Asymmetric *cis–trans* Photoisomerization of Cyclo-octene Sensitized by Chiral Aromatic Esters

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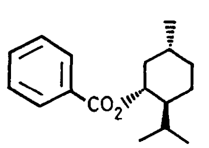
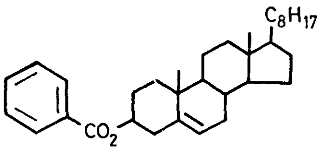
Summary The asymmetric *cis→trans* photoisomerization of cyclo-octene (**1**) in the presence of the chiral aromatic esters, (—)-menthyl benzoate (**2**), cholesteryl benzoate (**3**), or di-(—)-menthyl isophthalate (**4**) gave (*R*)-(—)-*trans*-cyclo-octene with a maximum enantiomeric excess of 4·0%.

Although asymmetric organic reactions have been of increasing interest in recent years, only to a limited extent have attempts been made at asymmetric induction of an achiral substrate by photosensitization with a chiral molecule.[1]

Our recent studies[2] on the *cis–trans* photoisomerization of cyclo-octene (**1**) have revealed, on the basis of the anomalously high *trans*: *cis* ratio at the photostationary state compared with those observed for the triplet sensitization and other kinetic evidence, that methyl benzoate and some other aromatic esters can promote the cyclo-octene molecule to its twisted, first excited singlet state *via* a singlet exciplex to give *cis–trans* isomerization on deactivation of the twisted singlet. This result prompted us to introduce chiral substituents into the alcoholic group of aromatic esters and to study the subsequent photosensitization with these chiral aromatic esters. We now present the first example of asymmetric *cis–trans* photoisomerization of cyclo-octene sensitized by chiral sensitizers.



(2)



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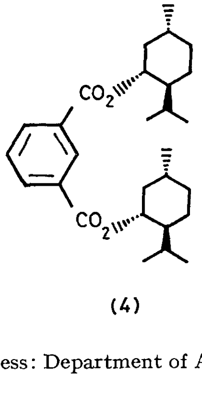

(4)

Three chiral aromatic esters, (—)-menthyl benzoate [(**2**), m.p. 51·0—52·0 °C, $[\alpha]_D^{19}$ —85·1° (EtOH)], cholesteryl benzoate [(**3**), m.p. 151—152 °C, $[\alpha]_D^{25}$ —13·7° ($CHCl_3$)], and di-(—)-menthyl isophthalate [(**4**), m.p. 70·5—71·0 °C, $[\alpha]_D^{25}$ —114·9° (CH_2Cl_2)], were employed as sensitizers in the photosensitized *cis–trans* isomerization of cyclo-octene (**1**). The photostationary state (pss) *trans* : *cis* ratios, $(t/c)_{pss}$, were determined for each sensitizer by the method described previously.[2a] As demonstrated in Table 1, the values $(t/c)_{pss}$ obtained for the chiral esters were comparable to those observed for the corresponding methyl esters, and were still anomalously high compared with triplet sensitization; compare the $(t/c)_{pss}$ ratios for aromatic esters with that obtained with benzene sensitization. It is thus likely that a change of the alcoholic

Table 1. Photostationary *trans* : *cis* ratio of cyclo-octene (**1**)[a]

Sensitizer	Concentration/M	$(t/c)_{pss}$
Methyl benzoate	0·004—0·4	0·25 ± 0·01
(**2**)	0·01	0·26
(**3**)	0·02	0·20
Dimethyl isophthalate	0·02	0·34
(**4**)	0·02	0·38
Benzene	0·01	0·05

[a] Concentration of (**1**) was 0·07 M; n-pentane was used as solvent.

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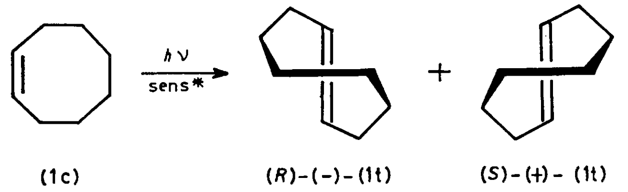
group in the aromatic ester into rather bulky chiral substituents has little influence on the mechanism of singlet sensitization *via* an exciplex.



SCHEME

The preparative scale photoisomerization of *cis*-cyclo-octene (**1c**) in the presence of the chiral esters (**2**)—(**4**) was carried out in an annular quartz vessel (80 ml) surrounding a 300 W high pressure mercury lamp at room temperature. Short irradiation times and therefore low conversion rates were employed since the reverse *trans*→*cis* photoisomerization might complicate the evaluation of the value of $[\alpha]_D$ (observed). Subsequent work-up,[3] followed by distillation under reduced pressure gave the product (**1t**), which was shown by g.l.c. to be >97—99% pure and free from the chiral sensitizer.‡ Table 2 shows that all the chiral esters gave the (*R*)-(−)-enantiomer of (**1t**) in slight excess. On sensitization with (−)-menthyl benzoate, only a little decrease in % e.e. (enantiomeric excess) was observed with increasing conversion rate up to 4%, and a change in solvent from pentane to methanol did not affect the optical yield. The effect of changing the chiral substituent in the aromatic esters was more marked; cholesteryl benzoate (**3**) was almost ineffective for asymmetric synthesis.

We consider that this singlet photosensitization of *cis*–*trans* isomerization by aromatic esters proceeds *via* an exciplex of an excited singlet ester with cyclo-octene.[2b] Once the exciplex is formed, the cyclo-octene unit of the exciplex starts to rotate about the C=C double bond to give two distinct diastereomeric exciplexes since the rotation brings about induced chirality to the twisted cyclo-octene unit. With further rotation, the exciplex finally dissociates leaving a ground state aromatic ester and a (+)- or (−)-twisted singlet of cyclo-octene. This chiral twisted singlet decays into *cis*- or chiral *trans*-cyclo-octene in its ground state. In all cases, the enantiomeric purities of the product (**1t**) are generally low as shown in Table 2, indicating the small free energy differences ($\Delta\Delta G^{\ddagger}$ *ca.* 0·05 kcal mol^{-1}) at the diastereomeric transition state. However, in spite of the lack of any covalent or hydrogen bond, even a weak interaction and a less rigid structure in an exciplex do contribute to the asymmetric induction of an achiral molecule.

TABLE 2. Partially asymmetric *cis–trans* photoisomerization of *cis*-cyclo-octene (**1c**) in n-pentane.

Chiral sensitizer (mM)	[(**1c**)]/M	Irradiation time/min	Conversion/%	Product (**1t**) Yield[a]/%	$[\alpha]_D$[b]/°	% e.e.
(**2**) (15)	4·2	30	1·9	0·9	−12·1 (*c* 4·78)	3·1
(**2**) (17)	4·2	50	2·8	1·0	−13·0 (*c* 4·59)	3·2
(**2**) (24)	4·2	80	4·0	1·5	−10·7 (*c* 4·2)[c]	2·8
(**2**) (13)[e]	1·7	20	2·0	1·1	−11·7 (*c* 3·41)	3·0
(**3**) (15)	4·2	40	1·9	1·2	−1·2 (*c* 16·7)	0·3
(**4**) (15)	4·0	30	1·5	0·5	−16·4 (*c* 4·15)	4·0

[a] Isolated yield of *trans*-cyclo-octene (**1t**) based on the *cis*-isomer used. [b] Measured in CH_2Cl_2 at 25 °C, unless otherwise stated. [c] Measured at 19 °C. [d] Enantiomeric excess based on the value of $[\alpha]_D^{25}$, 426° (*c* 0·41, CH_2Cl_2), (ref. 4), reported for the optically pure (−)−(**1t**); the values are corrected for the optical purity of the sensitizers employed and also for the purity (97—99%) of (**1t**) isolated. [e] Methanol was used as solvent.

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‡ The impurities, detected by g.l.c., were *cis*-cyclo-octene (<0·8%) and *cis*, *cis*-cyclo-octa-1,3-diene (0·5—2·0%), both of which are achiral compounds. Any other probable chiral impurities such as menthene, which might be produced *via* Norrish type II photocleavage of the sensitizers (**2**) and (**4**), were found by g.l.c. to be absent from the distilled samples.

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