Conformation of Methyl *trans*-3-Arylpropenoates in Triplet States and Their Reactivities

Kenichi NAKABAYASHI,* Kyouko OHASHI,† and Setsuo TAKAMUKU†
Department of Chemistry, Faculty of Education, Miyazaki University, Gakuen-kibanadai, Miyazaki 889-21
† The Institute of Scientific and Industrial Research, Osaka University, 8-1, Mihogaoka, Ibaraki, Osaka 567

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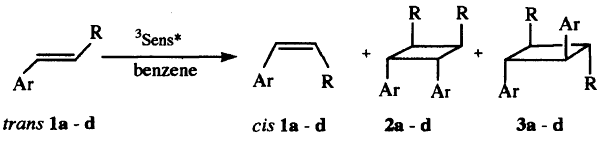
Synopsis. The photochemical *cis–trans* isomerization and cycloaddition of methyl *trans*-3-arylpropenoates in benzene via triplet state were investigated. The results of triplet sensitized *cis–trans* isomerization clearly indicated that the most stable conformation for methyl 3-phenylpropenoate is a twisted form while methyl 3-(4-biphenylyl)propenoate and methyl 3-(2-naphthyl)propenoate are in the equilibrium states between the *trans*-planar triplet and twisted form. Photoirradiation of these methyl 3-arylpropenoates in relatively high concentrated benzene solutions gave two isomeric cyclodimers of dimethyl *t*-3, *t*-4-diaryl-*r*-1, *c*-2-cyclobutanedicarboxylate and dimethyl *c*-3, *t*-4-diaryl-*r*-1, *t*-2-cyclobutanedicarboxylate as main products. The reactivities of cycloaddition are relatively high where the most stable conformation is twisted form.

The photochemical intermolecular [2 + 2] cycloaddition of α,β-unsaturated carbonyl compounds is one of the most extensively investigated and synthetically useful of photochemical reactions.[1)] The intermolecular [2+2] cycloaddition, in general, occurs competition with rapid unimolecular *cis–trans* photoisomerization.[2)] As a part of our investigation on the excited triplet state by γ- and electron-pulse radiolysis, we have reported the valence isomerization of aryl substituted quadricyclane and norbornadiene derivatives via the triplet state.[3)] In this paper, we have found that the reactivity of α,β-unsaturated carbonyl compounds toward the isomerization and the dimerization may strongly correlate with the conformation of the substrate in triplet state. In order to elucidate the relationship between conformation and reactivities in triplet state, we wish to report the photochemical reaction of methyl *trans*-3-arylpropenoates (**1a**—**d**) by direct and triplet sensitization (Chart 1).



a: Ar = phenyl, **b**: Ar = biphenylyl, **c**: Ar = 2-naphthyl, **d**: Ar = 1-naphthyl
R = CO_2CH_3

Chart 1.

Experimental

Apparatus. GLC analysis was carried out on Shimadzu GC-8A using a 50 cm×4 mm column of 2% Silicon OV-17 on Chromosorb W. ^{1}H and ^{13}C NMR were taken on a Bruker AM 360 for $CDCl_3$ solutions with tetramethylsilane used as an internal standard. A JMS-O1SG-2 was used for the analysis of the mass spectra. Elemental analyses were carried out at the Material Center of ISIR at Osaka University.

Materials. Syntheses of compounds, **1a**—**d**, have been described in a previous paper.[3b)] The structures of these compounds were satisfactorily confirmed by the spectral data. Benzophenone (BP) and azulene (Az) were purified by recrystallization from ethanol and sublimation. Spectral grade benzene was used without further treatment.

Photochemical Reaction. Photoirradiation was carried out with a 300 W high-pressure mercury lamp (Eikosha PIH 300) under cooling with water by the use of $BiCl_3$ solution filter and a *merry-go-round* turntable. A $BiCl_3$ solution (6.7 g dm^{-3} in 10% HCl aqueous solution, 10 mm path length) was used to isolate the 366 nm light. The identification of photoproducts and measurement of the yields were performed by GLC.

Syntheses and Identification of Cyclodimers. Irradiation of **1a**—**d** in benzene gave **2a**—**d** and **3a**—**d**. The isolation of the cyclodimers was carried out by column chromatography on silica gel with hexane and diethyl ether as the eluent. All the cyclodimers were obtained as colorless crystals after recrystallization from ethanol. Analytical data for **2a**, **3a**, **2d**, and **3d** were given in the literature.[2)] The isolation of **2b** and **3b** was not successful under these conditions.

Dimethyl *t*-3, *t*-4-di-(2-naphthyl)-*r*-1, *c*-2-cyclobutane Dicarboxylate (2c). Mp 131—132 °C, ^{1}H NMR δ=3.74 (s, 6H), 4.02 (d, J=7.1 Hz, 2H), 4.51 (d, J=7.1 Hz, 2H), 7.09 (m, 14H). Found: C, 79.05; H, 5.78%. Calcd for $C_{28}H_{24}O_4$: C, 79.23; H, 5.70%.

Dimethyl *c*-3, *t*-4-Di-(2-naphthyl)-*r*-1, *t*-2-cyclobutane Dicarboxylate (3c). Mp 89—91 °C, ^{1}H NMR δ=3.59 (d, J=9.5 Hz, 2H), 3.71 (s, 6H), 4.75 (d, J=9.5 Hz, 2H), 7.78 (m, 14H). Found: C, 79.20; H, 5.38%. Calcd for $C_{28}H_{24}O_4$: C, 79.23; H, 5.70%.

Results

Triplet Sensitized *cis-trans* Isomerization of 1a—d. The photosensitized *cis-trans* isomerization of *trans*-**1a**—**d** was investigated by irradiation at 366 nm light using benzophenone (BP) as triplet sensitizer. Benzene solutions of *trans*-**1a**—**d** (5 mmol dm^{-3}) containing BP (100 mmol dm^{-3}) were irradiated at 366 nm under an argon atmosphere. Under these conditions, an incident light was absorbed by BP (>98%) to generate efficiently the triplet state of BP. After the irradiation for 90 min the *cis*/*trans* ratios are shown in Table 1. The resulting photostationary ratios of the *cis*- and *trans*-isomers were accurately determined by GLC. The *cis*/*trans* ratios were nearly 1 : 1 in the cases of **1a**

Table 1. Triplet Sensitized *cis–trans* Isomerization of *trans*-**1**[a)] and Characterization of Triplet State of **1**

1	*cis* : *trans*[b)]			
	None[c)]	Az[d)]	O_2[e)]	Assignment of $^3\mathbf{1}^*$
trans-**1a**	48:52	48:52	48:52	twist
trans-**1b**	45:55	12:88	15:85	twist⇌planar
trans-**1c**	24:76	8:92	11:89	twist⇌planar
trans-**1d**	10:90	57:43	38:62	*cis*-planar⇌*trans*-planar

a) Irradiation of a benzene solution containing *trans*-**1** (5 mmol dm^{-3}) and BP (100 mmol dm^{-3}) at 366 nm for 90 min at room temperature. b) The *cis–trans* ratios at photostationary state. c) In the absence of quencher. d) In the presence of Az (10 mmol dm^{-3}). e) In the presence of O_2 (0.79 mmol dm^{-3}).

and **1b**, whereas *trans*-isomers were mainly formed in the cases of **1c** and **1d**.

Additive effect of azulene (Az) or oxygen molecule (O_2) was investigated by irradiating a benzene solution containing *trans*-**1a**—**d** (5 mmol dm^{-3}), BP (100 mmol dm^{-3}) and a given concentration of Az (1—10 mmol dm^{-3}) or O_2 (0.2—0.8 mmol dm^{-3}) at 366 nm for 90 min. The results are also shown in Table 1. With an increase of concentration of Az or O_2, the *trans–cis* isomer ratio increased in the cases of **1b** and **1c** whereas the ratio decreased in the case of **1d**. The *cis–trans* isomer ratio of **1a** was not affected by these additive.

Photodimerization of 1a—d. Dimerization occurred to some extents by irradiation at higher concentration of *trans*-**1a**—**d** as shown in Table 2, although the *cis–trans* isomerization exclusively occurred at low concentration of *trans*-**1a**—**d**. The photosensitized cyclodimerization of *trans*-**1a**—**d** was investigated by irradiation at 366 nm light using BP as triplet sensitizer. Irradiation of benzene solutions containing *trans*-**1a**—**d** (100 mmol dm^{-3}) and BP (100 mmol dm^{-3}) under an argon atmosphere at 366 nm for 10 h gave dimethyl *t*-3, *t*-4-diaryl-*r*-1, *c*-2-cyclobutanedicarboxylate (**2a**—**d**) and dimethyl *c*-3, *t*-4-diaryl-*r*-1, *t*-2-cyclobutanedicarboxylate (**3a**—**d**) along with *cis*-**1a**—**d**. The cyclodimers were isolated by column chromatography on silica gel and were assigned by the NMR and MS spectra of isolated compounds as described in the experimental section. Cleavage products and the other photoproducts were not detectable under our analytical conditions. In the case of **1b**, although GLC analysis indicated the presence of two type of cyclodimers, they could not be isolated by column chromatography. Relative yields and efficiencies of dimerization for *trans*-**1a**—**d** under triplet sensitization are summarized in Table 2. The yield of the cyclodimer shows the total amount of cyclodimers (**2** and **3**). In the case of **1c**, the yields of cyclodimers were four times greater than that of **1d** under the same reaction conditions.

Table 2. Product Distribution upon Irradiation of **1** in Benzene[a)]

Substrate	Product distribution/%[b)]		
	trans-**1**	*cis*-**1**	dimer (**2** : **3**)[c)]
trans-**1a**	27	20	53 (**2** : 98)
trans-**1c**	12	10	78 (**2** : 98)
trans-**1d**	49	32	19 (**5** : 95)

a) Irradiation of a benzene solution containing *trans*-**1** (100 mmol dm^{-3}) and BP (100 mmol dm^{-3}) for 10 h. b) Product analysis based on GLC. c) The values in parenthesis are isomer ratios of **2** and **3**.

Cyclodimerization was also observed by direct irradiation (>300 nm) in benzene. The photoirradiation of *trans*-**1a**—**d** (100 mmol dm^{-3}) in degassed benzene solution for 10 h gave two isomeric cyclodimers **2** and **3** as main products. In any cases, the *trans*-cyclodimers **3** were mainly obtained (90% for *trans*-**1a**, 74% for *trans*-**1c**, and 95% for *trans*-**1d**).

Since *trans*-cyclodimers were mainly obtained by direct irradiation in benzene, we assume the following mechanism for the photodimerization of **1** via triplet state (Scheme 1).

$$\begin{array}{rcll}
\mathbf{1} & \xrightarrow{h\nu} & {}^1\mathbf{1}^* & (1)\\
{}^1\mathbf{1}^* & \xrightarrow{a} & {}^3\mathbf{1}^* & (2)\\
{}^1\mathbf{1}^* & \xrightarrow{1-a} & \mathbf{1} & (3)\\
{}^3\mathbf{1}^* + \mathbf{1} & \xrightarrow{k_1} & \text{Complex} & (4)\\
{}^3\mathbf{1}^* & \xrightarrow{k_d} & \mathbf{1} & (5)\\
\text{Complex} & \xrightarrow{1-\alpha} & \mathbf{1}+\mathbf{1} & (6)\\
\text{Complex} & \xrightarrow{\alpha} & \mathbf{2}\text{ and }\mathbf{3}\text{ (Dimers)} & (7)
\end{array}$$

$$\frac{1}{\phi_{\mathrm{rel}}(\text{Dimer})} = \frac{1}{a\alpha}\left(1+\frac{k_d}{k_1[\mathbf{1}]}\right) \qquad (8)$$

Scheme 1.

Photocyclodimerization is a bimolecular reaction involving attack of an excited molecule on a ground-state substrate. Therefore, the rate of dimerization depend on the concentration of the reactant. Dimerization rate constants (k_1) were obtained from steady state kinetics. In the cases of **1a**, **1c**, and **1d**, linear plots were obtained, while no linear plot was observed in the case of **1b**. The 1/slope values of the plots and the triplet lifetimes ($\tau=1/k_d$) determined by the transient absorption spectra provide the dimerization rate constants, k_1 as shown in Table 3.

Discussion

From the results of transient spectra and steady state experiment, we assume the following potential energy surfaces of *cis–trans* isomerization for **1** as shown in Fig. 1. The results of triplet sensitized *cis–trans* isomerization clearly indicated that **1b** and **1c** undergo reversible isomerization between the *cis* and *trans* iso-

Table 3. Triplet Lifetime ($\tau=1/k_d$),[a] Stern–Volmer Constant (k_1/k_d) and Dimerization Rate Constant (k_1)

1	λ_{max} (T–T)	τ	k_1/k_d	k_1
	nm	μs	mol	$dm^3\,mol^{-1}\,s^{-1}$
trans-**1a**	315	0.065	52.5	3.3×10^7
trans-**1b**	440	0.080	—	—
trans-**1c**	390	0.43	10.3	2.4×10^7
trans-**1d**	480	4.2	0.6	1.4×10^5

a) Triplet lifetimes of *trans*-**1a**—**d** were determined by pulse radiolysis in benzene.

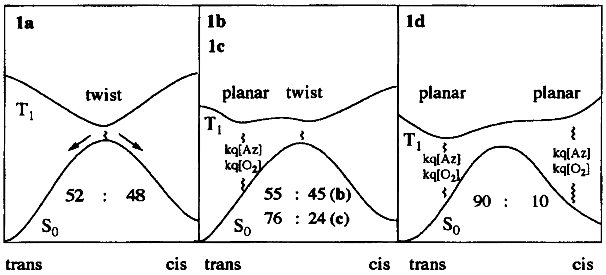


Fig. 1. Schematic potential energy surfaces for *cis*–*trans* isomerization of **1** via triplet state.

mers in the excited triplet state, and the *trans*-planar triplet ($^3t^*$) and the perpendicular triplet ($^3p^*$) are in an equilibrium as observed in stilbene (middle of Fig. 1).[4)] Since the photostationary state of **1a** was not affected by azulene and oxygen, *trans*- or *cis*-planar triplet were ruled out on the excited energy surface (left side of Fig. 1). On the other hand, in the case of **1d**, the *cis*-isomer was increased with increasing azulene and oxygen concentration. This fact suggests that in addition to the *trans*-planar triplet, a *cis*-planar triplet also exists (right side of Fig. 1).

In previous paper,[3)] the mechanism of the valence isomerization between norbornadiene and quadricyclane derivatives via triplet states was found to be correlated with the conformation of corresponding olefinic analogue (**1**). Therefore, the reactivity of twisted olefin (**1a**) is very high since the spin density seems to be mainly localized at the olefinic carbon atoms. On the other hand, the reactivity of planar triplet olefin (**1d**) is less reactive than a twisted olefin since the spin density is delocalized from the olefinic part of the molecule to aromatic substituent with a relatively low E_T value.[3b)] In the cases of **1b** and **1c**, contribution of both intermediates was estimated. Such a reactivity–conformation relationship was also observed in the triplet sensitized cyclodimerization of **1a**—**d**.

It is well-known that the intermolecular photodimerization of aromatic olefins such as styrenes,[5)] vinylnaphthalenes,[6)] follows the excited spin-state mechanism;[7)] that is, the excited singlet state gives *cis*-cyclodimer via an excimer, whereas the triplet state produces predominantly *trans*-cyclodimer via a 1,4-biradical intermediate. Since the *trans*-cyclodimers were mainly obtained and the Stern–Volmer plots showed good linearity except for *trans*-**1b**, the direct photodimerization of *trans*-**1a**, **c**, and **d** in benzene would also take place via the triplet state.[8)] The intermolecular reactivities of the triplet states of **1** (k_1 value) decreased in the order of **1a**>**1c**>**1d**. It is found that twisted olefins (**1a** and **1c**) exhibit a higher reactivity in intermolecular cyclodimerization than that of planar olefin (**1d**) though the lifetimes of the triplet **1a** and **1c** are short.

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