# Singlet Photosensitization of Simple Alkenes. Part 2.† Photochemical Transformation of Cyclo-octa-1,5-dienes sensitized by Aromatic Ester

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Irradiation of an oxygen-free pentane solution of *cis,cis*- or *cis,trans*-cyclo-octa-1,5-diene, (1*cc*) or (1*ct*), in the presence of methyl benzoate as sensitizer gave the *cis,trans*-isomer and tricyclo[3.3.0.0$^{2,6}$]octane. However, the tricyclo-octane was not an immediate product from (1*cc*), but was formed *via* (1*ct*). Kinetic evidence and energetic considerations indicate a non-vertical singlet sensitization mechanism involving a singlet exciplex, which in turn falls apart leaving a twisted, excited singlet of the cyclo-octadiene. Two exciplexes, $Ex_1$ and $Ex_2$, and therefore two twisted singlet cyclo-octadienes, $c,{}^1p$ and $t,{}^1p$, are postulated in order to rationalize the different reactivity of (1*cc*) and (1*ct*). No evidence for transannular interaction between the two double bonds was found from the quenching rate constants. Correlations between the quenching rate constants and the oxidation potentials of the cyclo-octadienes and cyclo-octenes suggest charge-transfer character for the exciplex. Asymmetric *cis–trans* photoisomerization sensitized by a chiral aromatic ester also supports the involvement of exciplex with a fairly rigid structure.

THE photochemical behaviour of *cis,cis*-cyclo-octa-1,5-diene (1*cc*) has been studied by sensitization with mercury ($^3P_1$) atoms in the vapour phase and by irradiation in the presence of copper(I) chloride in the liquid phase.[1-3] One of the most interesting features of these photoreactions is the conversion of *cis,cis*-cyclo-octa-1,5-diene into *cis,trans*- and *trans,trans*-cyclo-octa-1,5-diene, (1*ct*) and (1*tt*), and into tricyclo[3.3.0.0$^{2,6}$]octane (2); the *trans,trans*-diene (1*tt*) was obtained only upon irradiation of a pentane suspension of di-μ-chloro-bis-(*cis,cis*-cyclo-octa-1,5-diene)dicopper(I) (3),[3] and (1*ct*) and (2) were formed in all cases reported.[1-3] Although the basic mechanism for the formation of (2) upon the mercury photosensitization has been established, the mechanism of the copper-catalysed photochemical reaction in solution has not been clarified satisfactorily because of the complicated behaviour of (3) in solution.[3]

Our recent studies[4] on the *cis–trans*-photoisomerization of cyclo-octene have revealed that methyl benzoate and some other aromatic esters can non-vertically promote simple alkenes to a twisted alkene in the excited singlet state *via* a singlet exciplex. The results prompted us to use an aromatic ester as a singlet sensitizer for cyclo-octa-1,5-diene, where intramolecular competition towards singlet sensitization and transannular interaction between the two double bonds are expected. We report here a study on the methyl benzoate-sensitized photoisomerization of cyclo-octa-1,5-dienes in the liquid phase.

## EXPERIMENTAL

*Materials.*—Commercially available *cis,cis*-cyclo-octa-1,5-diene, which was free from its *cis,trans*-isomer, was purified by fractional distillation through a spinning-band column. The combined chemical impurities, as demonstrated by g.l.c., were $<0.4\%$. *cis,trans*-Cyclo-octa-1,5-diene was prepared by reported procedures[3, 5] at the beginning of the study but later by the methyl benzoate-sensitized photoisomerization of *cis,cis*-cyclo-octa-1,5-diene, which was found to be a more efficient preparative method. The procedure consists of the irradiation of a pentane solution (80 ml) of 0.1M-*cis,cis*-cyclo-octa-1,5-diene in the presence of 0.01M-methyl benzoate, followed by purifying the product by treatment with aqueous silver nitrate[6] and subsequent preparative g.l.c. to a purity of 99.0% (*cis,cis*-content 0.8%). Methyl benzoate employed as a sensitizer was purified by fractional distillation. The optically active sensitizer, (−)-methyl benzoate, was prepared in the reaction of (−)-menthol and benzoyl chloride followed by repeated recrystallization from methanol, m.p. 51.0—52.5 °C, $[\alpha]_D^{19}$ −85.1° (EtOH).[7] n-Pentane was treated with concentrated sulphuric acid, washed with water, dried over potassium carbonate, and fractionally distilled. Commercial benzene was distilled from phosphorus pentaoxide after sulphuric acid–water–hydrogencarbonate treatment. Spectrograde methanol (Tokyo Kasei Co.) was used without further purification.

*Analysis.*—G.l.c. analyses were carried out using a 2-m glass column of 10% 1,2,3-tris-(2-cyanoethoxy)propane at 60 °C or a 3 m glass column of 20% ββ′-oxydipropiononitrile at 70 °C. Preparative g.l.c. of the *cis,trans*-cyclo-octa-1,5-diene was performed by using a 2-m column of 5% Ucon LB 550X at 80 °C. The *cis*- and *trans*-isomers of cyclo-octa-1,5-diene were separated completely under these conditions. n-Octane and cyclo-octane were employed as internal standards.

*Photoisomerization Studies.*—Photoisomerizations were carried out at room temperature in a quartz tube, 1 cm in diameter, using a 300-W high-pressure mercury lamp. Under typical photolysis conditions, pentane solutions of 0.02M-cyclo-octa-1,5-diene containing 0.01M-methyl benzoate and 0.001M-cyclo-octane or -n-octane as an internal standard were flushed with nitrogen gas and then irradiated. In the Stern–Volmer experiments, the samples were degassed by four freeze–pump–thaw cycles on a vacuum line fitted with an oil diffusion pump (*ca.* $10^{-6}$ Torr). Stern–Volmer plots for the photosensitized isomerization of *cis,cis*- or *cis,trans*-cyclo-octa-1,5-diene were obtained by irradiating the samples containing 0.01M-methyl benzoate (0.1M in the case of *cis,trans*-cyclo-octa-1,5-diene) and 0.004—0.02M-cyclo-octa-1,5-diene in a merry-go-round

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† Part 1 is ref. 4*b*.

apparatus with a 300-W high-pressure mercury lamp, where conversions of the diene were <7%. The chemical actinometer employed was the methyl benzoate-sensitized photoisomerization of *cis*-cyclo-octene to the *trans*-isomer, the quantum yield of which was determined by ferrioxalate actinometry.

*Identification of the Products.*—*cis,trans*-Cyclo-octa-1,5-diene (1*ct*), tricyclo[3.3.0.0$^{2,6}$]octane (2) and *cis*-bicyclo-[3.3.0]oct-2-ene (4) were identified by direct comparison of the retention times of g.l.c., mass, i.r., and n.m.r. spectra with those of independently synthesized authentic samples. The *cis,trans*-diene and the tricyclo-octane were prepared by irradiating the pentane solution of *cis,cis*-cyclo-octa-1,5-diene in the presence of (3),[3] and (4) by potassium catalysed cyclization of cyclo-octa-1,3-diene.[8] 2-Methoxybicyclo-[3.3.0]octane (5) and 5-methoxy-*cis*-cyclo-octene (6) were isolated from the reaction mixture of (1*ct*) with acidic methanol by preparative g.l.c. and identified by their mass, i.r., and n.m.r. spectra.

*Oxidation Potential Measurements.*—Oxidation potentials were obtained by cyclic voltammetry using a platinum electrode with 0.1M-tetraethylammonium tetrafluoroborate in acetonitrile solutions, *versus* Ag–0.01M-AgClO$_4$. The oxidative process was not reversible and half-wave potentials were evaluated from cyclic voltammograms obtained at a 100 mV s$^{-1}$ sweep rate. Tetraethylammonium tetrafluoroborate used as a supporting electrolyte was prepared by the reaction of tetraethylammonium bromide with fluoroboric acid.[9] Recrystallization of the product from methanol–petroleum was carried out prior to use. Acetonitrile was distilled five times over phosphorus pentaoxide. The substrate (0.001M) was dissolved in acetonitrile. The solution was bubbled with nitrogen for 30 min, and the measurement was carried out under a nitrogen atmosphere.

*Asymmetric Induction.*—The preparative-scale photoisomerization of 0.1M-*cis,cis*-cyclo-octa-1,5-diene in the presence of 0.01M-(−)-menthyl benzoate was carried out at room temperature in a quartz vessel (80 ml) surrounding a 300-W high-pressure mercury lamp. A low conversion rate (4%) was employed in order to prevent influence of the reverse *trans*–*cis*-photoisomerization. Subsequent silver nitrate treatment[6] followed by purification by g.l.c. gave *cis,trans*-cyclo-octa-1,5-diene which was shown to be 98% pure by g.l.c. and was free from the chiral sensitizer. The specific rotation ($\alpha_D^{23}$) of the product (1*ct*) was measured by a Hitachi polarimeter (type PO–B) in methylene chloride.

## RESULTS AND DISCUSSION

*Participation of Excited-singlet Methyl Benzoate.*—The photolysis of a pentane solution containing 0.02M-*cis,cis*-cyclo-octa-1,5-diene (1*cc*) in the presence of 0.01M-methyl benzoate gave *cis,trans*-cyclo-octa-1,5-diene (1*ct*) and tricyclo[3.3.0.0$^{2,6}$]octane (2) along with polymeric products which precipitate from the pentane solution after prolonged irradiation.* The product yields are presented in Table 1, compared with benzene-sensitized photoisomerization of *cis,cis*-cyclo-octa-1,5-diene. Methyl benzoate was sufficiently effective as a sensitizer for the photoisomerization to give a relatively high yield of (1*ct*), while benzene failed to sensitize the *cis*–*trans*-photoisomerization. Taking into account the discussion in the preceding paper,[4b] this high yield for *cis*-*trans*-isomerization upon benzoate sensitization suggests the involvement of an excited singlet state of cyclo-octadiene produced by singlet sensitization by methyl benzoate.

TABLE 1

Photoisomerization of cyclo-octa-1,5-diene in pentane

| Compound | Sensitizer | Irradiation time (min) | Yield (%) [a] | | | |
|---|---|---|---|---|---|---|
| | | | (1*cc*) | (1*ct*) | (2) | Other |
| (1*cc*) | Methyl benzoate | 70 | 70 | 11 | 3.4 | Polymer |
| (1*ct*) | Methyl benzoate | 40 | 40 | 14 | 8.1 | Polymer |
| (1*cc*) | None | 120 | 100 | 0 | 0 | |
| (1*cc*) | Benzene (solvent) | 120 | Major | Trace | 0 | Polymer |

[a] Yields based on the amount of the starting material used.

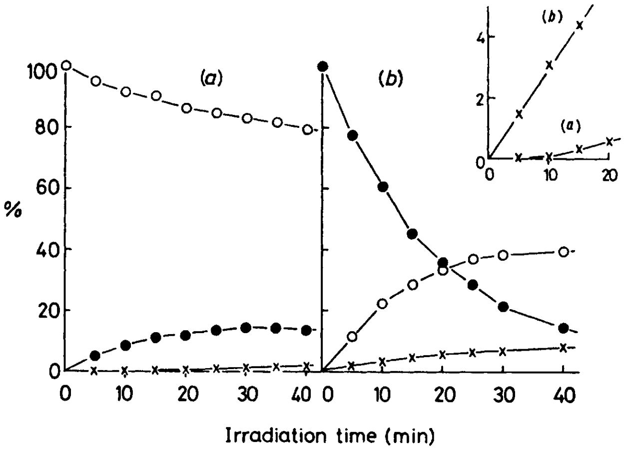

FIGURE 1 Yield of the tricyclo-octane (×), *cis,cis*- (○), and *cis,trans*-cyclo-octadiene (●), during the irradiation of (*a*) *cis,cis*- and (*b*) *cis,trans*-cyclo-octadiene in the presence of methyl benzoate. The insert gives yields of the tricyclo-octane on an expanded scale in the initial stages of irradiation.

*Pathway for Tricyclo-octane* (2) *Formation.*—In an effort to determine whether the tricyclo-octane (2) was formed from *cis,cis*-cyclo-octa-1,5-diene (1*cc*) or *cis,trans*-cyclo-octa-1,5-diene (1*ct*), the yields of (2) and the dienes were examined as a function of the irradiation period for the photoreaction of (1*cc*) or (1*ct*) with methyl benzoate under typical photolysis conditions (Figure 1).

Some significant facts emerge from the data in Figure 1. In the case of the irradiation of (1*cc*), the rate of the formation of (2) was initially zero, but became faster gradually with increasing amount of (1*ct*) produced in sharp contrast with the results for (1*ct*) where (2) was formed in the initial stage of the reaction. These results indicate that, while it is not formed from (1*cc*), (2) is formed predominantly from the photoreaction of (1*ct*) with methyl benzoate (Scheme 1).

*Photolysis in the Presence of Acidic Methanol.*—It has been shown that highly strained *trans*-cycloalkenes such as *trans*-cyclo-octene and *trans*-cycloheptene react rapidly with acidic methanol forming the corresponding methyl ethers as addition products.[10] Hence, the methyl benzoate-sensitized photolysis of (1*cc*) was performed in the presence of acidic methanol to try and

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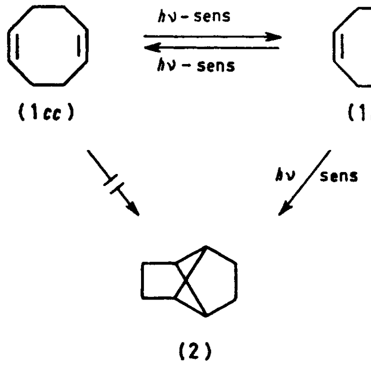
* No dimer could be detected.

TABLE 2

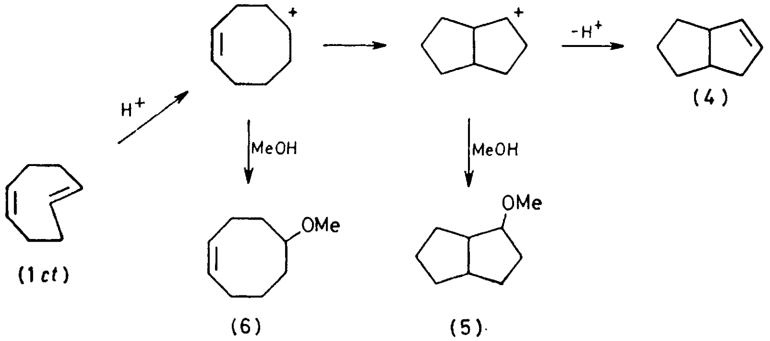
Photolysis of (1*cc*) in methanol and the reaction of (1*ct*) with acidic methanol

| Run | Compound (M) | [Methyl benzoate]/M | [$H_2SO_4$]/M | Irradiation time (h) | Treatment after irradiation | Product ratio (4) : (5) : (6) |
|---|---|---|---|---|---|---|
| a | (1*cc*) (0.1) | 0.01 | 0.03 | 2 | None | 2 : 3 : 2 |
| b | (1*cc*) (0.1) | 0.01 | 0 | 2 | Leave for 4 h at 0 °C, then add $H_2SO_4$ (0.03M) | 1.8 : 3 : 2.0 |
| c | (1*ct*) (0.1) | 0 | 0 | 0 | Add $H_2SO_4$ (0.03M) | 2.2 : 3 : 1.9 |

obtain the highly strained *trans,trans*-isomer (1*tt*).* The results of the photolysis of *cis,cis*-cyclo-octa-1,5-diene in neutral and also in acidic methanol showed that in the presence of acidic methanol only *cis*-bicyclo[3.3.0]oct-2-ene (4), 2-methoxybicyclo[3.3.0]octane (5), and 5-methoxy-*cis*-cyclo-octene (6) were obtained in a significant yield. In order to explore the precursor of products (4)—(6), the following three runs were compared: (a) photolysis of (1*cc*) in acidic methanol, (b) addition of acid after photolysis of (1*cc*) in neutral methanol, (c) thermal reaction of (1*ct*) with acidic methanol. The reaction conditions and product ratios are shown in Table 2. These three runs gave (4)—(6) as the main products in the identical ratio of 2 : 3 : 2, and other products such as 5-methoxy-*trans*-cyclo-octene and dimethoxycyclo-octane, which might be formed by a reaction of (1*tt*) with acidic methanol, could not be detected by g.l.c.† This result indicates that these three products were not formed from (1*tt*) but from (1*ct*) according to Scheme 2.[11] Furthermore, formation of (1*tt*) could not be detected by g.l.c. in a photolysed pentane solution of (1*cc*) or (1*ct*) and methyl benzoate even under comparable g.l.c. conditions ‡ to those of Whiteside *et al.*[3]



SCHEME 1



SCHEME 2

*Mechanism of Photoisomerization.*—Quantum yields for *cis–trans*-photoisomerization were measured at different cyclo-octa-1,5-diene concentrations and treated by the Stern–Volmer method by plotting $\phi^{-1}$ against [cyclo-octa-1,5-diene]$^{-1}$. As shown in Figure 2, the plots gave linear relationships, indicating that only one excited state of methyl benzoate is involved in the isomerization.

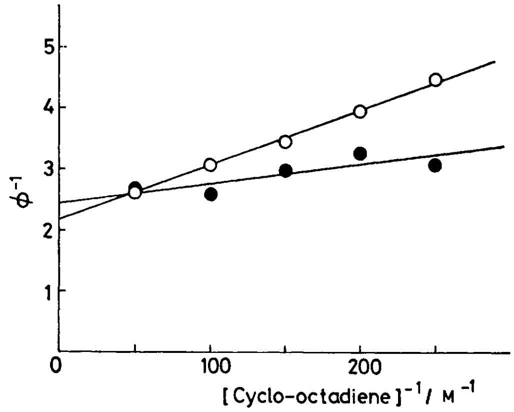


FIGURE 2 Reciprocal quantum yield of photoisomerization *versus* reciprocal cyclo-octadiene concentration in the methyl benzoate-sensitized *cis-trans*-photoisomerization of *cis,cis*- (○) and *cis,-trans*-cyclo-octa-1,5-diene (●) in n-pentane

The excited state involved is the excited singlet state of methyl benzoate, since the anomalously high yield of *cis–trans*-photoisomerization product upon benzoate sensitization of (1*cc*) cannot be accounted for in terms of triplet sensitization, which resulted in quite a low *cis–*

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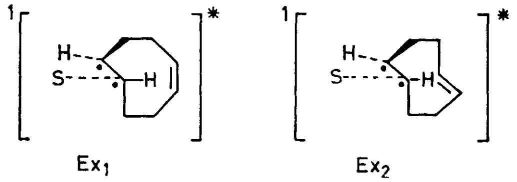
* The strain energy of (1*tt*) was calculated to be 27.8 kcal mol$^{-1}$ (see N. C. Allinger and J. T. Sprangue, *J. Amer. Chem. Soc.*, 1972, **94**, 5734).

† We also carried out the reaction of (1*cc*) with acidic methanol in the absence of light as a control experiment. No products could be detected by g.l.c.

‡ Under these conditions, we detected (1*tt*) by g.l.c. analysis of the irradiated pentane solution of (1*cc*) in the presence of (3).

*trans*-photoisomerization yield as shown in Table 1. However, the vertical singlet energy transfer from the excited singlet benzoate to cyclo-octadiene is energetically difficult because of the higher spectroscopic singlet energy of cyclo-octadienes than that (102 kcal $mol^{-1}$) of methyl benzoate. A mechanism *via* a singlet exciplex formed from excited singlet benzoate and cyclo-octadiene is proposed, by analogy with the exciplex from cyclo-octene.[4b] *cis,trans*-Cyclo-octa-1,5-diene has two kinds of double bonds which are distinguishable from each other, while (1*cc*) has only one type. Thus, an attack of excited singlet methyl benzoate to (1*ct*) may occur at the *cis*-double bond, *i.e. cis*-attack, and attack may also occur at the *trans*-double bond, *i.e. trans*-attack. For (1*cc*), of course, only *cis*-attack is possible. *cis*-Attack of the sensitizer (S) on (1*cc*) leads to an exciplex ($Ex_1$) which is stabilized by having the *cis*-double bond of the diene twisted to a nearly orthogonal position.[4] This exciplex has the same conformation as that obtained by *trans*-attack on (1*ct*) and subsequent rotational relaxation of the *trans*-double bond. On the other hand, *cis*-attack on (1*ct*) leads to the other exciplex ($Ex_2$) where the *cis*-double bond is twisted with retention of the *trans*-double bond.



SCHEME 3

With further rotation of up to *ca.* 90°, each exciplex falls apart generating a ground-state sensitizer and a twisted, excited singlet of cyclo-octadiene $c,{}^1p$ or $t,{}^1p$, only one double bond of which is twisted with retention of the *cis*- or *trans*-configuration on the other double bond.

The twisted singlet cyclo-octene $c,{}^1p$ decays to (1*cc*) or (1*ct*) in the ratio $\beta/(1-\beta)$, while the other twisted singlet $t,{}^1p$ decays to (1*ct*) or (2) instead of (1*tt*). This latter decay path is supported by the fact[3] that direct irradiation of (1*tt*) gives (2) in good yield, since the intermediate of direct photolysis should be the twisted singlet $t,{}^1p$.

On the basis of the above considerations, we propose the singlet sensitization mechanism of reactions (1)—(6) in order to account for the methyl benzoate-sensitized photoisomerization of cyclo-octa-1,5-diene,* where $c,{}^1p$

$$S \xrightarrow{h\nu} {}^1S \qquad (1)$$

$$^1S \xrightarrow{k_d} {}^3S, S \qquad (2)$$

$$(1cc) + {}^1S \xrightarrow{k_c} Ex_1 \qquad (3)$$

$$(1ct) + {}^1S \xrightarrow{k_t} \alpha Ex_1 + (1-\alpha)Ex_2 \qquad (4)$$

$$Ex_1 \longrightarrow c,{}^1p \longrightarrow \beta(1cc) + (1-\beta)(1ct) \qquad (5)$$

$$Ex_2 \longrightarrow t,{}^1p \longrightarrow \gamma(2) + (1-\gamma)(1ct) \qquad (6)$$

and $t,{}^1p$ represent the two kinds of twisted singlets of cyclo-octadiene. A steady state treatment of sequence (1)—(6) leads to relationships (7)—(9), where $\phi_{c\to t}$,

$$1/\phi_{c\to t} = \frac{1}{1-\beta}\left\{1 + \frac{k_d}{k_c[(1cc)]}\right\} \qquad (7)$$

$$1/\phi_{t\to c} = \frac{1}{\alpha\beta}\left\{1 + \frac{k_d}{k_t[(1ct)]}\right\} \qquad (8)$$

$$1/\phi_{t\to(2)} = \frac{1}{\gamma(1-\alpha)}\left\{1 + \frac{k_d}{k_t[(1ct)]}\right\} \qquad (9)$$

$\phi_{t\to c}$, and $\phi_{t\to(2)}$ represent initial quantum yields for the conversion of (1*cc*) into (1*ct*), (1*ct*) into (1*cc*), and (1*ct*) into (2), respectively.

As shown in Figure 2, the plots of the reciprocal of the quantum yield for the photoisomerization against the reciprocal of the diene concentration gave linear relationships. The slope of the plot should be $(k_q\tau)^{-1}$, where $k_q$, *i.e.* $k_c$ or $k_t$, is the quenching rate constant and $\tau$ the lifetime of excited singlet methyl benzoate in the absence of cyclo-octa-1,5-diene. The intercept should be $(\phi^\infty)^{-1}$, the reciprocal of the limiting quantum yield for the isomerization at infinite diene concentration. Using the limiting quantum yields from (1*cc*) ($\phi^\infty_{(1cc)\to(1ct)}$ 0.46) and (1*ct*) ($\phi^\infty_{(1ct)\to(1cc)}$ 0.41 and $\phi^\infty_{(1ct)\to(2)}$ 0.06 †), we calculated parameters $\alpha$, $\beta$, and $\gamma$. The results are summarized in Table 3, along with those for cyclo-octene.[4b]

TABLE 3

Results of Stern–Volmer studies in pentane

| Compound | $k_q\tau$/ l $mol^{-1}$ | Excitation ratio $k_c/k_t$ | Decay ratio $(1-\beta)/\beta$ | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|---|---|
| (1*cc*) | 250 | 0.29 | 0.85 | 0.76 | 0.54 | 0.25 |
| (1*ct*) | 860 | | | | | |
| *cis*-Cylco-octene | 140 | 0.25 | 0.76 | | 0.57 | |
| *trans*-Cyclo-octene | 590 | | | | | |

The decay ratio $(1-\beta)/\beta$ from $c,{}^1p$ is 0.85, indicating that decay to (1*cc*), the more stable isomer, is slightly favoured, while the decay ratio $\gamma/(1-\gamma)$ from $t,{}^1p$ is 0.33. The ratio $(1-\alpha)/\alpha$ for the intramolecular selectivity for attack by $^1S$ on the two kinds of double bonds of (1*ct*) is 0.32, which is comparable to the intermolecular excitation selectivity ratio (*cis*/*trans* 0.24) for *cis*- and *trans*-cyclo-octenes. This demonstrates that excited singlet methyl benzoate much prefers the *trans*-double bond to the *cis* as shown for cyclo-octenes in the preceding paper.[4b] In addition, since the sum of $k_q\tau$ (730 l $mol^{-1}$) for *trans*-cyclo-octene (590) and *cis*-cyclo-octene (140) is very close to that for (1*ct*) (860), and $k_q\tau$ for (1*cc*) (250) was about twice that for *cis*-cyclo-octene (140), it was

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* We are not sure so far whether or not the exciplexes directly decay to (1*cc*), (1*ct*), or (2).

† Since low conversion rates were employed for the Stern–Volmer studies, we could not directly measure the yield of (2). However, the constant product ratio of (2) : (1*cc*) maintained throughout the initial stage of the reaction (Figure 1) allow us to evaluate the $\phi^\infty_{t\to(2)}$ value.

shown that each double bond of *cis,cis*- or *cis,trans*-cyclo-octa-1,5-diene acts independently of the other during attack by excited singlet methyl benzoate. No evidence in support of transannular interaction between the two double bonds was observed during photosensitization.

In order to obtain an insight into the characteristics of the exciplex, we have measured the oxidation potentials of cyclo-octa-1,5-diene and attempted to correlate them with the relative quenching rate constants. The results are summarized in Table 4, together with those for cyclo-octenes. Although the quenching rate constants for both cyclo-octa-1,5-dienes or cyclo-octenes increased with the decrease of $E^{\mathrm{Ox}}_{1/2}$ in each system, this relation between the uncorrected $k_q\tau$ and $E^{\mathrm{Ox}}_{1/2}$ was not observed throughout all the compounds in Table 4. However, this kind of direct comparison between these $k_q\tau$ values and the oxidation potentials is meaningless, since only one of the two double bonds, that with the lower oxidation potential, is responsible for the observed oxidation potential of cyclo-octadiene. If the $k_q\tau$ value can be distributed between the respective double bonds of the cyclo-octadienes, the fractional $k_q\tau$ for the *trans*-double bond in (1*ct*) and the fractional $k_q\tau$ for a *cis*-double bond in (1*cc*) should be correlated with the oxidation potential for each diene. The corrected $k_q\tau$ values are equal to $860\alpha = 654$ l mol$^{-1}$ for (1*ct*) and $250/2 = 125$ l mol$^{-1}$ for (1*cc*). As shown in Table 4, the $k_q\tau$ value increases with decreasing oxidation potential of the alkene. This result indicates the existence of a charge-transfer interaction between excited singlet benzoate and the cyclo-octadienes and also demonstrates that the two double bonds of cyclo-octa-1,5-diene act independently during the attack of the sensitizer singlet.

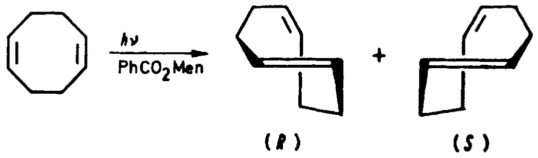
TABLE 4

Oxidation potentials and the quenching rate constants for cyclo-octa-1,5-dienes and cyclo-octenes

| Compound | $E^{\mathrm{Ox}}_{1/2}$/V [a] | $k_q\tau$/l mol$^{-1}$ Observed | $k_q\tau$/l mol$^{-1}$ Corrected [b] |
|---|---|---|---|
| (1*cc*) | 1.82 | 250 | 125 |
| (1*ct*) | 1.48 | 860 | 654 |
| *cis*-Cyclo-octene | 1.76 | 140 [c] | 140 |
| *trans*-Cyclo-octene | 1.56 | 590 [c] | 590 |

[a] Oxidation potentials were measured under the conditions reported in the Experimental section. [b] These corrected values can be correlated with $E^{\mathrm{Ox}}_{1/2}$; see text. [c] See ref. 4*b*.

*Asymmetric Photoisomerization.*—We have recently reported on novel asymmetric *cis–trans*-photoisomerization of cyclo-octene sensitized by chiral aromatic esters.[7] In order to extend the scope of this asymmetric induction method, we have applied the method to the photochemical *cis–trans*-isomerization of cyclo-octa-1,5-diene. (−)-Menthyl benzoate was employed as a chiral sensitizier. Upon photosensitization of (1*cc*), this chiral ester acted as a sensitizer as effectively as methyl benzoate did, and, after work-up of the photolysed solution, gave the (−)-enantiomer of (1*ct*) in slight excess; $[\alpha]_D^{23}$ −2.43° (*c* 3.7, $CH_2Cl_2$); e.e. 1.6%.*



SCHEME 4

This result demonstrates that, when the diene unit of an encounter complex between the excited benzoate and (1*cc*) starts to rotate about the C=C double bond into the more stable exciplex, the direction of rotation of the C=C double bond is influenced by the chiral ester moiety, and hence gives further support for the involvement of an exciplex with a fairly rigid structure in the course of photoisomerization.

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* e.e. = Enantiomeric excess based on the value of $[\alpha]_D^0$ −152° (see A. C. Cope, J. K. Hecht, H. W. Johnson, H. Keller, and H. J. S. Winler, *J. Amer. Chem. Soc.*, 1966, **88**, 761).