

Enantiodifferentiating photoisomerization of 1-methylcyclooct-1-ene sensitized by chiral alkyl benzenecarboxylates: steric effects upon stereodifferentiation

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Enantiodifferentiating *Z*-to-*E* photoisomerizations of 1-methylcyclooct-1-ene (**2**) sensitized by (–)-menthyl benzene(poly)carboxylates were performed at varying temperatures and the steric effects of the methyl group introduced to the parent cyclooctene (**1**) upon both isomerization and enantiodifferentiation processes were studied. The photostationary state **2E**:**2Z** ratio, $(E/Z)_{\text{pss}}$, was shown to decrease dramatically with decreasing irradiation temperature and increasing steric hindrance in the sensitizer. Kinetic analyses of the sensitized photoisomerization demonstrated that the temperature- and sensitizer-dependent $(E/Z)_{\text{pss}}$ ratios originate solely from the quenching process. The steric effect on the $(E/Z)_{\text{pss}}$ values of the introduced methyl group is much greater for the (*Z*)-isomer (**2Z**) than for the (*E*)-isomer (**2E**), as compared with the cyclooctene case reported previously. The optical purities (%*op*) of photoproduct **2E** were found to be relatively low (< 10%) in general, and the increased steric hindrance induced by the methyl group does not appear to enhance the product's optical purity. However, the temperature dependence studies revealed that the differential activation enthalpy ($\Delta\Delta H^\ddagger$) and entropy ($T\Delta\Delta S^\ddagger$) as functions of the number of chiral groups in the benzene(poly)carboxylate sensitizer give a quite similar profile to those parameters obtained for parent **1**, showing uniform increases for **2** of 0.4 and 0.15 kJ mol⁻¹ in $\Delta\Delta H^\ddagger$ and $T\Delta\Delta S^\ddagger$, respectively, for all chiral sensitizers.

The enantiodifferentiating photosensitization, requiring only a catalytic amount of chiral sensitizer, has long fascinated photochemists as an attractive method for transferring and multiplying chirality through the electronically excited state.¹⁻³ After considerable efforts for nearly three decades,³⁻¹⁹ since Hammond and Cole's first report on the photosensitized enantiodifferentiating *cis*-*trans* isomerization of 1,2-diphenylcyclopropane,³ it has turned out that achieving efficient chiral recognition in the excited state is quite difficult. Hence, the product's highest optical purity (%*op*) was reported to be as low as 6.7%³ until very recently. This was thought to be inherent in the photosensitized enantiodifferentiation and the low *op* values obtained are the natural consequence, since the excited-state interaction between chiral sensitizer and prochiral substrate is too weak and short-lived to guarantee sufficient intimate molecular recognition.

However, recent reports from our laboratories have demonstrated that the enantiodifferentiating *Z*-*E* photoisomerizations of cyclooctene (**1**), sensitized by several optically active benzenepolycarboxylates afford much higher *op* values, up to 64%.²⁰⁻²² Examining the molecular structure of the sensitizers which afford high *op* values, we have reached a tentative conclusion that one of the most effective strategies for improving optical purity is to introduce two or more bulky ester moieties into the benzenepolycarboxylate sensitizer at the *ortho* positions.^{21,22} This is simply because the high *op* values obtained in these cases are a consequence of the enormous contribution of the entropic factor, arising most probably from the synchronized dynamic conformational changes of both **1Z** and the sensitizer during the enantiodifferentiating rotational relaxation of **1Z** within the exciplex intermediate. In this context, the steric repulsion within the exciplex intermediate

seems to be a crucial factor in the enantiodifferentiating photosensitization.

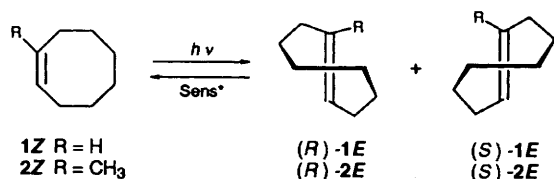
More recently, in a series of investigations on the photochemical *Z*-*E* isomerization of cycloalkenes,^{11,12,23} we have found that cyclooctene (**1**) and 1-methylcyclooct-1-ene (**2**), though displaying quite analogous behaviour in the direct and triplet-sensitized photoisomerizations, give completely different photostationary state *E*:*Z* ratios, $(E/Z)_{\text{pss}}$, only upon singlet photosensitization with benzenepolycarboxylates. Thus, the less hindered methyl benzoate, as a singlet sensitizer, affords comparable $(E/Z)_{\text{pss}}$ ratios for **1** and **2**, while the ratio for the more hindered **2** decreased much more rapidly with increasing alkoxy carbonyl groups in the sensitizer than that for parent **1**.^{23e}

The above observations indicate that the sensitizer-substrate interaction in the excited state is greater in singlet than in triplet sensitization, and prompted us to extend the scope of our study on the photosensitized enantiodifferentiating isomerization to the sterically more congested substrate **2**. In the present study, the steric effects of the methyl group introduced into **2** upon both *Z*-*E* isomerization and *R*-*S* enantiodifferentiation are investigated at varying temperatures and the results are discussed in terms of the activation parameters obtained in the temperature-dependence studies.

Experimental

General

IR spectra were recorded on a JASCO IR-810 instrument. ¹H and ¹³C NMR spectra were recorded on a JEOL GX-400 spectrometer in [²H]chloroform. *J* Values are given in Hz.



Scheme 1

Optical rotations were measured in a thermostatted conventional 10 cm cell, using a Perkin-Elmer polarimeter model 243B and are given in units of $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$. Gas chromatographic analyses were performed using a Shimadzu 6A instrument.

Materials

(*Z*)-1-Methylcyclooct-1-ene (**2Z**) was prepared by the Grignard reaction of cyclooctanone with methyl magnesium iodide and the subsequent spontaneous dehydration of the product 1-methylcyclooctan-1-ol upon distillation. (*E*)-1-Methylcyclooct-1-ene (**2E**) was prepared by the photoisomerization of **2Z**, sensitized by methyl benzoate, and was isolated and purified by the selective extraction with aqueous silver nitrate in 7.1% yield, according to the procedures described previously.²⁴

(-)-Menthyl benzenepolycarboxylates used as chiral sensitizers were synthesized from the corresponding acid chlorides and (-)-menthol and were purified by repeated recrystallization from methanol.²⁵

1-Methylcyclooctane-1,2-diol. A pyridine solution (3 cm³) of (*E*)-1-methylcyclooct-1-ene (0.25 g, 2.01 mmol), prepared by enantiodifferentiating photoisomerization of **2Z** sensitized by di(-)-menthyl terephthalate at 25 °C, was added to a stirred pyridine solution (2 cm³) of osmium tetroxide (0.51 g, 2.01 mmol) and stirred for 5 h at room temperature. To the resulting solution was added a solution of 1.0 g sodium bisulfite in 15 cm³ water and 10 cm³ pyridine, and the mixture was extracted with two 20 cm³ portions of dichloromethane. After removal of pyridine by extraction with a saturated aqueous copper sulfate solution, the dichloromethane extract was washed with water and brine, dried over sodium sulfate and evaporated under reduced pressure. The crude product obtained was purified by column chromatography over silica gel with hexane-ethyl acetate (50:50) eluent to give 1-methylcyclooctane-1,2-diol (0.23 g, 78% yield): ν/cm^{-1} 3420 (s), 2930 (s), 2860, 1470, 1450, 1380, 1160, 1130, 1060, 1025, 980, 970, 930 and 890; δ_{H} 1.15 (s, 3 H), 1.35–1.49 (m, 3 H), 1.55–1.77 (m, 8 H), 1.84 (m, 1 H), 2.24 (br s, 2 H) and 3.90 (dd, J 2.6, 10.4, 1 H); δ_{C} 21.19, 21.74, 25.01, 25.47, 29.94, 32.58, 39.02, 74.44 and 75.56.

2-Acetoxy-1-methylcyclooctan-1-ol. A pyridine solution (3 cm³) of 1-methylcyclooctane-1,2-diol (225 mg, 1.52 mmol) and acetic anhydride (778 mg, 7.62 mmol) was stirred for 5 h at room temperature and then 5 cm³ water was added. The reaction mixture was extracted with three 15 cm³ portions of ether. The crude product, obtained by similar work-up procedures described above, was purified with MPLC over SiO₂ with hexane-ethyl acetate (30:70) eluent to give 2-acetoxy-1-methylcyclooctan-1-ol (252 mg, 83% yield): ν/cm^{-1} 3470 (m), 2925 (s), 2850, 1725 (s), 1475, 1465, 1450, 1370 (m), 1260 (m), 1060, 1035 (m), 970, 960 and 905; δ_{H} 1.21 (s, 3 H), 1.46–1.85 (m, 12 H), 2.04 (br s, 1 H), 2.08 (s, 3 H) and 5.08 (t, J 5.9, 1 H); δ_{C} 21.35, 21.39, 23.32, 25.34, 25.99, 28.66, 31.01, 38.08, 74.64, 79.43 and 171.20.

Photolysis

All irradiations were carried out in a water (50–0 °C) or methanol (–20 to –78 °C) bath thermostatted at the desired temperature (within ± 1 °C). A pentane solution of **2Z** (30–200 mmol dm⁻³) and a chiral sensitizer (5–10 mmol dm⁻³), containing cyclooctane (10 mmol dm⁻³) as an internal

standard, was irradiated under an argon atmosphere in a quartz tube (1 cm id) or in an annular vessel (300 cm³), using a 30 W mercury resonance lamp (Eikosha) fitted with a Vycor filter.

Gas chromatographic analyses of the irradiated solutions were performed over a 3 m column of 20% polyethylene glycol-300 at 65 °C, the injection-port temperature being kept at ca. 100 °C in order to prevent the thermal *E*–*Z* isomerization of strained product **2E**. The peaks of **2Z**, **2E** and cyclooctane were separated satisfactorily under these gc conditions.

Results

Photosensitized *Z*–*E* isomerization

In the preceding paper,^{23e} we have shown that upon singlet sensitization with benzenecarboxylates, the (*E*/*Z*)_{ps} ratio obtained for 1-methylcyclooct-1-ene (**2**) is much more sensitive to the sensitizer's steric hindrance than that for cyclooctene (**1**), while the ratios are quite comparable with both substrates upon triplet sensitization by aromatic hydrocarbons. This seems reasonable as the singlet sensitization proceeds through the postulated exciplex intermediate, in which greater interaction is expected to occur.²¹ In order to gain further insight into the nature of the sensitizer–substrate interaction in the exciplex intermediate, the singlet-sensitized photoisomerizations of **2** were performed at a variety of temperatures ranging from –78 to +50 °C in the presence of a series of (poly)-(-)-menthyl benzenepolycarboxylates as sensitizers, and the results are discussed in comparison to those of **1**.

As was the case with the parent compound **1Z**, the major course of the photosensitization of **2Z** was the geometrical isomerization to the (*E*)-isomer, **2E**, in good to excellent chemical yields in most cases, ultimately affording a photostationary-state *Z*–*E* mixture upon prolonged irradiation, as shown in Table 1. The ultimate *E*:*Z* ratios, (*E*/*Z*)_{ps}, obtained for **1** and **2** at some temperatures are summarized in Table 2. The (*E*/*Z*)_{ps} ratio for less hindered **1** does not appear to suffer any suppressing effect even when the reaction temperature is lowered or the number of bulky (-)-menthoxy-carbonyl groups in the sensitizer is increased. In contrast, the ratio for more congested **2** decreases dramatically at lower temperatures, especially upon sensitization with the polysubstituted benzenecarboxylates such as isophthalate, terephthalate and trimesate.

Determination of optical purity of **2E**

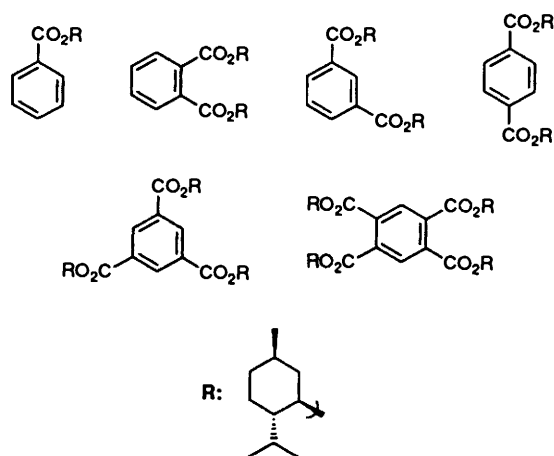
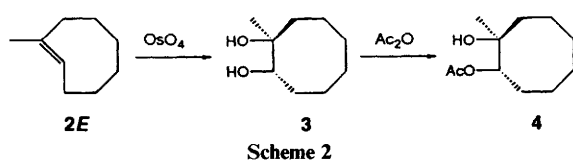
Since the specific rotation of optically pure (*R*)- or (*S*)-**2E** has not been reported so far, we first evaluated this value through the chemical derivatization of the optically active **2E** produced photochemically and the subsequent determination of its enantiomeric excess (ee) using a chiral NMR shift reagent. As illustrated in Scheme 2, the photochemically produced **2E** of $[\alpha]_{\text{D}}^{25} = 5.3$ (CH₂Cl₂, c 0.549) was oxidized to the corresponding 1,2-diol (**3**) with osmium tetroxide, which was then acetylated with acetic anhydride to give the monoacetate (**4**). The purified acetate **4** was subjected to the NMR measurement in the presence of an optically active lanthanoid shift reagent, *i.e.*, tris[3-(heptafluoropropyl)hydroxymethylene]-(+)-camphorato] europium(III), Eu(hfc)₃. The gradual addition of Eu(hfc)₃ up to 3 mol% to the solution of **4** in [²H]chloroform led to a good separation of the methyl protons in the enantiomeric acetate **4** with accompanying substantial downfield shifts. From the integration of each peak, the ee value of **4**, and therefore **2E**, was determined to be 5.0%. Using this ee value and the $[\alpha]_{\text{D}}^{25}$ value of the starting material, the specific rotation of the optically pure (+)-**2E** is calculated to be +106.

Note that the chemical shifts of **2E** were not affected by the

Table 1 *Z-E* Photoisomerization of 1-methylcyclooct-1-ene (**2Z**) sensitized by (–)-menthyl benzenecarboxylates in pentane

Sensitizer	<i>T</i> /°C	Irrad. time/h	Conv. (%)	Yield (%) ^a	<i>E/Z</i>
Benzoate	25	1	14.6	93	0.16
		4	19.6	83	0.20
	–40	1	9.9	98	0.11
		6	19.3	87	0.21
	–70	1	9.7	95	0.10
		7	21.2	73	0.20
Phthalate	50 ^b	2	3.0	50	0.015
	25	0.5	2.6	27	0.008
		7	5.4	20	0.012
		4	<1	<i>c</i>	<0.005
Isophthalate	25	1	12.2	85	0.12
		4	18.9	76	0.18
	–40	1	6.9	91	0.067
		6	14.0	84	0.14
	–70	1	4.7	98	0.050
		7	12.9	71	0.11
Terephthalate	50 ^b	0.5	5.6	98	0.059
		2	10.8	70	0.080
	25	1	5.7	70	0.043
		4	9.1	62	0.062
		1	2.9	62	0.018
	0	4	5.9	64	0.041
		0.5	3.2	44	0.015
	–40	4	6.4	44	0.029
		0.5	1.3	<i>c</i>	0.006
	Trimesate	25	1	11.2	67
6			17.4	60	0.13
–40		1	7.2	78	0.060
		4	11.0	82	0.10
–78		1	4.7	96	0.047
		6	10.1	69	0.078
Pyromellitate	–78	10	3	<i>c</i>	<0.005

^a Chemical yield of **2E** based on **2Z** consumed. ^b Irradiation performed in hexane. ^c Not determined due to low conversion.



addition of representative chiral shift reagents, *i.e.*, Eu(hfc)₃ and Pr(hfc)₃, while mere peak broadening, rather than separation, was observed with the diol **3** upon gradual addition of both shift reagents up to 5 mol%.

Enantiodifferentiating photoisomerization

The product **2E** obtained in the sensitized photoisomerization of **2Z** was isolated by selective extraction with aqueous silver nitrate solution,²⁴ and the specific rotation of the isolated **2E** was measured to calculate its optical purity (%*op*) based on the

specific rotation of pure enantiomer estimated above: $[\alpha]_D^{25} = 106$.

As can be seen from Table 3, the %*op* value is a critical function of the irradiation temperature and also of the sensitizer structure or, more precisely, the number and position of the (–)-menthoxy carbonyl group introduced. Although the %*op* values are not very high in general, it is interesting to point out that (–)-menthyl benzoate, isophthalate, and terephthalate as sensitizers, give (+)-**2E** as the dominant enantiomer, while the trimesate, though possessing the same chiral ester moieties, affords the antipodal (–)-**2E** at the low temperatures. Note also that an inversion of the product chirality is expected to occur upon extrapolation to the higher temperatures.

Discussion

Photostationary state *E:Z* ratios $[(E/Z)_{\text{ps}}]$

Assuming a twisted phantom singlet (¹p) as common intermediate, the *Z-E* photoisomerizations of cyclooctenes **1** and **2** sensitized by aromatic ester (S) is expressed by the following equations:

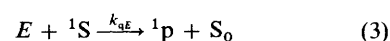
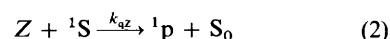
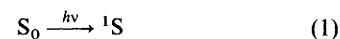


Table 2 Photostationary state $E:Z$ ratio, $(E/Z)_{\text{pss}}$, of cyclooctene (**1**) and 1-methylcyclooct-1-ene (**2**) upon photosensitization with (–)-menthyl benzenecarboxylates

Sensitizer	Substrate	$T/^\circ\text{C}$						
		50	25	0	–20	–40	–70	–78
Benzoate	1Z		0.24			0.29		
	2Z		0.20			0.21	0.20	
Phthalate	1Z		0.050			0.14		0.20
	2Z	0.015	0.012					<0.005
Isophthalate	1Z		0.38			0.38		0.28
	2Z		0.18			0.14	0.11	
Terephthalate	1Z		0.31			0.37		
	2Z	0.080	0.062	0.041	0.029	0.017		
Trimesate	1Z					0.42		0.22
	2Z		0.13			0.10		0.078
Pyromellitate	1Z		0.10			0.66		
	2Z							<0.005

Table 3 Enantiodifferentiating photoisomerization of 1-methylcyclooct-1-ene sensitized by (–)-menthyl benzenecarboxylates

Sensitizer	$T/^\circ\text{C}$	Irrad. time/h	Conv. (%)	Yield (%)	E/Z	$[\alpha]_{\text{D}}^{25}$ (c)	% <i>op</i> ^a
Benzoate	25	27	17.8	13.6	0.165	3.38 (0.21)	3.2
	–40	40	15.5	15.1	0.176	6.39 (1.01)	6.0
	–78	66	14.0	13.3	0.152	7.78 (1.08)	7.3
Isophthalate	25	45	13.3	12.4	0.147	0.92 (0.98)	0.9
	–40	61	11.7	8.7	0.098	3.94 (0.51)	3.7
	–78	86	7.6	6.9	0.075	5.10 (0.51)	4.8
Terephthalate	25	40	7.0	4.6	0.050	5.28 (0.55)	5.0
Trimesate	25	20	5.1	5.0	0.065	0.00 (1.19)	0.0
	–40	67	6.9	6.2	0.067	–1.72 (0.99)	–1.6
	–78	86	8.0	5.2	0.057	–5.65 (1.03)	–5.3

^a Calculated on the basis of the specific rotation of optically pure (+)-**2E**: $[\alpha]_{\text{D}}^{25} = 106$; the sign corresponds to that of the specific rotation.

where Z and E represent the (Z)- and (E)-isomers of **1** or **2**, respectively, and the superscript refers to the multiplicity of the excited state.

According to the steady-state treatment, the $(E/Z)_{\text{pss}}$ ratio is expressed as a product of the quenching rate ratio, $k_{\text{qZ}}/k_{\text{qE}}$, and the decay rate ratio, $k_{\text{dE}}/k_{\text{dZ}}$.

$$(E/Z)_{\text{pss}} = (k_{\text{qZ}}/k_{\text{qE}})(k_{\text{dE}}/k_{\text{dZ}}) \quad (6)$$

As has been demonstrated previously in the study of singlet photosensitization of **1**,¹¹ the decay ratio can be assumed to be very close to unity in the present case of **2**, since the decay process from the phantom singlet ¹p is inherently independent of the sensitizer used and the ¹p state produced in the singlet sensitization must be equivalent to that produced in the direct excitation.^{23e} Energetically, the quenching process is slightly endothermic, while the decay process from the phantom singlet ¹p to the ground-state (Z)- or (E)-isomer is highly exothermic.¹¹ Hence, the $(E/Z)_{\text{pss}}$ ratio is considered to be determined solely by the quenching ratio, $k_{\text{qZ}}/k_{\text{qE}}$, and we may reduce eqn. (6) to (7).

$$(E/Z)_{\text{pss}} \approx k_{\text{qZ}}/k_{\text{qE}} \quad (7)$$

The contrasting behaviour of the $(E/Z)_{\text{pss}}$ ratios for the less hindered **1** and the more congested **2**, shown in Table 2, can be reasonably accounted for as a consequence of the increased steric hindrance for **2** in the quenching process. The effect is more drastic for the photosensitizations with highly substituted benzenecarboxylates and at lower temperatures. The much decreased $(E/Z)_{\text{pss}}$ ratios for **2** upon sensitization, especially with benzenepolycarboxylates, clearly indicate that the steric

hindrance caused by the methyl group introduced in the substrate is more effective towards **2Z** than **2E**, affording much smaller quenching ratios, $k_{\text{qZ}}/k_{\text{qE}}$, and therefore smaller $(E/Z)_{\text{pss}}$ ratios.

The Arrhenius treatment of each quenching rate constant leads to eqn. (8). A plot of $\ln(E/Z)_{\text{pss}}$ vs. $1/T$ gives an excellent

$$\begin{aligned} \ln(E/Z)_{\text{pss}} &\approx \ln(k_{\text{qZ}}/k_{\text{qE}}) \\ &= \ln(A_{\text{qZ}}/A_{\text{qE}}) - (E_{\text{qZ}} - E_{\text{qE}})/RT \end{aligned} \quad (8)$$

straight line for each sensitizer as shown in Fig. 1. The differential activation energy ($\Delta E_{\text{q}} = E_{\text{qZ}} - E_{\text{qE}}$) and the relative frequency factor ($A_{\text{qZ}}/A_{\text{qE}}$) for the quenching process are calculated from the slope and intercept of the plot; the parameters obtained are listed in Table 4.

As can be seen from Table 4, the activation parameters are not apparently correlated with the sensitizer's singlet energy (E_{S}) but are rather sensitive to the number and position of the additional substituent(s) introduced in the sensitizer. It is shown that the relatively low $(E/Z)_{\text{pss}}$ ratios around 0.2 obtained upon benzoate sensitization do not arise from the activation energy difference ΔE_{q} between **2Z** and **2E**, but mainly from the unfavourable frequency factor for **2Z**. This is somewhat unexpected since the constrained (E)-isomer **2E** possesses a lower singlet energy than the (Z)-isomer **2Z** and is therefore considered to be energetically advantageous over **2Z** in the quenching process. In the quenchings of more substituted benzenepolycarboxylates, the increased steric hindrance causes inevitable differences in E_{q} , part of which is however cancelled by the increased relative frequency factor. The much larger ΔE_{q} value, and the extremely low $(E/Z)_{\text{pss}}$ ratio as its logical consequence, observed for the phthalate may be attributable to

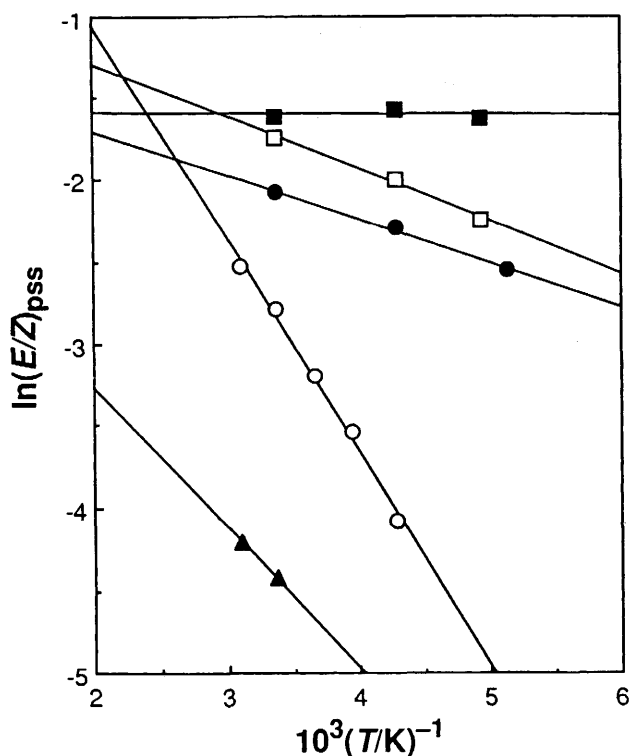


Fig. 1 Temperature dependence of photostationary $E:Z$ ratio of 1-methylcyclooct-1-ene upon photosensitization with (–)-menthyl benzoate (■), phthalate (▲), isophthalate (□), terephthalate (○) and trimesate (●)

the bulky menthoxy carbonyl groups in the adjacent positions. These bulky groups make the approach of $2Z$ rather than $2E$ more difficult, since $2Z$ with a higher singlet energy than $2E$ requires a closer approach to form an exciplex stable enough to execute energy transfer. The relatively low ΔE_q values for the *meta*-substituted sensitizers, *i.e.* isophthalate and trimesate, are reasonably understood in the framework of the above hypothesis. However, the exact reason(s) for the large ΔE_q value for the terephthalate is not known at present. Experimentally, the extremely low $(E/Z)_{\text{pss}}$ ratio as a consequence of the large ΔE_q makes it quite difficult to isolate $2E$ in an amount sufficient to measure the specific rotation by a conventional polarimeter.

Activation parameters for enantiodifferentiating process

Our previous studies²¹ have shown that the actual enantiodifferentiating process in the photosensitized isomerization of **1** is not the quenching process, but the rotational relaxation of the alkenic double bond of $1Z$ to the phantom singlet state within the exciplex intermediate. Although the individual rate constant for each process must be substantially affected by the introduction of a methyl group, a similar enantiodifferentiation mechanism proposed for **1**²¹ is inferred to be applicable to the present enantiodifferentiating photoisomerization of **2**. Then, the relative rate constant (k_+/k_-) for the production of (+)- and (–)- $2E$ is analysed by the Eyring equation to give the differential enthalpy ($\Delta\Delta H^\ddagger$) and entropy ($\Delta\Delta S^\ddagger$) of activation. According to eqn. (9), the

$$\begin{aligned} \ln(k_+/k_-) &= -(\Delta H^\ddagger_+ - \Delta H^\ddagger_-)/RT + (\Delta S^\ddagger_+ - \Delta S^\ddagger_-)/R \\ &= -\Delta\Delta H^\ddagger/RT + \Delta\Delta S^\ddagger/R \end{aligned} \quad (9)$$

logarithm of the relative rate constant k_+/k_- , which is

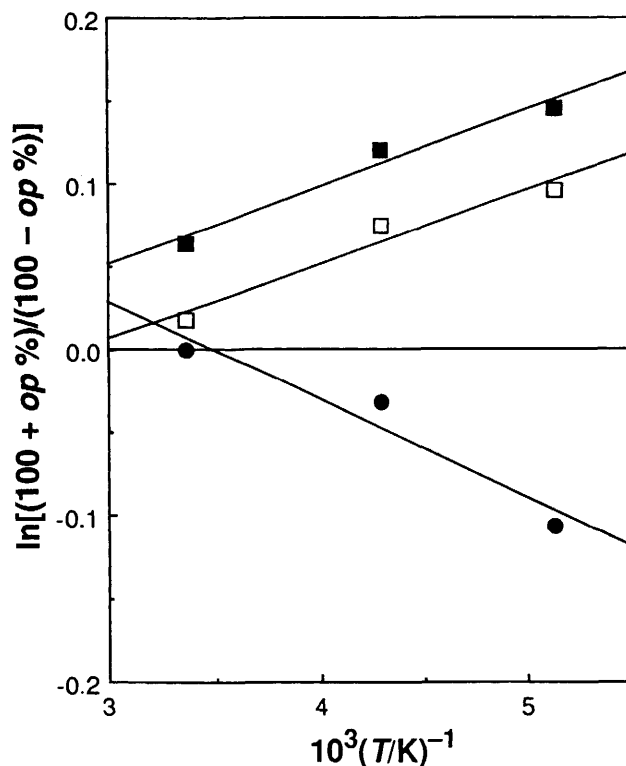


Fig. 2 Plots of $\ln(k_+/k_-)$, or $\ln[(100 + \%op)/(100 - \%op)]$, versus reciprocal temperature for (–)-menthyl benzoate (■), isophthalate (□), terephthalate (○) and trimesate (●)

Table 4 Differential activation energies, $E_{qZ} - E_{qE}$, and relative frequency factors, A_{qZ}/A_{qE} , for the photoisomerization of 1-methylcyclooct-1-ene **2** sensitized by (–)-menthylbenzene(poly)carboxylates

Sensitizer	$E_S^a/$ kJ mol ⁻¹	$E_{qZ} - E_{qE}/$ kJ mol ⁻¹	A_{qZ}/A_{qE}
Benzoate	428	0.02	0.20
Phthalate	425	7.04 ^b	0.21 ^b
Isophthalate	416	2.67	0.52
Terephthalate	406	10.79	4.67
Trimesate	415	2.20	0.31

^a Singlet energy of sensitizer; ref. 21. ^b Calculated using only two data points.

experimentally equivalent to $\ln[(100 + \%op)/(100 - \%op)]$, is plotted as a function of reciprocal temperature only for those sensitizers that give sufficient amounts of $2E$ even at low temperatures: *i.e.* (–)-menthyl benzoate, isophthalate and trimesate. The plots give good straight lines for these sensitizers, as shown in Fig. 2. Eqn. (9) and the slope and intercept obtained from the plot provide us with the differential activation parameters, listed in Table 5, for the enantiodifferentiating photoisomerization of **2**.

In order to analyse quantitatively the steric effect induced by the methylation of cyclooctene upon the photosensitized enantiodifferentiation process, a systematic comparison of the activation parameters is made between **1** and **2**. As can be seen from Table 5, the methylation of cyclooctene obviously enhances the absolute values of both $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ for the benzoate, affording higher $\%op$ values for **2** than for **1**, but substantially diminishes both parameters for the trimesate. Furthermore, the signs of the $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ values for isophthalate are inverted with **1** and **2**. These observations may

Table 5 Differential enthalpy ($\Delta\Delta H^\ddagger$)^a and entropy ($T\Delta\Delta S^\ddagger$)^b of activation for enantiodifferentiating photoisomerization of **1** and **2** sensitized by (–)-menthyl benzenecarboxylates in pentane ($T = 298\text{ K}$)

Sensitizer	Substrate	$\Delta\Delta H^\ddagger$ / kJ mol ⁻¹	$T\Delta\Delta S^\ddagger$ / kJ mol ⁻¹
Benzoate	1	0.063	-0.075
	2	-0.39	-0.22
Isophthalate	1	0.32	0.11
	2	-0.37	-0.31
Trimesate	1	0.97	0.84
	2	0.49	0.51

$$^a \Delta\Delta H^\ddagger = \Delta H^\ddagger_+ - \Delta H^\ddagger_- \quad ^b \Delta\Delta S^\ddagger = \Delta S^\ddagger_+ - \Delta S^\ddagger_-$$

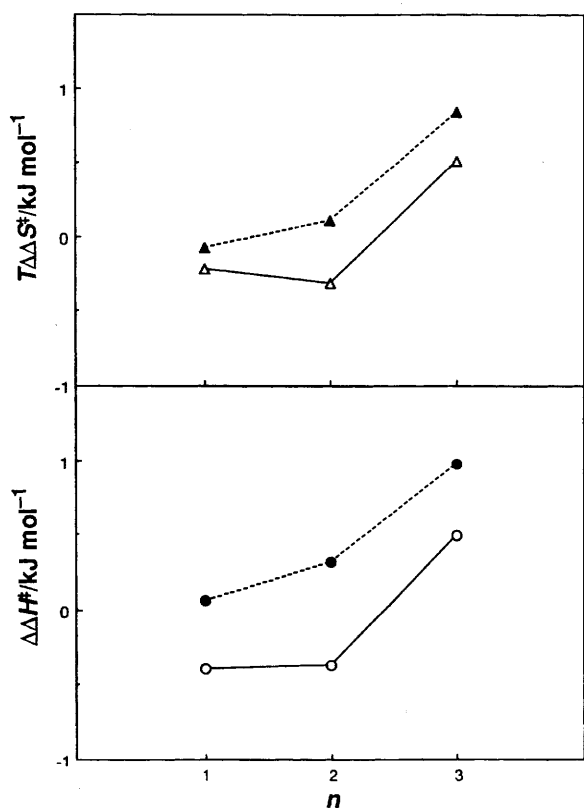


Fig. 3 Differential activation enthalpy $\Delta\Delta H^\ddagger$ (○, ●) and entropy changes $T\Delta\Delta S^\ddagger$ (△, ▲) for the enantiodifferentiating photoisomerization of cyclooctene **1** (●, ▲) and of 1-methylcyclooct-1-ene **2** (○, △) as a function of the number (n) of *meta*-substituted menthoxy carbonyl groups in the sensitizer; 1: benzoate; 2: isophthalate; 3: trimesate

seem confusing and *ad hoc* explanations for the individual sensitizers appear to be needed.

These sensitizers, possessing a varying number of chiral group(s) at the *meta* position(s) of benzoate, may be correlated structurally with each other. Then, the parameters obtained are plotted against the number (n) of (–)-menthoxy carbonyl groups at the *meta* position. Although, as mentioned above, the individual activation parameters listed in Table 5 do not appear to show any general tendencies, the changing profiles of $\Delta\Delta H^\ddagger$ and $T\Delta\Delta S^\ddagger$ shown in Fig. 3 are quite similar for **1** and **2**. The only difference observed for **2** is the parallel downward deviations in both $\Delta\Delta H^\ddagger$ and $T\Delta\Delta S^\ddagger$ by 0.4–0.7 and 0.15–0.4 kJ mol⁻¹, respectively. These results clearly indicate that the seemingly unpredictable changes in the product's optical purity caused by the methylation of cyclooctene are not random at all, but remarkably systematic and consistent throughout the series of

menthyl benzenecarboxylates employed. We may conclude therefore that the increased steric hindrance can be used as a tool for enhancing the enantiodifferentiation efficiency as measured by the activation parameters, although the %*op* value at a specific temperature is not necessarily enhanced. Hence, it is emphasized once again that the enantiodifferentiating ability of the chiral sensitizer should not be judged by a single run at ambient temperature.

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