A Novel *Cis–Trans* Photoisomerization of Vinylidenecyclopropanes via Excited Singlet and Triplet States

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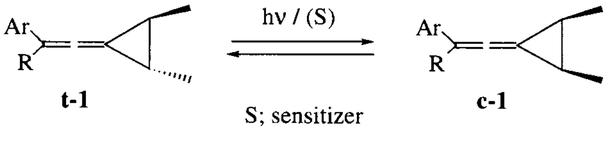
Photoisomerization of *cis*- and *trans*-1-diarylvinylidene-2,3-dimethylcyclopropanes is described. The formation of different photostationary state mixtures of *cis* and *trans* isomers generated by direct and triplet-sensitized photoreactions clearly shows that the photoisomerization proceeds via their excited singlet and triplet states, respectively.

Recently, much attention has been focused on the photochemical reactivity of small ring compounds such as cyclopropanes, methylenecyclopropanes, cyclobutanes, and so on from the mechanistic and synthetic viewpoints.[1] The *cis–trans* photoisomerization of 1,2-diarylcyclopropanes via the excited singlet and triplet states, or their radical cations has been extensively investigated.[2-4] The photorearrangement of methylenecyclopropanes via trimethylenemethane intermediates is also wellknown.[5] However, little is known about the photochemical reactivity of vinylidenecyclopropanes, which have strained structures with reactive sites.[6] We now report a novel *cis–trans* photoisomerization of 1-diarylvinylidene-2,3-dimethylcyclopropanes to give the different photostationary state (PSS) depending on the excited species.[7]

Irradiation of a benzene solution containing *cis*-2,3-dimethyl-1-(2',2'-diphenylvinylidene)cyclopropane (**c-1a**) through Pyrex filter (> 280 nm light) under argon atmosphere gave a 50:50-PSS mixture of **c-1a** and its *trans* isomer (**t-1a**). Similar irradiation of **t-1a** afforded a PSS mixture in the same ratio.[8] The product ratio was monitored by 270-MHz ^{1}H NMR spectrum. Quantum yield for the photoisomerization from **c-1a** to **t-1a** and that from **t-1a** to **c-1a** were determined at 313 nm as 0.08 and 0.07, respectively. Photoisomerization of **c-1a** and **t-1a** also occurs in more polar solvents such as acetonitrile, chloroform, and ethyl acetate to give the same PSS as that in benzene. The photoisomerization was not quenched by adding triplet quenchers such as molecular dioxygen, 2-methyl-1,3-butadiene, and 1,3-cyclohexadiene. These results support the singlet mechanism.



1a; Ar = R = Ph, **1b**; Ar = R = 4-MeC$_6$H$_4$, **1c**; Ar = R = 4-ClC$_6$H$_4$
1d; Ar = R = 4-MeOC$_6$H$_4$, **1e**; Ar = 2-Naph, R = Ph, **1f**; Ar = Ph, R = Me

Whereas, the photoreaction sensitized by triplet sensitizers such as acetophenone (E_T = 309 kJ mol^{-1}), benzophenone (E_T = 288 kJ mol^{-1}), thioxanthen-9-one (E_T = 265 kJ mol^{-1}), Michler's ketone (MK; E_T = 259 kJ mol^{-1}), and 1-acetonaphthone (E_T = 236 kJ mol^{-1}) gave a 30:70 PSS mixture of **c-1a** and **t-1a**. Although pyrene (E_T = 203 kJ mol^{-1}) did not sensitize this reaction, the photoisomerization of **c-1a** to **t-1a** occurred slowly in the presence of 9-fluorenone (E_T = 211 kJ mol^{-1}). Thus, this photoreaction proceeds also through the triplet mechanism, and the triplet energy of **1** is estimated as 220–230 kJ mol^{-1}. Some results are shown in Table 1. Quantum yields in the presence of MK at 366 nm were determined as 0.62 and 0.19 for the isomerization of **c-1a** to **t-1a** and that of **t-1a** to **c-1a**, respectively.

Table 1. The *cis-trans* photoisomerization of vinylidenecyclopropanes

Entry	1	*cis* : *trans* ratio on PSS[a]		
		Direct irradn	Triplet-sensitizer[b]	Triplet-sensitized irradn
1	**c-1a**	50 : 50	MK[c] (259)	30 : 70
2	**t-1a**	50 : 50	MK	30 : 70
3	**c-1a**		acetophenone (309)	30 : 70
4	**c-1a**		benzophenone (288)	27 : 73
5	**c-1a**		pyrene (203)	>99 : <1
6	**c-1b**	50 : 50	MK	27 : 73
7	**c-1c**	54 : 46	MK	27 : 73
8	**c-1d**	46 : 54	MK	29 : 71
9	**c-1e**	25 : 75	MK	27 : 73
10	**t-1f**	45 : 55	MK	25 : 75

[a] Determined by 270 MHz ^{1}H NMR. [b] The values in parentheses are the excited triplet energies of sensitizers (E_T / kJ mol^{-1}). [c] Michler's ketone.

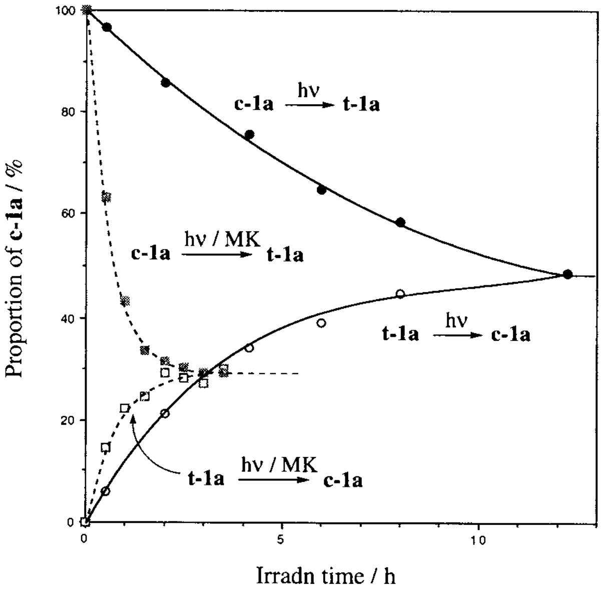
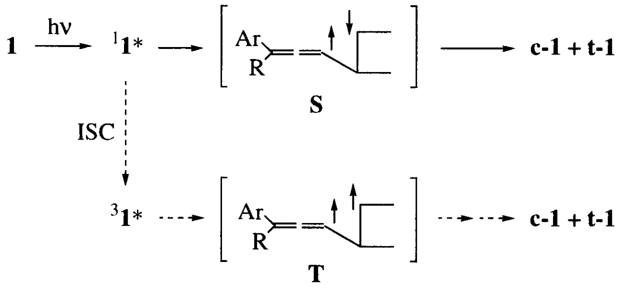


Figure 1. Photoisomerization of **c-1a** and **t-1a** in benzene. ○; *trans* - direct irradiation, ●; *cis* - direct irradiation, □; *trans* - MK sensitization, ■; *cis* - MK sensitization.

Figure 1 shows the plots of the composition of **c-1a** and **t-1a** versus the irradiation time in the direct and MK-sensitized photoreactions. The triplet-sensitized photoisomerization proceeds more efficiently than the direct one. The photoisomerization of the other vinylidenecyclopropanes **1b–f** is also investigated. Their MK-sensitized photoreaction (366 nm light) gave approximately 30:70 to 25:75 (*cis:trans*) PSS mixtures. On the other hand, the direct irradiation (>280 nm light) of these vinylidenecyclopropanes gave 50:50 to 45:55 PSS mixtures, except **1e**. The PSS ratios in both direct and triplet-sensitized photoreactions were found not to depend on the *p*-substituents on phenyl rings. In the case of **1e**, both direct and triplet-sensitized photoreaction afforded the same PSS mixture (**c-1e** : **t-1e** = 30 : 70).

From these results, we propose the simple mechanism involving the excited singlet and triplet biradical intermediates (**S** and **T**) as shown in Scheme 1. In the case of triplet mechanism, the triplet 1,3-biradical intermediate **T** may have relatively long lifetime and is efficient for the isomerization. The 30:70 *cis-trans* PSS can be derived from the difference for the stability between the *cis* and *trans* isomers.



Scheme 1.

On the other hand, **S** probably reproduces cyclopropane ring before intersystem crossing (ISC) to **T** occurs. This is supported by the observation that the isomerization by direct irradiation was not retarded by triplet quenchers such as 1,3-cyclohexadiene. The difference of quantum yields between the direct and triplet-sensitized photoisomerization can be explained by the difference of lifetimes of **S** and **T**. In the case of **1e**, the photoisomerization in the absence of a triplet sensitizer probably occurs via **T** by rapid ISC of the singlet states of naphthalene moiety to its triplet states, though the phosphorescence of **1e** was not observed.

$$\mathrm{Sens} \xrightarrow{h\nu} {}^1\mathrm{Sens}^* \longrightarrow {}^3\mathrm{Sens}^*$$

$$\mathbf{1} + {}^3\mathrm{Sens}^* \longrightarrow {}^3\mathbf{1}^* + \mathrm{Sens}$$

$$^3\mathbf{1}^* \longrightarrow \mathbf{T} \longrightarrow \longrightarrow \textbf{c-1} + \textbf{t-1}$$

Scheme 2.

We conclude that the cis–trans photoisomerization of **1** proceeds via both singlet and triplet biradical intermediates independently and the PSS ratio of *cis*-**1** to *trans*-**1** from the excited singlet state is different from that generated from the excited triplet state.

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