BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (12), 3578—3583 (1976) [Vol. 49, No. 12

The Solution Photodimerization of (*E*)-*p*-Nitrocinnamates

Tatsuzo Ishigami, Tomoji Murata, and Tadashi Endo
Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University,
Chitosedai, Setagaya-ku, Tokyo 157

(Received May 12, 1976)

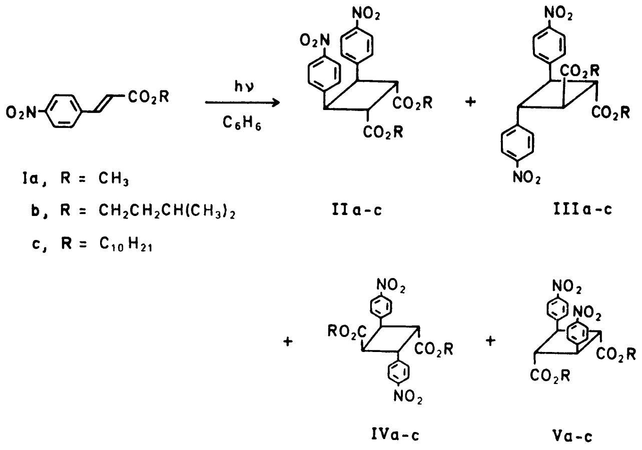
The solution photodimerization of methyl (*E*)-*p*-nitrocinnamate has been studied under various conditions. *Cis* and *trans* dimers of head-to-head configuration were formed predominantly, the ratio of the dimers being highly dependent on the concentration and the solvent. The sensitization, the quenching phenomena, and the external heavy-atom effect were observed in this photodimerization. It appears likely that the excited multiplicity responsible for the formation of the *trans*-dimer is the triplet π,π^* state and that both the singlet and the triplet π,π^* states contribute to the production of the *cis*-dimer.

The formation of four-membered rings through the irradiation of olefins, especially of the α,β-unsaturated carbonyl compounds, is one of the oldest photoreactions in organic chemistry. The photocyclodimerization of the *crystalline* cinnamic acids is a classic illustration of this type of reaction.1) The crystallographically different α- and β-forms of (*E*)-cinnamic acid exclusively give α-truxillic acid (head-to-tail dimer) and β-truxinic acid (heat-to-head dimer), respectively. The stereospecificity of this cycloaddition is shown to depend mainly upon the packing arrangement of the nearest neighbours in the monomer lattice. Further, cyrstallographic studies have made it clear that, in order for dimerization to occur in either crystal form, the reacting centers must be separated by no more than 4 Å.1) On the other hand, in *solution* or in the *liquid* state of cinnamic acid, ultraviolet light merely causes an equilibration between the *Z* and *E* isomers.2) The absence of photodimerization in solution is attributable to the lack of a situation in which the intermolecular carbon-carbon double bonds lie close together, *e.g.*, within 4 Å.

As a fundamental study on the control of photoreactions, this paper deals with the solution photodimerization of (*E*)-*p*-nitrocinnamates giving the two head-to-head photocyclodimers whose ratios vary largely, depending on the irradiation conditions, and also with the mechanistic aspects of this photodimerization.

Results

*Photodimerization of Substituted (*E*)-Cinnamates in Benzene.* An argon-saturated benzene solution (0.05 mol dm^{-3}) of methyl (*E*)-*p*-nitrocinnamate (Ia) was externally irradiated with a 450-watt high-pressure mercury arc for 3 h at 10 °C. The resulting solution was subjected to TLC to give the *cis*- (IIa, 14%) and *trans*-head-to-head cyclodimers (IIIa, 29%), together with only a trace amount (1%>) of the *cis*- (IVa) and *trans*-head-to-tail cyclodimers (Va). When the irradiation was effected by the Pyrex-filtered light, the yields of IIa and IIIa were 13 and 36%, respectively. The structures of these cyclobutane derivatives were established by an examination of their NMR and mass spectra.3) It was also confirmed that both IIa and IIIa are extremely stable under all the irradiation conditions employed.



The *Z*, *E* isomerization of the carbon-carbon double bond generally competes with photodimerization. In the above photoreaction, the rapid equilibration between Ia and its *Z* isomer (VIa) was confirmed by the gas-chromatographic analysis of the reaction mixture; the ratio of Ia to VIa was 0.94 when Ia was irradiated for 10 min and 1.13 under a 3-h irradiation.

In contrast, methyl (*E*)-cinnamate and its derivatives possessing the *p*-chloro, *p*-methoxyl, *p*-methyl, *p*-isopropyl, and *p*-dimethylamino groups underwent only *Z*, *E* isomerization and gave no cyclodimers when irradiated under the conditions described above. However, the prolonged irradiation (65 h) of a more concentrated solution (0.5 mol dm^{-3}) of methyl (*E*)-cinnamate gave the corresponding *cis*- and *trans*-head-to-head cyclodimers in 16 and 37% yields, respectively.

When the bulky isopentyl (Ib) or decyl group (Ic) is the ester moiety, the ratio of the corresponding two cyclodimers (II/III) was found to be 0.26 or 0.20, respectively (Table 1). This can be explained by the greater steric repulsion between the two alkyl groups in II than that in III.

Solvent Effect on the Photodimerization of Ia. The data in Table 2 indicate the dependence of the product distribution on the solvent polarity. The amount of IIa proved to increase with an increase in the dielectric constants4) or dipole moments5) of the solvents employed.6) No relationship existed between the selectivity in this photodimerization and the coefficients of the viscosity5) of the solvents or the reaction temperature.7) The use of the polar solvents such as pyridine, acetone, and acetonitrile, raised the yields of the head-to-tail cyclodimers (IVa and Va) considerably in comparison with the use of the nonpolar solvents.

TABLE 1. PHOTODIMERIZATION OF I[a)]

Compound	Filter	Conversion (%)	Yield (%)[b)] II	III	IV, V	II/III
Ia	Quartz	54	14	29	1	0.48
Ia	Pyrex	62	13	36	2	0.36
Ib	Quartz	55	6	23	1>	0.26
Ic	Quartz	65	8	40	1	0.20

a) Irradiated in a benzene solution (0.05 mol dm^{-3}) under an argon atmosphere with a 450-watt high-pressure mercury lamp for 3 h. b) Based on I employed.

TABLE 2. SOLVENT EFFECTS ON THE PHOTODIMERIZATION OF Ia[a)]

Solvent	ε[b)]	μ[c)]	Conversion (%)	Yield (%)[d)] IIa	IIIa	IVa, Va	IIa/IIIa
1,4-Dioxane	2.21	0.45	58	8	16	2	0.50
C_6H_6	2.28	0	54	14	29	1	0.48
$CH_3CO_2C_2H_5$	6.02	1.88	55	15	26	2	0.58
Pyridine	12.4	2.37	64	19	24	5	0.79
CH_3COCH_3	20.7	2.69	63	21	22	8	0.95
CH_3CN	37.5	3.44	82	27	26	8	1.04
CH_2Cl_2	8.93	1.14	49	3	26	1	0.12
$CHCl_3$	4.81	1.15	48	2	25	1	0.08
CH_2Br_2	4.78	1.23	59	1	30	1	0.03

a) Irradiated under the same conditions as in the case of Table 1. b) Dielectric constant at 20 °C. c) Dipole moment at 25 °C. d) Based on Ia employed.

TABLE 3. CONCENTRATION EFFECTS AND SOLID-STATE IRRADIATION

Solvent[a)]	Concn. (mol dm^{-3})	Conversion (%)	Yield (%)[b)] IIa	IIIa	IIa/IIIa
Solid-state	—	100	95	0	—
C_6H_6	1×10^{-1}	73	41	16	2.56
C_6H_6	5×10^{-2}	69	15	22	0.68
C_6H_6	5×10^{-3}	69	2	6	0.33

a) Irradiated under an oxygen atmosphere with a 450-watt high-pressure mercury lamp for 3 h. b) Based on Ia employed.

The irradiation of Ia in the halogenated hydrocarbons resulted in the predominant formation of the *trans*-cyclodimer (IIIa) probably by means of the external heavy-atom effect.[8)] In the case of dibromomethane, the heavy-atom effect was remarkable, the IIa/IIIa value being 0.03. However, at a lower concentration (5 mol% dibromomethane in benzene) the halogen-containing compounds showed no significant effect.

Effect of Concentration. As is shown in Table 3, the concentration of the reactant (Ia) proved to influence the ratio of the photodimers remarkably. The IIa/IIIa value increased from 0.68 to 2.56 with an increase in the concentration of benzene solution under an oxygen atmosphere. In the case of a dilute solution (5×10^{-3} mol dm^{-3}), polymerization prevailed. These results led us to investigate the solid-state photodimerization. The irradiation of crystalline Ia afforded a single topochemical *cis*-head-to-head cyclodimer (IIa) almost quantitatively. On the other hand, the *trans*-head-to-head cyclodimer was formed as the sole product in only a 7% yield on the irradiation of crystalline methyl (*E*)-*p*-methoxycinnamate. The formation of this "nontopochemical product"[9)] might be explained in terms of local melting and the disruption of the lattice control.

Quenching and Sensitization Experiments. The quenching effects of oxygen, azulene, ferrocene, and hydroquinone were also examined (Table 4). In the presence of oxygen, the formation of IIIa was suppressed considerably, the yield of IIa being unaffected. When an argon-saturated 0.05 mol dm^{-3} benzene solution of Ia was irradiated in the presence of azulene (10 mol%, $E_T=30.9$ kcal/mol[10)]), an efficient triplet quencher, the yield of IIIa (10%) turned out to be about one-third that (29%) in the non-quenching solution, the yield of IIa being less affected.

To elucidate the nature of the excited state involved in the formation of IIa and IIIa, the ferrocene quenching[11)] was studied in detail. Figures 1 and 2 illustrate the Stern-Volmer plots of the Φ^0/Φ values against the ferrocene concentration for two cyclodimers IIIa and IIa, respectively. With low concentrations of ferrocene ([FcH]$<2.5\times10^{-2}$ mol dm^{-3}) the plot in Fig. 1 is approximately linear, but with higher concentrations ([FcH]$>3.5\times10^{-2}$ mol dm^{-3}) the plot showed an extreme curvature. On the contrary, the relationship between Φ^0_{IIa}/Φ_{IIa} and the ferrocene concentration shown in Fig. 2 is quite different from that of $\Phi^0_{IIIa}/\Phi_{IIIa}$. The quenching plot leveled off once ($\Phi^0_{IIa}/\Phi_{IIa}=1.43$) at the concentrations of ferrocene between 5.0×10^{-3} and 3.5×10^{-2} mol dm^{-3}, and again showed a linear increment at higher concentrations.

Table 4. Results of quenching experiments[a)]

Solvent	Additive (mol/mol)	Filter[b)]	Ia/VIa after[c)] irradiation	Yield (%)[d)]			IIa/IIIa
				IIa	IIIa	IVa, Va	
C_6H_6	None	Q	1.13	14	29	1	0.48
C_6H_6	O_2[e)]	Q	1.06	15	22	1>	0.68
C_6H_6	Az(0.1)[f)]	Q	0.57	10	10	1>	1.00
CH_3CN	None	P	1.59	40	26	7	1.54
CH_3CN	FcH(0.1)[g)]	P	0.50	32	7	2	4.57
CH_3CN	FcH(0.7)	P	0.19	28	1	1>	28.0
CH_3CN	None	Q	1.44	27	26	8	1.04
CH_3CN	HQ(1.0)[h)]	Q	0.48	23	8	0	2.88

a) Irradiated under the same conditions as in the case of Table 1. b) Q=quartz and P=Pyrex. c) Determined by GLPC. d) Isolation yield based on Ia employed. e) Saturated with oxygen. f) Azulene. g) Ferrocene. h) Hydroquinone.

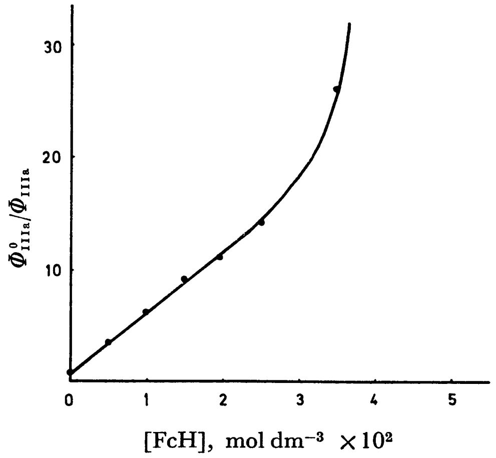


Fig. 1. A Stern-Volmer plot of the IIIa formation as a function of the ferrocene concentration in acetonitrile.

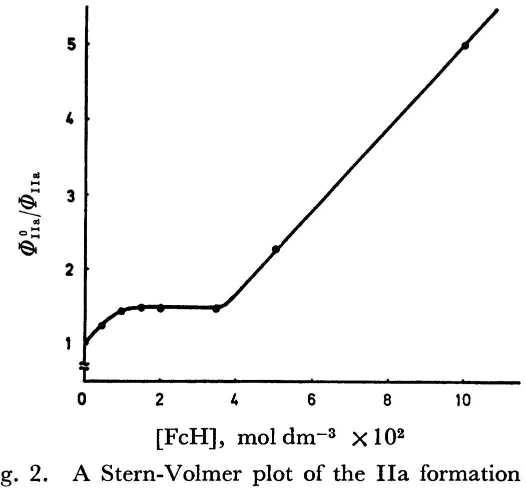


Fig. 2. A Stern-Volmer plot of the IIa formation as a function of the ferrocene concentration in acetonitrile.

The irradiation of Ia in acetonitrile in the presence of an equimolar amount of hydroquinone (an excellent radical scavenger) caused a drastical reduction in the yield of IIIa, along with a slight decline in IIa. It was found that the formation of the head-to-tail cyclodimers (IVa and Va) was suppressed completely by the addition of such a radical scavenger. Further, the rate of the *Z,E* isomerization of Ia was lowered significantly by both the quenchers.

In relation to the possibility of excimer formation in this dimerization, the luminescence of Ia was investigated. No fluorescence from Ia could be observed in benzene at room temperature, probably because of the self-quenching by the methoxycarbonyl or nitro group.[12)] The triplet energy of Ia was estimated to be *ca.* 54 kcal/mol based on the phosphorescence measurement of Ia in EPA glass at 77 K. This E_T value suggests that 2,3-butanedione (E_T=56.3 kcal/mol)[13)] or 4,4'-bis(dimethylamino)benzophenone (Michler's ketone, E_T=62 kcal/mol)[14)] may be an efficient sensitizer. When a benzene solution of Ia (0.05 mol dm^{-3}) and 2,3-butanedione (1.0 mol dm^{-3}) was irradiated (λ>430 nm) for 8 h, the triplet sensitization was observed and the yields of IIa and IIIa were 2 and 17%, respectively. Contrary to our expectations, neither photodimerization nor *Z,E* isomerization of Ia was observed in the Michler's ketone sensitized irradiation (λ>330 nm). This was also the case with the use of dimethylaniline (E_T=76 kcal/mol)[15)] in place of Michler's ketone. The quenching by these dimethylamino-containing compounds can be explained by the assumption that the short-lived singlet or triplet exciplex is formed between the nitrophenyl and dimethylaminophenyl moieties and that the excited π-complex consequently undergoes a radiative or radiationless decay to the ground state before the reaction takes place.

Discussion

Increasing solvent polarity favored *cis*-head-to-head cyclodimer formation, while decreasing solvent polarity favored *trans*-head-to-head dimerization. Although neither fluorescence nor triplet excimer[16)] phosphorescence from Ia could be observed, it seems probable that this predominant formation of the *cis*-cyclodimer can be interpreted by the hypothesis[17,18)] that polar solvents and a concentrated solution generally aid a ground- or excited-state aggregation, leading to a singlet excimer. However, monomer association was not detected in any of the UV spectra at various concentrations (1.0×10^{-5} to 1.0×10^{-1} mol dm^{-3}) in benzene and acetonitrile.

Another possible explanation of these observations is the following.[19] Since *cis*-head-to-head dimerization is accompanied by a net increase in the dipole moment, and since *trans* dimerization proceeds with its reduction, solvents of appreciable dipole moments stabilize the transition state[20] (a 1,4-biradical intermediate or weak association between two Ia molecules of the *cis*-head-to-head type orientation), leading to the polar dimer (IIa). This explanation is consistent with the concentration dependence of the *cis* dimerization described before. Concerning the relationship between the concentration and the solvent polarity, Ruhlen and Leermakers have reported that "macroscopic" and "microscopic" polarity decreases as the concentration is reduced.[21] As is shown in Table 2, the effectiveness of *trans* cyclodimerization varied little with the solvents. For *cis* dimerization, however, a change in the solvent from benzene to acetonitrile caused a remarkable two-fold rate acceleration.

The excited-state multiplicities and reaction pathways in this cyclodimerization were studied through sensitization and quenching experiments. The 2,3-butanedione-sensitized irradiation afforded IIIa (IIa/IIIa=0.12) mainly. In the presence of azulene or hydroquinone, the quenching against the IIIa formation is larger than that against the IIa (Table 4). The dissolved oxygen only suppressed the production of IIIa; it had no effect on the yield of IIa.[22] These sensitization and qualitative quenching data suggest that IIIa is formed exclusively from a 1,4-biradical intermediate *via* triplet-excited Ia and IIa mainly from the less-quenchable singlet state with a partial contribution of the triplet-excited state. The linearity of the Stern-Volmer plot for IIIa is a further indication that only one excited state (the triplet state) is involved in the IIIa formation. At the point of $[\text{FcH}]=3.5\times10^{-2}\ \text{mol dm}^{-3}$, the IIIa formation ($\Phi^0_{\text{IIIa}}/\Phi_{\text{IIIa}}=25.8$) and the *Z,E* isomerization of Ia (Ia/VIa=0.188) are quenched almost completely. For IIa, the quenching plot of $\Phi^0_{\text{IIa}}/\Phi_{\text{IIa}}$ is once leveled off at the ferrocene concentrations between 5.0×10^{-3} and $3.5\times10^{-2}\ \text{mol dm}^{-3}$, then it shows a linear increment. The former quenching effect is probably based on the quenching of the triplet state of Ia, and the latter on the singlet quenching (Fig. 2). From the Stern-Volmer plot shown in Fig. 2, the contribution of the triplet state to the IIa formation can be estimated to be 30%; therefore, 70% of the IIa may be formed *via* a singlet state of Ia.

Moreover, the formation of the singlet-derived dimer (IIa) was found to be enormously suppressed in dichloromethane, chloroform, and dibromomethane. This can be ascribed to the heavy-atom solvent, which promotes intersystem crossing, hence providing a higher steady-state concentration of the Ia triplet and resulting in a low efficiency of dimerization from the singlet state (external heavy-atom effect).[23] Considering the heavy-atom effect, which is known to promote the $\text{S-T}_{\pi,\pi}$ transition, but not the $\text{S-T}_{n,\pi}$ transition,[24] it is likely that the $^3\pi,\pi^*$ state participates in the photodimerization of the aromatic nitro compound Ia to IIa and IIIa. Recent study has shown that the liquid state dimerization of ethyl cinnamate is photosensitized by picramide and *p*-nitroaniline,[25] each of which has a nitro group on its benzene ring. In addition to this fact, our observation described above on the extremely facile photodimerization of Ia should be noted in comparison with methyl (*E*)-cinnamates, which have no nitro group. One possible explanation for these phenomena is that the nitro group in Ia acts as a built-in photosensitizer.

The rapid *Z,E* isomerization of Ia competes with its photodimerization, and the photo-stationary value (Ia/VIa) is 1.35 in benzene. Accordingly, there is a very fair possibility that IIa and IIIa might be produced by the turn-over[26] of the VIa-derived intermediate biradicals with the alleviation of the steric intricacy.

In conclusion, we propose the following multipathway mechanism, which is consistent with all of the experimental observations:[27,28] where S=Ia, $^1(\text{S}\cdots\text{S})$=singlet excimer, D=dimers (IIa and IIIa), HA=halo-solvent, Sens=2,3-butanedione, and Q=quencher.

$$\text{S} + h\nu \rightarrow {}^1\text{S}$$
$$^1\text{S} + \text{S} \rightarrow {}^1(\text{S}\cdots\text{S})$$
$$^1(\text{S}\cdots\text{S}) \rightarrow \text{D (IIa)}$$
$$^1\text{S} + \text{S} \rightarrow \text{D (IIa)}$$
$$^1\text{S} \rightarrow {}^3\text{S}$$
$$\text{S} + {}^3\text{Sens} \rightarrow {}^3\text{S} + \text{Sens}$$
$$^1\text{S} + \text{HA} \rightarrow {}^3\text{S} + \text{HA}$$
$$^3\text{S} + \text{S} \rightarrow \text{D (IIa and IIIa)}$$
$$^3\text{S} + \text{Q} \rightarrow \text{S} + {}^3\text{Q}$$
$$^3\text{S} \rightarrow \text{VIa}$$
$$\text{VIa} + h\nu \rightarrow {}^1\text{VIa}$$
$$^1\text{VIa} \rightarrow \text{S}$$

It appears most likely that the IIIa formation proceeds through a biradical intermediate derived from the triplet state (π,π^*) of Ia. In contrast, two different mechanisms are probably concerned with the IIa formation. The major possible pathway is the contribution of a concerted $[_\pi2_s+_\pi2_s]$ transition state or the geminate reaction of the 1,4-biradical intermediate stabilized in the solvent cage,[29] which is known not to be quenched by a radical scavenger, *via* the singlet excimer of Ia; the minor pathway being the ring closure of the intermediary 1,4-biradical by way of the triplet state (π,π^*) of Ia.

Experimental

General. (*E*)-*p*-Nitrocinnamic acid was prepared from *p*-nitrobenzaldehyde[30] and malonic acid by the method of Wiley and Smith.[31] The following (*E*)-cinnamic acid derivatives were prepared according to the known procedures: *p*-methoxy-,[32] *p*-methyl-,[33] *p*-isopropyl-,[33] *p*-chloro-,[32] and *p*-dimethylamino-(*E*)-cinnamic acid.[34] The esterification of each acid was performed in the presence of sulfuric acid.[35] Acetonitrile was purified in the usual manner.[36] Benzene was purified by two successive distillations. The other reagents were obtained commercially, the liquids were distilled, and the solids were recrystallized, before use. The NMR spectra were taken with a Hitachi R-20 spectrometer in a CDCl_3 solution with tetramethylsilane as the internal standard. The mass spectra were made on a Hitachi RMU-

6M mass spectrometer at 70 eV using a heating inlet system. Analytical GLPC chromatography was performed on a Hitachi Model 063 instrument with a flame-ionizaion detector and nitrogen as the carrier gas. The column (3-mm × 1-m) used was 10% silicone SE-30 on Chromosorb W. Analytical and preparative thin layer chromatography (TLC) was carried out on silica gel plates (Merck silica gel 60 F_{254} pre-coated plates).

Irradiation Procedure. All irradiations of solutions were conducted in a 20-ml syrindrical quartz vessel with a neck to accommodate a three-way stopcock. Stirring was effected magnetically. For irradiation with or without a Pyrex filter, a reaction vessel was placed 5 cm away from a light source (Ushio 450 watt UM-452 high-pressure mercury lamp) placed in a water bucket for cooling. In the case of the 313 nm light, the sample solution was irradiated through a Pyrex filter sleeve and a 1-cm path of a 2.0×10^{-3} mol dm^{-3} potassium chromate solution filter.[37] A Toshiba filter V-Y45 was used for the 2,3-butanedione sensitization. The solids were irradiated on Pyrex glass plates at a distance of *ca.* 15 cm at 20 °C.

Irradiation of Ia in Solution. The general execution of the present photodimerization is typically illustrated by the procedure for the conversion of Ia to IIa and IIIa. A benzene solution (20 cm^3) of Ia (207 mg, 1.0 mmol) was saturated with argon after evacuation and then irradiated for 3 h. A quantitative determination by GLPC indicated the recovery of Ia and the yield of VIa to be 23 and 24%, respectively. The reaction mixture was concentrated *in vacuo*, and the residue was subjected to preparative tlc with hexane–ethyl acetate (5:1 v/v) as the eluent to give pure IIa (14%) and IIIa (27%). The identification of IIa and IIIa was made on the basis of the following NMR and mass spectral data by the method given in the literature.[3]

Compound IIa: NMR (60 MHz, $CDCl_3$) δ 3.80 (s, 6H, CH_3), 3.80—4.75 (AA'BB', 4H, cyclobutane ring), 7.24 ($d_{J=9.0\,Hz}$, 2H, aromatic ring), and 8.03 ($d_{J=9.0\,Hz}$, 2H, aromatic ring); mass *m/e* (rel. intensity) 414 (6.8, M$^+$, $C_{20}H_{18}O_8N_2$), 270 (5.3, $C_{14}H_{10}O_4N_2$), and 207 (100, M/2, $C_{10}H_9O_4N$).

Found: C, 57.88; H, 4.46; N, 6.53%. Calcd for $C_{20}H_{18}O_8N_2$: C, 57.97; H, 4.38; N, 6.76%.

Compound IIIa: NMR (60 MHz, $CDCl_3$) δ 3.82 (s, 6H, CH_3), 3.40—4.10 (AA'BB', 4H, cyclobutane ring), 7.60 ($d_{J=9.0\,Hz}$, 2H, aromatic ring), and 8.20 ($d_{J=9.0\,Hz}$, 2H, aromatic ring); mass *m/e* (rel. intensity) 414 (4.2, M$^+$, $C_{20}H_{18}O_8N_2$), 270 (12.7, $C_{14}H_{10}O_4N_2$), and 207 (100, M/2, $C_{10}H_9O_4N$).

Found: C, 58.15; H, 4.35; N, 6.88%. Calcd for $C_{20}H_{18}O_8N_2$: C, 57.97; H, 4.38; N, 6.76%.

Despite all our efforts to separate the mixture of IVa and Va, we could not isolate the two isomers in a pure form. Therefore, the structures of IVa and Va were determined by means of the NMR and mass spectra of the mixture. The quantitative analysis of Ia and VIa was performed by the cut-and-weigh integration of GLPC traces using a known amount of benzophenone as the external standard for the correction of the detector response differences.

Actinometry. A conventional method of actinometry was employed; it eliminated errors due to light fluctuations and may inherently give good quantum yield ratios for the Stern-Volmer plot. The actinometer solution, which contained 0.05 mol dm^{-3} Ia in acetonitrile, was photolyzed simultaneously with sample solutions containing 0.05 mol dm^{-3} Ia and varying concentrations of ferrocene. No quantum-yield value was assumed for the actinometer solution. Instead, the ratio (Y^0/Y) of the yields of the dimer in the actinometer and in the sample solutions was used directly. The light absorbed and the time of photolysis were the same for both solutions, so the Y^0/Y value should be equal to the ratio of the quantum yields (Φ^0/Φ).

The support of this work by the Matsunaga Science Foundation is gratefully acknowledged.

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26) The phenomenon of "turn over" is known (Ref. 1) even in the solid state: the crystalline (*Z*)-cinnamic acid photodimerizes only after photochemical isomerization to (*E*)-cinnamic acid *via* a metastable complex between an excited monomer and its nearest neighbor.

27) The deactivation processes from excited states are omitted in this scheme.

28) The isomerization of Ia to VIa proceeds *via* a triplet state and that of VIa to Ia *via* a singlet state; T. Ishigami, T. Murata, M. Uehara, and T. Endo, unpublished result.

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