **4e**, **5e**, and **6e** were isolated by column chromatography on silica gel and were characterized by ^{1}H NMR and mass spectroscopy.

Thus, the ^{1}H NMR spectra of the cyclobutane protons for the above compounds exhibited a characteristic A_2B_2 pattern (for **4c**, **3d**, **4d**, **4e**, and **5e**) or one four-proton singlet (for **3c**, **3e**, and **6e**). The A_2B_2 patterns for **4c**, **4e**, and **5e** were calculated by a personal computer.[16,17] It was found for **4c** and **4e** that $J_{12} = 11.0$, $J_{34} = 10.0$, $J_{14} = J_{23} = 8.0$, and $J_{13} = J_{24} = -0.1$ Hz. For **5e**, it was estimated that $J_{12} = J_{23} = J_{34} = J_{14} = 10.0$ and $J_{13} = J_{24} = 0.0$ Hz. According to the literature,[15b] coupling constants for stilbene dimers are $J_{12\text{cis}} = 10$, $J_{12\text{trans}} = 6.5$, and $J_{13} \sim 0$ Hz. Therefore, the J values for **4c**, **4e**, and **5e** are consistent with their assigned structures.

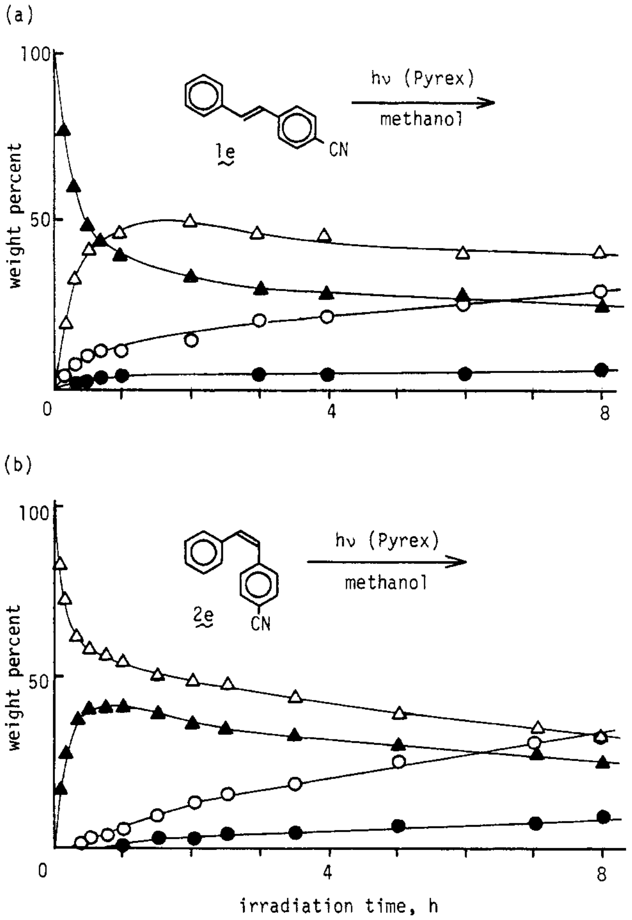
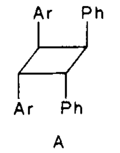


Figure 3. Time course for the photolysis of (a) *trans*-4-cyanostilbene (**1e**) and (b) *cis*-4-cyanostilbene (**2e**) in methanol. The initial concentrations of **1e** and **2e** are 4.9 × 10^{-2} M; ▲, trans (**1e**); △, cis (**2e**); ○, cis-anti-cis (**3e** + **4e**); ●, all trans (**5e** + **6e**).

Unambiguous differentiation between the cis-anti-cis structure (**3** and **4**) and the all-trans structure (**5** and **6**) was made by the difference in the chemical shift of the cyclobutane protons (see Experimental Section). It is reported that the cyclobutane protons of stilbene dimers appear around δ 4.5 for the cis-anti-cis adducts and around δ 3.7 for the all-trans adducts.[4,15] Distinction between the head-to-tail structure (**3** and **5**) and the head-to-head structure (**4** and **6**) was done by mass spectroscopy.[15c] The mass spectra of the head-to-tail adducts (**3c**, **3e**, **5e**) gave a peak corresponding to [PhCH=CHAr]$^{\bullet+}$, while those of the head-to-head adducts (**4c**, **4e**, **6e**) gave additional peaks corresponding to [PhCH=CHPh]$^{\bullet+}$ and [ArCH=CHAr]$^{\bullet+}$. Although the structure A is also possible for the cis-anti-cis dimer **4**, this possibility seems to be less likely, since the photodimerization occurs only from excitation of the *trans*-stilbenes (Figure 3). In general, stilbene cycloaddition with alkenes proceeds with retention of stereochemistry.[18]



A

Attempts to isolate other dimers were not carried out. They were characterized by the ^{1}H NMR spectra of the mixtures.

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[13] Solute–solvent complexation in the ground and excited states in alcoholic solvents is often claimed to occur.[14] Interpretation of our results in terms of such a complex formation cannot be ruled out.

[14] (a) Tanimoto, Y.; Inoue, K.; Furukawa, Y.; Segawa, Y.; Itoh, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1601. (b) Tamaki, T. *Ibid.* **1982**, *55*, 3321. (c) Suter, G. W.; Wild, U. P.; Schaffner, K. *J. Phys. Chem.* **1986**, *90*, 2358.

[15] (a) Shechter, H.; Link, W. J.; Tiers, V. D. *J. Am. Chem. Soc.* **1963**, *85*, 1601. (b) Ulrich, H.; Rao, D. V.; Stuber, F. A.; Sayigh, A. A. R. *J. Org. Chem.* **1970**, *35*, 1121. (c) Green, B. S.; Heller, L. *Ibid.* **1974**, *39*, 196. (d) Laarhoven, W. H.; Cuppen, T. J. H. M.; Nivard, R. J. F. *Tetrahedron* **1970**, *26*, 1069.

[16] A computer program LAOCOON III[17] was used after modification for our personal computer NEC PC-9801 VM21.

[17] Bothner-By, A. A.; Castellano, S. In *Computer Programs for Chemistry*; De Tar, D. F., Ed.; Benjamin: New York, 1968; Vol, 1, p 10.

[18] Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152.

Experimental Section

^{1}H NMR spectra were measured on a Varian FT-80A, Varian Gemini-200, or JEOL GX-400 spectrometer with $CDCl_3$ as the solvent. IR, UV, emission, and mass spectra were recorded with JASCO FT/IR-5M, JASCO UVIDEC-610, Shimadzu RF-500, and JEOL JMS-DX 300 spectrometers, respectively.

Photolyses in Organic Solvents. Solutions containing 0.01–6 × 10^{-2} M of *trans*-stilbenes **1a–f** or *cis*-stilbenes **2c** and **2e** in various organic solvents (10–100 mL) were irradiated with a 400-W high-pressure mercury lamp through a Pyrex filter. All the irradiations were carried out for 8 h under bubbling nitrogen. The reaction mixtures were analyzed by HPLC (JASCO Twincle, Cosmosil $5C_{18}$ 4.6 × 150 mm, $MeOH-H_2O$) and/or NMR.

Photolyses in Water. Solutions containing ~10^{-4} M of *cis*-stilbenes **2c** and **2e** in water (100 mL) were ultrasonicated (Branson B-220) for 0.5 h at ambient temperature. Irradiations and analyses were done in a similar manner to that described above.

Sensitization. A solution containing 4-acetylstilbene (**1c**) (5.9 × 10^{-3} M) and Michler's ketone (5.9 × 10^{-2} M) in 20 mL of MeOH–benzene (7:3 v/v) was irradiated with a 400-W high-pressure mercury lamp through a Riko U-360 glass filter (mainly 366 nm). The irradiation was performed for 40 h under bubbling nitrogen, and the reaction was followed by HPLC. The trans–cis isomerization was observed, reaching a photostationary state after 13 h of the irradiation (**2c**/**1c** = 1.3). The cyclobutane dimers were undetectable even after 40 h.

Quenching. A solution containing 4-acetylstilbene (**1c**) (9.8 × 10^{-3} M) and 2,5-dimethyl-2,4-hexadiene (4.9 × 10^{-2} M) in methanol (20 mL) was irradiated with a 400-W high-pressure mercury lamp through a Pyrex filter (>280 nm). The irradiation was continued for 0.5 h under bubbling nitrogen, and the reaction was monitored by HPLC. The trans–cis isomerization was observed and reached a photostationary state after 13 min of the irradiation (**2c**/**1c** = 5.2). The yield of the cyclobutane dimers **3c** and **4c** increased gradually with the irradiation time (final yield, 5.2%).

An essentially indistinguishable result was obtained by irradiation in the absence of the diene quencher.

Isolation of Cyclobutane Dimers. Reaction mixtures obtained from irradiations of **1c–e** (~5 × 10^{-2} M) in methanol or methanol–benzene (7:3 v/v) were separated by repeated column chromatography on silica gel (Wako gel C-200) to furnish corresponding cyclobutane dimers **3–6** in a satisfactory purity. An attempt to obtain an analytically pure sample was not carried out. Physical and spectroscopic data are as follows.

3c: oil; ^{1}H NMR (400 MHz) δ 2.51 (6 H, s), 4.53 (4 H, s, cyclobutane), 7.08-7.20 (14 H, m), 7.74 (4 H, d,[19] J = 8.4 Hz); MS, m/e (relative intensity) 222 ($M^+/2$, 100); UV (MeOH) λ 262 (ϵ 34 000) nm; IR (KBr) 1681 cm^{-1}.

4c: oil; ^{1}H NMR (400 MHz) δ 2.51 (6 H, s), 4.49–4.52 and 4.55–4.58 (4 H, A_2B_2, cyclobutane), 7.08–7.21 (14 H, m), 7.74 (4 H, d,[19] J = 8.4 Hz); MS, m/e (relative intensity) 264 (0.3), 222 ($M^+/2$, 100), 180 (4); UV (MeOH) λ 255 (ϵ 29 000) nm; IR (KBr) 1682 cm^{-1}.

3d or **4d**: oil; ^{1}H NMR (400 MHz) δ 2.46 (6 H, s), 4.49–4.60 (4 H, A_2B_2, cyclobutane), 7.05–7.18 (10 H, m), 7.21–7.31 (4 H, m), 7.66 (2 H, d,[19] J = 7.6 Hz), 7.68 (2 H, s[19]); MS, m/e (relative intensity) 222 ($M^+/2$, 100).

3d or **4d**: oil; ^{1}H NMR (400 MHz) δ 2.47 (6 H, s), 4.52–4.58 (4 H, A_2B_2, cyclobutane), 7.06–7.18 (10 H, m), 7.21–7.30 (4 H, m), 7.64 (2 H, d,[19] J = 7.6 Hz), 7.72 (2 H, s[19]); MS, m/e (relative intensity) 222 ($M^+/2$, 100).

3e: white solid melted at 68–69 °C; ^{1}H NMR (400 MHz) δ 4.50 (4 H, s, cyclobutane), 7.04–7.21 (14 H, m), 7.42 (4 H, d,[19] J = 8.4 Hz); MS, m/e (relative intensity) 410 (M^+, 0.2), 205 (100);[20] UV (MeOH) λ 243 (ϵ 34 000) nm; IR (KBr) 2227 cm^{-1}.

4e: white solid melted at 59–62 °C; ^{1}H NMR (400 MHz) δ 4.43–4.46 and 4.54–4.57 (4 H, A_2B_2, cyclobutane), 7.05–7.20 (14 H, m), 7.46 (4 H, d,[19] J = 8.5 Hz); MS, m/e (relative intensity) 410 (M^+, 0.3), 230 (0.2), 205 (100), 180 (4); UV (MeOH) λ 236 (ϵ 32 000) nm; IR (KBr) 2227 cm^{-1}.

5e: oil; ^{1}H NMR (200 MHz) δ 3.55–3.77 (4 H, A_2B_2, cyclobutane), 7.2–7.35 (14 H, m), 7.57 (4 H, d, J = 8.4 Hz); MS, m/e (relative intensity) 410 (M^+, 0.05), 205 (100);[20] UV (MeOH) λ 242 nm; IR (KBr) 2227 cm^{-1}.

6e: oil; ^{1}H NMR (200 MHz) δ 3.69 (4 H, s, cyclobutane), 7.2–7.38 (14 H, m), 7.61 (4 H, d, J = 8.4 Hz); MS, m/e (relative intensity) 410 (M^+, 0.1), 230 (0.05), 205 (100), 180 (5); UV (MeOH) λ 244 nm; IR (KBr) 2227 cm^{-1}.

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(19) Fine splittings (J = 1–2 Hz) are observable.

(20) A very small peak that corresponds to $[PhCH{=}CHPh]^{\bullet+}$ was present at m/e 180. However, a peak that corresponds to $[ArCH{=}CHAr]^{\bullet+}$ was not detected.

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