Singlet Photosensitization of Simple Alkenes. Part 1. *cis–trans*-Photoisomerization of Cyclo-octene sensitized by Aromatic Esters †

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The use of aromatic carboxylic esters, *e.g.* methyl benzoate, as sensitizers gave an unusual *cis–trans*-photoisomerization of cyclo-octene, in which the *trans* : *cis*-ratio in the photostationary state was anomalously high, provided the usual triplet sensitization is operating (Table 1). From Stern–Volmer quenching studies and the consequent comparison of the decay ratios for three different sensitizers in two different solvents with those for direct or triplet-sensitized photoisomerizations (Table 4), it is concluded that the present photoisomerization takes place *via* a singlet mechanism which involves non-vertical singlet energy transfer from an excited aromatic ester to the cyclo-octene moiety in an exciplex resulting in 90° twisted cyclo-octene (^1p), which in turn decays to ground state *cis*- or *trans*-cyclo-octene in the ratio of 0.56 : 0.44. The asymmetric *cis–trans*-photoisomerization induced by chiral aromatic esters also supports the involvement of an exciplex.

ALTHOUGH singlet sensitization by naphthalene and other aromatic hydrocarbons has been well established, most of these are accomplished only by using dienes or diphenylcyclopropanes as an acceptor.[1] No singlet sensitization of simple mono-olefins has been reported so far.

We have been interested in the *cis–trans*-photoisomerization of cyclo-octene,[2] the *trans*-isomer of which has considerably higher strain energy by 9.3 kcal mol^{-1} than the *cis*-isomer.[3] This compound is an ideal system for the detection of singlet sensitization because triplet sensitization and direct excitation at 185 nm give completely different *trans* : *cis* ratios in the photostationary state, $(t/c)_{pss}$ 0.05 and 0.96 respectively,[2] while simple mono-olefins, *e.g.* but-2-ene, are believed to afford $(t/c)_{pss}$ values of *ca.* 1 for both singlet and triplet photoisomerization.

We now report a study of an unusual *cis–trans*-photoisomerization of cyclo-octene sensitized by aromatic esters and present a singlet mechanism for this photoisomerization. To the best of our knowledge, this is the first example of singlet photosensitization where aromatic esters act as singlet sensitizers and simple alkenes as acceptor molecules.

EXPERIMENTAL

Materials.—*cis*- and *trans*-Cyclo-octene used in the kinetic studies were prepared as described previously.[2b] The purity of both isomers was determined by g.l.c. to be >99.5 and 99.6%, respectively. *trans*-Piperylene was fractionally distilled prior to use.

Commercially available sensitizers were purified by fractional distillation or repeated recrystallization. Optically active sensitizers, *i.e.* cholesteryl benzoate, (−)-menthyl benzoate, and di-(−)-menthyl isophthalate, were obtained commercially or, in the case of the menthyl esters, prepared by the reaction of (−)-menthol and the corresponding acid chlorides followed by repeated recrystallization from methanol. (−)-Menthyl benzoate had m.p. 51.0—52.5°, $[\alpha]_D^{19}$ −85.1° (*c* 0.67, EtOH), cholesteryl benzoate had m.p. 151—152°, $[\alpha]_D^{25}$ −13.7° (*c* 0.9, $CHCl_3$), and di-(−)-menthyl isophthalate had m.p. 70.5—71.0°, $[\alpha]_D^{25}$ −114.9° (*c* 0.51, CH_2Cl_2).

Pentane used as solvent was stirred over sulphuric acid until the acid layer no longer turned yellow, washed with water, dried over potassium carbonate, and fractionally distilled. Spectrograde methanol (Tokyo Kasei Co.) was used without further purification.

Analysis.—G.l.c. analyses of the reaction mixture were performed on a 3 m column of 20% ββ′-oxydipropiononitrile or on a 3 m column of 15% polyethylene glycol 6000, on which the *cis*- and *trans*-isomers of cyclo-octene were separated completely. n-Octane and cyclo-octane were employed as internal standards.

Fluorescence Studies.—Emission spectra of the aromatic esters were taken on a Hitachi MPF-2A spectrofluorimeter at room temperature.

Photoisomerization Studies.—The photostationary state determinations were carried out at 20 ± 2 °C in quartz tube, 1 cm in diameter, using a 300 W high pressure mercury lamp. A pentane or methanol solution of 0.07M-cyclo-octene of a given isomer composition containing various sensitizers and an internal standard was flushed with nitrogen gas and then irradiated. The sensitizers are shown in Table 1 along with the concentrations employed. The *trans* : *cis*-ratios after u.v. irradiation were determined by periodic analysis by g.l.c. The photostationary states were reached from both sides after irradiation for up to 6 h. With some sensitizers, the samples were degassed by five freeze–pump–thaw cycles on a vacuum line fitted with an oil diffusion pump (*ca.* 10^{-6} Torr). Samples both deaerated and containing N_2 showed no difference in the isomerization yield; non-treated, air-saturated samples however showed slightly reduced yields.

The Stern–Volmer plots of photosensitized isomerization of pure *cis*- or *trans*-cyclo-octene were obtained by irradiating samples containing 0.01M-sensitizer and 0.004—0.4M-cyclo-octene on a merry-go-round in a water-bath with a 300 W high pressure or 30 W low pressure mercury lamp. Methyl benzoate, t-butyl benzoate, and dimethyl isophthalate were employed as sensitizers in the kinetic studies. Since the isomerizations were carried out to very low extent (<5%) to prevent back reactions, corrections for back reactions were not made.

Quenching experiments by up to 0.05M-*trans*-piperylene were carried out under nitrogen in the presence of 0.1M-*cis*-cyclo-octene in pentane solution containing 0.4M-methyl benzoate. Under these conditions most incident light is absorbed by the sensitizer, although the diene has a weak absorption at *ca.* 250 nm.

† Preliminary report, Y. Inoue, S. Takamuku, Y. Kunitomi, and H. Sakurai, *J.C.S. Chem. Comm.*, 1978, 1024.

The quantum yields for isomerization were determined at 254 and 265 nm using a 30 W low pressure or 300 W high pressure mercury lamp fitted with a Baush and Lomb high intensity monochrometer. The intensity of incident light was monitored by potassium ferrioxalate actinometry.[4]

Preparative scale photoisomerizations of *cis*-cyclo-octene were run to obtain the *trans*-isomer. A pentane solution (80 ml) containing 1.0M-*cis*-cyclo-octene (9.0 g) and 0.009M-methyl benzoate or -dimethyl isophthalate as sensitizer was placed in a quartz vessel, flushed with nitrogen gas, and irradiated for 19 h by a 300 W high pressure lamp. Work-up as described previously [2] gave *trans*-cyclo-octene of 99.6% purity. The isolated yields for the benzoate and isophthalate sensitizations were 1.4 g (15% based on *cis*-cyclo-octene used) and 1.6 g (18%), respectively. The i.r. and n.m.r. spectra of the product were in good agreement with authentic *trans*-cyclo-octene independently synthesized.[5]

Asymmetric *cis–trans*-photoisomerizations of *cis*-cyclo-octene were carried out in the presence of the chiral sensitizers. The apparatus and the procedures were similar to those used in the preparative photoisomerization except for the higher *cis*-cyclo-octene concentrations and therefore lower conversion rates. The specific rotations of the isolated *trans*-cyclo-octene were measured in methylene chloride and were compared with the value of $-426°$ (CH_2Cl_2) [6] to give the excess of one enantiomer, corrected for the optical purity of the sensitizers and also for the purity of the *trans*-cyclo-octene produced.

RESULTS

The trans : cis *Ratios in the Photostationary State*, $(t/c)_{\text{pss}}$.—Irradiation of a cyclo-octene (0.07M) solution in the presence of a variety of aromatic esters (0.004—0.4M) led to *cis–trans*-isomerization as the only major photochemical reaction. Regardless of the sensitizer used, only negligible disappearance (0.4—1.9% h^{-1}) of the combined *cis* and *trans*-cyclo-octenes was detected on g.l.c. After prolonged irradiation (4—6 h) of a given *cis–trans*-mixture, the photostationary state was achieved for each sensitizer from both sides of the final $(t/c)_{\text{pss}}$ value. Most experiments were carried out in pentane solution under nitrogen, but methanol and acetonitrile were used in some cases. Deaeration of the samples had no effect on the photostationary ratios. A variety of aromatic esters with various substituents were used as sensitizers. The photostationary *trans* : *cis*-ratios are shown in Table 1 along with the sensitizers and the concentrations employed. The $(t/c)_{\text{pss}}$ value for methyl benzoate was independent of the sensitizer concentration in the range 0.004—0.4M. As can be seen from Table 1, a change from methyl to t-butyl benzoate has little effect on the $(t/c)_{\text{pss}}$ values. Substitution on the aromatic ring had a drastic effect on the value. Apart from the phthalates, substitution by either electron-donating or -withdrawing groups in any position reduced the $(t/c)_{\text{pss}}$ ratio dramatically, *e.g.* as shown by *p*-methoxy- and *p*-cyano-benzoate. Most phthalates gave comparable or higher $(t/c)_{\text{pss}}$ values than that for methyl benzoate. Dimethyl phthalate, however, gave quite a low $(t/c)_{\text{pss}}$ value, whilst phthalic anhydride was very efficient giving a $(t/c)_{\text{pss}}$ value of 0.28.

The use of polar solvents also gave a drastic increase in the $(t/c)_{\text{pss}}$. In methanol or acetonitrile, methyl benzoate and/or dimethyl isophthalate gave much higher $(t/c)_{\text{pss}}$ ratios up to 0.52 (34% *trans*) than those in pentane.

TABLE 1

Photostationary *trans* : *cis* ratios $(t/c)_{\text{pss}}$

Sensitizer	Concentration (M)	$(t/c)_{\text{pss}}$ (% *trans*)
(n-Pentane)		
Benzoic acid	0.036	0.26 (21)
Methyl benzoate	0.40	0.25 (20)
	0.080	0.25 (20)
	0.010	0.25 (20)
	0.004	0.25 (20)
Ethyl benzoate	0.070	0.26 (21)
t-Butyl benzoate	0.028	0.24 (19)
	0.010	0.26 (21)
(−)-Menthyl benzoate	0.010	0.26 (21)
Cholesteryl benzoate	0.020	0.20 (17)
Dimethyl phthalate	0.031	0.07 (6)
Phthalic anhydride	0.008	0.28 (22)
Dimethyl isophthalate	0.020	0.34 (25)
Di-(−)-menthyl isophthalate	0.020	0.38 (28)
Dimethyl terephthalate	0.006	0.27 (22)
Tetramethyl pyromellitate	0.005	0.10 (9)
Pyromellitic anhydride	0.005	0.02 (1.6)
Methyl salicylate	0.019	0.07 (6)
Methyl acetyl salicylate	0.030	0.09 (9)
p-Methoxybenzoic acid	0.003	0.01 (1)
Methyl *o*-methoxybenzoate	0.035	0.05 (4)
Methyl *p*-methoxybenzoate	0.047	0.06 (6)
Methyl *o*-methylbenzoate	0.037	0.09 (8)
Methyl *p*-methylbenzoate	0.061	0.11 (10)
Methyl *p*-cyanobenzoate	0.005	0.12 (11)
1,4-Dicyanobenzene	0.004	0.02 (2)
(Methanol)		
Methyl benzoate	0.010	0.36 (27)
Dimethyl isophthalate	0.010	0.52 (34)
(Acetonitrile)		
Methyl benzoate	0.010	0.35 (26)

Fluorescence Studies.—In order to reveal the involvement of excited singlet state of aromatic esters, attempts to detect fluorescence were carried out with methyl benzoate, dimethyl iso-, or tere-phthalate in cyclohexane or methanol. However, as mentioned in the literature,[7] these aromatic esters did not show any emission at room temperature, probably due to the n,π^* character of the lowest excited singlet state of the esters.

Stern–Volmer Studies.—Irradiation of a series of pentane solution containing 0.01M-methyl benzoate and pure *cis*- or *trans*-cyclo-octene of various concentrations (0.004—0.1M) on a merry-go-round apparatus and subsequent treatment gave Stern–Volmer plots of reciprocal yield *versus* reciprocal concentration for the *cis–trans*-photoisomerization of cyclo-octene sensitized by methyl benzoate. As shown in Figure 1, good linear relationships were obtained. Additionally, similar experiments were run with t-butyl benzoate and dimethyl isophthalate in pentane and also with methyl benzoate in methanol. Over the entire concentration range employed the Stern–Volmer plot gave a good linear relationship for each sensitizer, which indicates that only one excited state of the aromatic ester is involved in the photoisomerization. From the slopes and the intercepts of these plots and the Stern–Volmer equation, we calculated the k_c/k_d and k_t/k_d values and the limiting quantum yield ϕ^∞ for each sensitizer in a specific solvent (Table 2).

Piperylene Quenching Experiment.—The photoisomerization of 0.1M-*cis*-cyclo-octene sensitized by 0.4M-methyl benzoate was run in the presence of up to 0.05M-*trans*-piperylene. As shown in Figure 2, a plot of the reciprocal quantum yield of *trans*-cyclo-octene produced *versus* the piperylene concentration gave a good straight line over the entire quencher concentration employed. An analysis of the line gave the following values: intercept 2.50, slope 140 mol^{-1}.

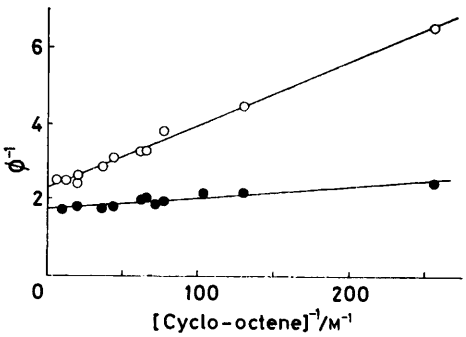

FIGURE 1 Reciprocal quantum yield of photoisomerization *versus* reciprocal cyclo-octene concentration in the methyl benzoate-sensitized *cis–trans*-photoisomerization of *cis*-(○) and *trans*-cyclo-octene(●) in n-pentane

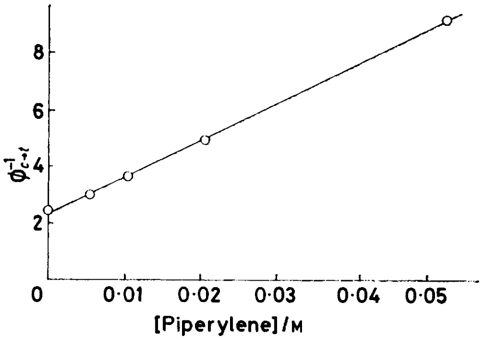

FIGURE 2 Effect of *trans*-piperylene on the *cis–trans*-photoisomerization of *cis*-cyclo-octene (0.1M) sensitized by methyl benzoate (0.4M)

TABLE 2

Summary of Stern–Volmer study

Sensitizer	Solvent	k_c/k_d	k_t/k_d	$1-\alpha$ $\phi^{\infty}_{c\to t}$	α $\phi^{\infty}_{t\to c}$
$PhCO_2Me$	n-Petane	140	590	0.43	0.57
$PhCO_2Me$	MeOH	130	340	0.42	0.53
$PhCO_2Bu^t$	n-Pentane	170	600	0.37	0.48
m-$C_6H_4(CO_2Me)_2$	n-Pentane	430	870	0.40	0.51

The preparative scale photoisomerization of *cis*-cyclo-octene in the presence of chiral sensitizer followed by the usual work-up gave *trans*-cyclo-octene, which was 97—99% pure and free from the chiral ester or its decomposition products. All the chiral esters gave (*R*)-(−)-enantiomer of *trans*-cyclo-octene in slight excess. The results are summarized in Table 3.

The effect of the reverse *trans–cis*-isomerization was checked by changing the irradiation period. However, no significant decrease of the optical yield was observed upon increasing the conversion rate up to 4%. A change in solvent from pentane to methanol also had little effect. The effect of changing the chiral substituent in the aromatic ester was drastic; cholesteryl benzoate was almost ineffective in asymmetric synthesis.

DISCUSSION

Recently, we reported a comparative study on direct and sensitized *cis–trans*-photoisomerization of cyclo-octene and showed that sensitized isomerization by a variety of triplet sensititizers with $E_T > 72$ kcal mol^{-1} give an extremely low *trans* : *cis* ratio in the photostationary state, *i.e.* $(t/c)_{pss}$ *ca.* 0.05, while direct photoisomerization at 185 nm gives a high $(t/c)_{pss}$ value of 0.96.[2a] This striking difference in the $(t/c)_{pss}$ ratios for direct and sensitized photoisomerization was reasonably interpreted in terms of the potential curves for the excited singlet (S_1) and triplet (T_1) states shown in Figure 3.

TABLE 3

Partially asymmetric *cis–trans*-photoisomerization

[Chiral sensitizer] [a]/M		[*cis*-Cyclo-octene]/M	Solvent	Conversion (%)	% E.e.[b]
$PhCO_2Men$	0.015	4.2	Pentane	1.9	3.1
	0.017	4.2	Pentane	2.8	3.2
	0.024	4.2	Pentane	4.0	2.8
	0.013	1.7	Methanol	2.0	3.0
$PhCO_2Chol$	0.015	4.2	Pentane	1.9	0.3
m-$C_6H_4(CO_2Men)_2$	0.015	4.0	Pentane	1.5	4.0

[a] Men = Menthyl; Chol = cholesteryl. [b] Enantiomeric excess of the isolated *trans*-cyclo-octene.

One-step Synthesis of trans-*Cyclo-octene*.—The aromatic ester sensitization gave a fairly high $(t/c)_{pss}$ ratio by irradiation at 254 nm, while direct irradiation at 254 nm without sensitizer did not result in *cis–trans*-isomerization. This method is an alternative, simple route to direct irradiation at 185 nm [2c] for preparing moderate amounts of *trans*-cyclo-octene. *trans*-Cyclo-octene of 99% purity was prepared in 15 or 18% isolated yield by methyl benzoate or dimethyl isophthalate sensitized photoisomerization.

Asymmetric cis–trans-*Photoisomerization*.—Three chiral aromatic esters, menthyl benzoate, cholesteryl benzoate, and dimenthyl isophthalate, were used as sensitizers in asymmetric *cis–trans*-photoisomerization. The $(t/c)_{pss}$ ratios for these chiral sensitizers (Table 1) are comparable to those obtained for the corresponding methyl esters. Unexpectedly, the use of methyl benzoate (E_T 78.7 kcal mol^{-1}) [8] as a sensitizer * increased the $(t/c)_{pss}$ value to 0.25. As can be seen from Table 1, the effect of changing the ester group of the benzoate is very small and these benzoates also give higher $(t/c)_{pss}$ values than does triplet sensitization. As for ring substitution, most sensitizers with either an electron-donating or -withdrawing group are ineffective in giving high

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* Although it is known that photochemical reactions of aromatic esters with alkenes give oxetans (T. S. Cantrell, *J.C.S. Chem. Comm.*, 1973, 468) and/or cycloadducts with an aromatic ring (Y. Katsuhara, T. Nakamura, A. Shimizu, Y. Shigemitsu, and Y. Odaira, *Chem. Letters*, 1972, 1215), a study of the properties of aromatic esters as sensitizers is lacking.

$(t/c)_{\text{pss}}$ ratios, while only dimethyl iso- and tere-phthalates and phthalic anhydride are as or more effective as methyl benzoate. These anomalously high $(t/c)_{\text{pss}}$ values suggest the involvement of a twisted singlet state (^1p) of cyclo-octene as an intermediate of the photoisomerization; the decay ratio of ^1p to *cis*- and *trans*-cyclo-octene is known to be almost unity.[2]

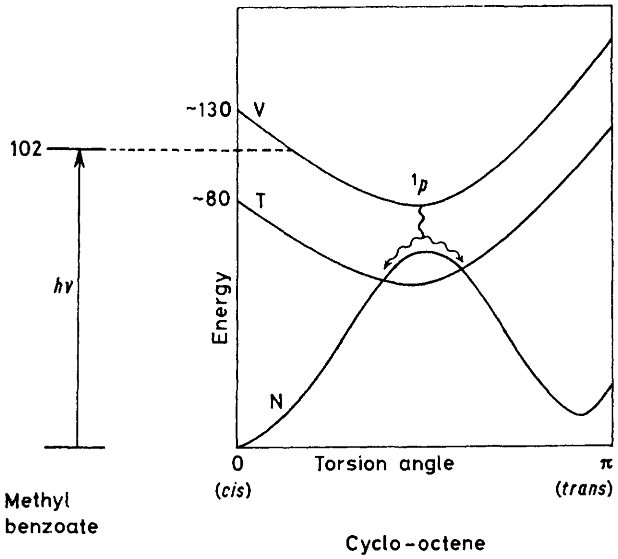
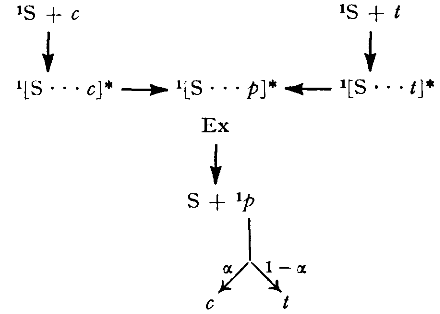


FIGURE 3 Energy diagram for the excited singlet state of methyl benzoate and potential surfaces for the excited singlet and triplet states and the ground state of cyclo-octene as a function of the torsional angle [2b]

The Stern–Volmer plots for typical sensitizers gave good straight lines suggesting that only one excited state of the sensitizer is involved in the photosensitization. This should be an excited singlet state of the aromatic esters, since the triplet energy transfer producing triplet cyclo-octene results in the extremely low $(t/c)_{\text{pss}}$ value of 0.05 and the possible 1,4-biradical, 'Schenck' intermediate which could be formed between excited benzoate and cyclo-octene falls apart regenerating the *cis*-isomer predominantly,[2a] because of the higher strain energy of the *trans*-isomer. Although these aromatic esters, unfortunately, show no fluorescence, we find additional support for the singlet mechanism in the decay ratio described later.

We consider the energetics before presenting a singlet sensitization mechanism. The singlet energy of methyl benzoate is reported to be 102 kcal mol^{-1},[8] while that of the Franck–Condon singlet of disubstituted alkenes is believed to be *ca.* 130 kcal mol^{-1}, although the potential curves for ^{1}S shows an energy minimum for the 90° twisted singlet (^1p) as shown in Figure 3. Therefore, a simple vertical singlet energy transfer mechanism fails to account for the photoisomerization. We propose a singlet exciplex mechanism which involves non-vertical singlet energy transfer from the aromatic ester to cyclo-octene *via* an exciplex producing a twisted, excited singlet cyclo-octene, ^1p, directly.

The reaction can be written as in Scheme 1. The interaction of the excited singlet (^{1}S) of the aromatic ester with the ground state *cis*- or *trans*-cyclo-octene, *c* or *t*, leads to encounter complexes with retention of the original configurations. Rotation about the C=C double bond stabilizes the complexes to give a common exciplex (Ex), where the double bond of the cyclo-octene (now represented by *p*) is twisted by *ca.* 90°. The results for asymmetric *cis–trans* photoisomerization sensitized by chiral esters can be taken as support for the involvement of an exciplex in the photoisomerization. In the case of the asymmetric photoisomerization, once an encounter complex is formed, the cyclo-octene moiety of the complex rotates about the double bond to give two distinct diastereoisomeric exciplexes since rotation brings about induced chiralty in the twisted cyclo-octene; asymmetric induction in the cyclo-octene must take place at this stage of the reaction. The preferred direction of rotation is prescribed by the chiral substituent of the sensitizer, although we cannot elucidate the detailed transition state geometry in the exciplex. With further rotation of up to *ca.* 90°, the exciplex finally falls apart leaving a ground state aromatic ester and a (+)- or (−)-twisted singlet of cyclo-octene ^1p. This chiral twisted singlet decays into *cis*- or chiral *trans*-cyclo-octene in the ground state.



SCHEME 1

This leads to the sequence in Scheme 2 where S, ^{1}S, and ^{3}S represent the ground, excited singlet, and triplet states of the aromatic ester, respectively. A steady-state treatment of the sequence gives the expressions (i)—(iii) for the reciprocal quantum yields of isomerization from *cis* to *trans* and *trans* to *cis* and also for the photostationary state *trans* : *cis*-ratio.

$$
\begin{aligned}
\mathrm{S} &\xrightarrow{h\nu} {}^1\mathrm{S} \\
{}^1\mathrm{S} &\xrightarrow{k_\mathrm{d}} {}^3\mathrm{S}, \mathrm{S} \\
c + {}^1\mathrm{S} &\xrightarrow{k_c} \mathrm{Ex} \\
t + {}^1\mathrm{S} &\xrightarrow{k_t} \mathrm{Ex} \\
\mathrm{Ex} &\longrightarrow {}^1p + \mathrm{S} \\
{}^1p &\longrightarrow \alpha c + (1 - \alpha)t
\end{aligned}
$$

SCHEME 2

$$1/\phi_{c\rightarrow t} = \frac{1}{1-\alpha}\left(1 + \frac{k_\mathrm{d}}{k_c[c]}\right) \qquad \text{(i)}$$

$$1/\phi_{t\rightarrow c} = \frac{1}{\alpha}\left(1 + \frac{k_{\mathrm{d}}}{k_t[t]}\right) \qquad \text{(ii)}$$

$$(t/c)_{\mathrm{pss}} = \frac{1-\alpha}{\alpha}\cdot\frac{k_c}{k_t} \qquad \text{(iii)}$$

The decay ratio $(1-\alpha)/\alpha$ and the excitation ratio k_c/k_t for each sensitizer can be obtained from the values shown in Table 2. The calculated decay and excitation ratios are shown in Table 4. It should be noted that, in spite of the steric and electronic differences of the sensitizers and also the difference of solvent polarity, the three sensitizers give the same decay ratio, *i.e.* $(1-\alpha)/\alpha = 0.78$. This strongly indicates the presence of a common intermediate as an immediate precursor of the photoisomerization. On the other hand, the excitation ratio, k_c/k_t, which is responsible for the higher $(t/c)_{\mathrm{pss}}$ values for the polar solvent, is dependent on the solvent or sensitizer. The higher quenching constant for the *trans*-isomer, *i.e.* $k_t > k_c$, can be interpreted in terms of the higher strain energy or the lower ionization potential of the *trans*-isomer.[9] The increased k_c/k ratios upon using a polar solvent or isophthalate as a sensitizer suggest some charge transfer interaction in the encounter complex; further discussion is given in the following paper.[10] Additionally, the $(t/c)_{\mathrm{pss}}$ values calculated from equation (iii) were consistent with the observed values (see Table 4). The facts that (1) three sterically and electronically different sensitizers in different solvents give the same decay ratio and (2) the decay ratio observed is in good agreement with the ratio from the excited singlet state (^1p) obtained in the direct excitation at 185 nm of cyclo-octene,[2] are strongly in favour of the electronically excited state which leads to *cis–trans*-isomerization, being the twisted, excited singlet state of cyclo-octene.*

TABLE 4

Kinetic parameters

Sensitizer	Solvent	Decay ratio $(1-\alpha)/\alpha$	Excitation ratio, k_c/k_t	$(t/c)_{\mathrm{pss}}$ Calc.*	Obs.
$\mathrm{PhCO_2Me}$	n-Pentane	0.76 ± 0.03	0.24 ± 0.04	0.18	0.25
$\mathrm{PhCO_2Me}$	MeOH	0.79 ± 0.01	0.38 ± 0.02	0.30	0.36
$\mathrm{PhCO_2Bu}^t$	n-Pentane	0.77 ± 0.02	0.28 ± 0.03	0.22	0.26
m-$\mathrm{C_6H_4(CO_2Me)_2}$	n-Pentane	0.78 ± 0.02	0.49 ± 0.03	0.38	0.34
Direct excitation at 185 nm		0.88 ± 0.08			
Triplet sensitization		0.049 ± 0.002			

* $(t/c)_{\mathrm{pss}}$ calculated by equation (iii).

Piperylene quenching studies of the photoisomerization gives additional kinetic values. Piperylene is known as a quencher of the n,π^* excited singlet of alkanones,[11] although this compound is well established as a triplet quencher. In the presence of *trans*-piperylene (*t*-P), quenching path in Scheme 3 should be added to Scheme 2. A steady-state treatment of the whole sequence leads to expression (iv) for the reciprocal quantum yield for the *cis–trans*-isomerization of cyclo-octene where the concentration of *cis*-cyclo-octene is

$$1/\phi^{\mathrm{P}}{}_{c\rightarrow t} = \frac{1}{1-\alpha}\left(1 + \frac{k_{\mathrm{d}} + k_{\mathrm{q}}[t\text{-P}]}{k_{\mathrm{c}}[c]}\right) \qquad \text{(iv)}$$

0.1M. Using equation (iv) and the $(1-\alpha)$ value in Table 2, we can evaluate the relative rate constants

$$^1\mathrm{S} + t\text{-P} \xrightarrow{k_{\mathrm{q}}} \mathrm{S} + {}^1\mathrm{P}$$

$$^1\mathrm{P} \longrightarrow c\text{-P} + t\text{-P}$$

SCHEME 3

k_{q}/k_c from the slope in Figure 2; $k_{\mathrm{q}}/k_c = 6.0$. The value k_{q}/k_t of 1.5 is derived as the product of k_{q}/k_c and k_c/k_t (Table 4). It should be noted that the quenching constant for *trans*-cyclo-octene is comparable with that for the diene, though quenching by *cis*-cyclo-octene is much more slower as expected.

We conclude that the use of an aromatic ester as a sensitizer enables us to produce the excited singlet state of a simple alkene by irradiation at 254 instead of 185 nm. Since the excitation constitutes non-vertical activation directly to a twisted singlet state, there is little possibility of side reactions, which, in the case of the direct irradiation at 185 nm, may take place *via* the Rydberg state.[2a] The decay from the twisted singlet is ' strain-free ', and therefore this method may be useful especially in carrying out *cis–trans*-photoisomerizations where formation of one of the isomers is unfavourable for triplet sensitization due to the strain energy. Furthermore, this could be a general method for generating excited singlet state of simple alkene.

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* One might suppose that direct decay from the exciplex takes place prior to the generation of ^1p. However, the above facts make such an assumption unlikely, because it is improbable that there is the same decay ratio for exciplexes with different structures and/or energies. This kind of argument can be applied to eliminate the possibility of a triplet exciplex as an intermediate of the photoisomerization.

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