Highly Enantiodifferentiating Photoisomerization of Cyclooctene by Congested and/or Triplex-Forming Chiral Sensitizers

Yoshihisa Inoue,*,† Noritsugu Yamasaki, Taizo Yokoyama, and Akira Tai

Group PRESTO, JRDC, Department of Material Science, Himeji Institute of Technology, Kamigori, Hyogo 678-12, Japan

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In an effort to generate photoproducts with higher optical purities (op), two novel strategies, i.e., intra/intermolecular triplex formation and increased steric hindrance, have been employed in the enantiodifferentiating $Z \rightarrow E$ photoisomerization of cyclooctene (1) sensitized by optically active (ar)alkyl benzene(poly)carboxylates 2–5 at temperatures ranging from 25 to −90 °C. The newly synthesized benzenepolycarboxylates, possessing extremely bulky and/or electron-donating (ar)-alkyl groups, gave products with the highest op's ever reported for the enantiodifferentiating photosensitizations, not only at low temperatures (up to 64% op at −89 °C) but also at ambient temperature (50% op). Both strategies to fix the sensitizer conformation and to induce more dynamic conformational changes in the exciplex/triplex intermediate are shown to function well and to give very high op's. The temperature-dependence studies also demonstrate that the temperature switching of the product chirality is not an extraordinary but rather a general phenomenon, which is attributed to the significant contribution of the entropy factor in the enantiodifferentiating process, caused by the dynamic structural change in the excited complex.

Enantiodifferentiating photochemical reactions of prochiral substrates sensitized by catalytic amounts of optically active compounds have attracted the interest of a broad spectrum of (photo)chemists from the theoretical, mechanistic, and synthetic points of view as an attractive and chiral source-efficient method for transferring and multiplying optical activity.[1,2] However, in spite of the considerable efforts devoted to enantiodifferentiating photosensitized isomerizations,[3-10] elimination,[11] rearrangements,[12,13] and cycloaddition reactions,[14,15] the optical purities (op) of the photoproducts obtained at ambient temperatures did not exceed the original op (6.7%) reported in the pioneering work by Hammond and Cole,[3a] except for the 1,2-diphenylcyclopropane case (10% op) reported recently.[10] Even at lower temperatures, the optical purities obtained in recent studies were only slightly higher (10–15%).[12,14]

Recently, we reported an unusual and fairly efficient enantiodifferentiating photosensitizing system involving an exciplex intermediate. The Z–E photoisomerization of cyclooctene (1), sensitized by chiral polyalkyl benzenepolycarboxylates as illustrated in Scheme I, not only gives the optically active (E)-isomer 1E in op's of up to 40–50% at −88 °C but also exhibits unusual temperature-switching behavior of the product chirality at the equipodal temperature (T_0), depending upon the sensitizer employed.[16] It was also revealed that this seemingly curious, unprecedented behavior is actually the natural consequence of the appreciable differential entropy of activation ($\Delta\Delta S^{\ddagger} \neq 0$), possessing the same sign as the differential enthalpy of activation ($\Delta\Delta H^{\ddagger}$), for the photosensitized enantiodifferentiating process.[16b] The significant contribution of the entropy term has been attributed to the dynamic conformational changes of the adjacent alkyl moieties of the ortho-substituted benzenepolycarboxylate, which synchronize with the enantiodifferentiating rotational relaxation of cyclooctene around the double bond within the intervening exciplex.[16b]

As an intriguing logical extension of this work, we have examined the effects of conformational fixation, in both ground and excited states, of the otherwise mobile ester moieties in the sensitizer molecule upon the product's op and the activation parameters. In principle, substituents that make the ground-state structure more rigid should induce more dynamic structural changes in the exciplex to afford greater $\Delta\Delta S^{\ddagger}$, while conformational fixation in the excited state would provide a more defined exciplex geometry which may lead to a higher $\Delta\Delta H^{\ddagger}$.

In the present study, we employed two different strategies to control conformational changes in the exciplex intermediate: the donor–acceptor interaction and increased steric hindrance within the sensitizer molecule. The introduction of an electron-donating phenyl group to the ester moieties of the sensitizer at the appropriate

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Scheme I

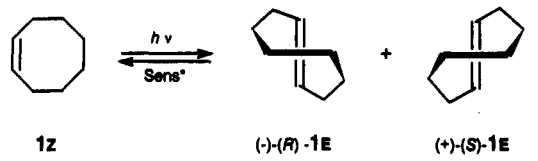
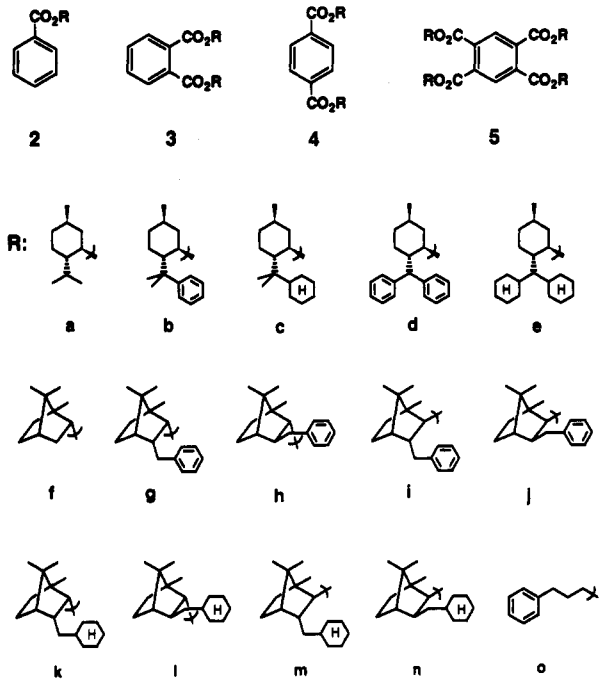


Chart I. Optically Active Polyalkyl Benzenepolycarboxylates



position leads to the formation of an intramolecular exciplex upon excitation, which in turn forms a structurally less flexible intra/intermolecular triplex [A–D···D′] between the donor–acceptor sensitizer (A–D) and the substrate cyclooctene (D′). On the other hand, increased steric hindrance, caused by highly bulky alkyl groups introduced in the ester moieties, also reduces the freedom of the ester moieties, at least in the ground state, but renders the rotational relaxation within the exciplex more dynamic.

These two approaches functioned indeed quite effectively; the introduction of bulky and/or electron-donating (ar)alkyl groups in the sensitizer led to cooperative changes in both the enthalpy and entropy terms, affording the highest op's over a wide range of temperatures in the optimized cases.

Results and Discussion

Absorption and Fluorescence Spectra. The newly synthesized photosensitizers, illustrated in Chart I, were first examined spectroscopically in order to evaluate the effects of highly bulky and electron-donating substituents in these sensitizers upon ground- and excited-state properties. The measurements were conducted in nonpolar pentane and polar acetonitrile solutions. As can be seen from Table I, neither the bulky nor the electron-donating substituents have any detectable influence on the apparent 0–0 absorption band, irrespective of the substituent structures **a**–**n** in **3** and **5** (Chart I), as the corresponding methyl esters **3** and **5** (R = Me) display practically the same absorption maxima.[17] The comparable absorption maxima observed in both polar and nonpolar solvents further indicate that, in the ground state, there is no appreciable intramolecular charge-transfer interaction between the core and peripheral aromatic moieties of the phenyl-substituted alkyl phthalate **3b** and benzenetetracarboxylates **5b**, **5d**, and **5g**–**5j**.

Table I. Absorption and Fluorescence Spectra of Some Bulky and Electron-Donating Alkyl Phthalate and 1,2,4,5-Benzenetetracarboxylates[a]

compd	solvent	absorption λ_{max},[b] nm	fluorescence λ_{max}, nm	fluorescence τ, ns	Stokes shift	ref
3b	pentane	285	*c*			*d*
	CH_3CN	283	(375)[e]			*d*
5a	pentane	292	332	0.2	40	*d*,*f*
	CH_3CN	291	331	0.2	40	*d*,*f*
5b	pentane	295	377	0.5	82	*d*
	CH_3CN	294	445	2.1	151	*d*
5c	pentane	293	326		33	*d*
5d	pentane	294	384	1.0	90	*d*
	CH_3CN	293	455		162	*d*
5f	pentane	293	331	0.2	38	*f*
	CH_3CN	291	331		40	*f*
5g	pentane	292	380		88	*d*
	CH_3CN	292	445		153	*d*
5h	pentane	292	355		63	*d*
	CH_3CN	292	450		158	*d*
5i	pentane	292	365		73	*d*
	CH_3CN	292	445		153	*d*
5j	pentane	292	385		93	*d*
	CH_3CN	292	445		153	*d*

[a] Spectra measured with 1.7–2.5 × 10^{-5} M aerated solutions at 22 ± 2 °C; excitation at 250 nm. [b] Broad apparent 0–0 band. [c] No appreciable fluorescence detected. [d] This work. [e] Very weak. [f] References 16b and 17.

By contrast, the fluorescence spectrum reveals dramatic effects of both the substituent structure as well as the solvent polarity. The highly congested 8-cyclohexylmenthyl benzenetetracarboxylate **5c** shows a smaller Stokes shift (33 nm) than the less-congested **5a** (40 nm), **5f** (38 nm), or methyl ester **5** (R = Me) (40 nm).[17] This finding indicates that the highly congested ester **5c** enjoys only limited relaxation in the excited state, most likely due to the increased steric hindrance between the adjacent ester moieties. In other words, the highly bulky substituents introduced in **5c** do contribute toward reducing the conformational flexibility of the excited sensitizer.

Interestingly, phenyl substitution in the ester moieties of **5** leads to much larger Stokes shifts for **5b**, **5d**, and **5g**–**5j** both in pentane and, particularly, in acetonitrile, demonstrating that considerable structural and electronic changes occur in the excited state. In pentane, the observed Stokes shift, ranging from 63 nm (**5h**) to 93 nm (**5j**), is a sensitive function of the stereochemistry of the alkyl group (R), and it appears that a wide variety of both stabilities and degrees of conformational change must exist in the excited states of **5g**–**5j**. The energy difference calculated from the fluorescence maxima of **5h** and **5j** amounts to 6.2 kcal/mol. Obviously, those emissions with the larger Stokes shifts originate from the intramolecular exciplex formed through the π–π interaction accessible only to the sensitizers possessing phenyl groups in the ester moieties; the emission maxima are governed by the extent of the π–π interaction determined by the substituent's stereochemistry. The interaction between the core and peripheral aromatic moieties is charge transfer (CT)

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Table II. Fluorescence Quenching of Some Tetraalkyl 1,2,4,5-Benzenetetracarboxylates (5) with (Z)- and (E)-Cyclooctene (1Z and 1E)[a]

alkyl (R) group in 5	solvent	τ,[b] ns	quencher	$k_q\tau$,[c] M^{-1} s^{-1}	k_q,[d] 10^9 s^{-1}	exciplex fluorescence λ_{max}, nm	exciplex fluorescence rel int[e]	ref
methyl	pentane	0.2	1Z	0.65	3.3	415	0.76	f
			1E	2.70	13.5	445	0.17	f
menthyl (5a)	pentane	0.2	1Z	0.28	1.4	410	≡1.00	f
			1E	2.08	10.4	455	0.05	f
	CH_3CN	0.2	1Z	0.83	4.2	445	0.44	g
bornyl (5f)	pentane	0.2	1Z	0.21	1.1	415	0.89	f
			1E	1.80	9.0	455	0.09	f
8-phenylmenthyl (5b)	pentane	0.5	1Z	0.26	0.52	h		g
			1E	2.57	5.1	h		g
	CH_3CN	2.1	1Z	0.67	0.32	h		g
			1E	8.7	4.2	h		g

[a] Measured with 2.0×10^{-4} M aerated solutions of 5 at 25 °C. [b] Fluorescence lifetime of 5 in aerated solutions at 22 ± 2 °C. [c] Stern–Volmer constant obtained in quenching experiment with 1Z (0.05–0.65 M) or 1E (0.01–0.20 M); intensity change measured at the peak maximum, unless stated otherwise. [d] Quenching rate constant calculated by using the lifetimes (τ) of 5. [e] Intensity of [A···D] exciplex peak, relative to that observed in the quenching of 5a with 1Z at the same concentration. [f] Reference 16b. [g] This work. [h] No new emission attributable to [A–D···D'] triplex observed.

in nature, as demonstrated by the dramatic bathochromic shift in polar solvents. Judging from the Stokes shifts in pentane, the sensitizers 5g and 5j, with endo–endo or exo–exo stereochemistry between the benzyl and carboxyl groups, are more stabilized, and probably immobilized, in the excited state than their epimers 5h and 5i, possessing a staggered benzyl group. It has been shown, therefore, that the conformational fixation of the chiral ester moiety in the excited sensitizer is achieved through the intramolecular CT interaction producing an intramolecular exciplex. The extent of CT interaction, and therefore conformational fixation, is governed by the stereochemistry of the (ar)alkyl substituents introduced.

On the other hand, the use of acetonitrile as solvent leads to tremendous Stokes shifts of up to 151–162 nm for the phenyl-substituted sensitizers 5b, 5d, and 5g–5j. These extremely large shifts indicate that, in this polar solvent, the excited sensitizers gain additional stabilization through intramolecular electron transfer, producing radical ion pairs composed of anionic core and cationic peripheral phenyl groups. Another important feature of this experiment is that, unlike those observed in pentane, the Stokes shifts observed in acetonitrile are practically independent of the stereochemistry of the ester moiety; the energy differences are almost negligible (≤0.5 kcal/mol). Thus, intramolecular electron transfer produces the equally-stabilized ion pairs of 5b, 5d, and 5g–5j, in which the specific stereochemistry does not appear to play a significant role, probably owing to the elongated interionic distance.

The fluorescence lifetimes of some selected benzenetetracarboxylates were also measured by means of the time-correlated single-photon counting method; the results are included in Table I. In contrast to the solvent polarity- and structure-independent lifetimes of about 0.2 ns for methyl, bornyl, and menthyl benzenetetracarboxylate,[17] the electron donating 8-phenylmenthyl ester 5b gives much longer, highly solvent polarity-dependent lifetimes of 0.5 ns in pentane and 2.1 ns in acetonitrile. This unique behavior of 5b is very compatible with the above conclusion that only the phenyl-substituted alkyl esters gain additional stabilization through the intramolecular CT interaction in the excited state specifically in the polar solvent.

Fluorescence Quenching. Since the intramolecular CT interaction induced by the phenyl group dramatically alters the fluorescence maxima and lifetimes of benzenetetracarboxylates, it is essential to examine the quenching behavior of these donor–acceptor sensitizers in both polar and nonpolar solvents. Comparative fluorescence quenching experiments of 8-phenylmenthyl benzenetetracarboxylate 5b (0.2 mM) with 1Z (0.05–0.7 M) and 1E (0.01–0.2 M) were performed in aerated pentane and acetonitrile. The fluorescence quenching of menthyl ester 5a in pentane and acetonitrile was also examined. The addition of 1Z or 1E as a quencher led to a gradual decrease in fluorescence intensity, without accompanying the development of a new emission at longer wavelengths. In accordance with the conventional Stern–Volmer treatment, the relative fluorescence quantum yield (Φ°/Φ) has been plotted against quencher concentration to give good straight lines of different slopes for 5a and 5b, as shown in Figure 1.

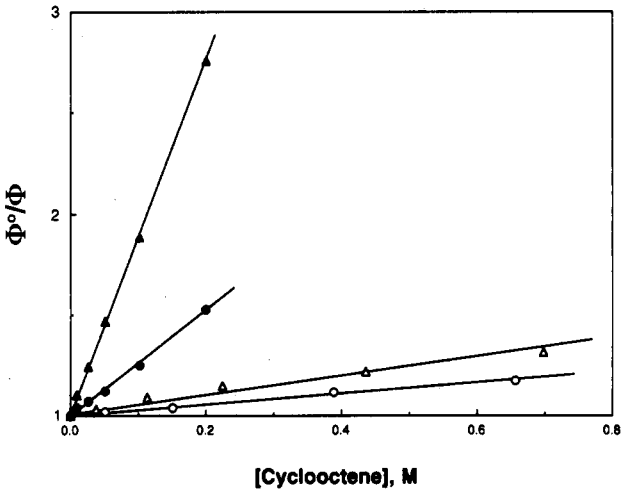


Figure 1. Stern–Volmer plot for the fluorescence quenching of tetrakis(8-phenylmenthyl) 1,2,4,5-benzenetetracarboxylate 5b with 1Z (○) and 1E (●) in pentane and with 1Z (△) and 1E (▲) in acetonitrile.

The Stern–Volmer constants ($k_q\tau$) and the quenching rate constants (k_q) are calculated from the reciprocal slopes of the plots and the fluorescence lifetime (τ) measured under comparable conditions in the absence of quencher. The constants obtained are listed in Table II, along with those for the simpler methyl, menthyl (5a), and bornyl (5f) esters in pentane solutions.[16b]

The fluorescence quenching of benzenetetracarboxylate 5 by (E)-cyclooctene 1E occurs at nearly diffusion-controlled rates of $5–13 \times 10^9$ M^{-1} s^{-1}, while the (Z)-isomer 1Z quenches fluorescence less efficiently at rates of 0.3–

$3.3 \times 10^9\ M^{-1}\ s^{-1}$. In pentane, the k_q value slowly decreases with increasing bulkiness of the (ar)alkyl group and the intramolecular exciplex formation in **5b** does not significantly affect the quenching rate. Thus, in the quenching process, the 8-phenylmenthyl group in **5b** acts merely as a substituent of increased bulkiness surrounding the exciplex-forming fluorescent core that is stabilized electronically. In acetonitrile, the k_q value for the quenching of menthyl ester **5a** with **1Z** triples from $1.4 \times 10^9\ M^{-1}\ s^{-1}$ in pentane to $4.2 \times 10^9\ M^{-1}\ s^{-1}$, indicating enhanced CT interaction which facilitates quenching. Unexpectedly, the phenylmenthyl ester **5b** affords almost comparable k_q values in pentane and acetonitrile. This result may indicate that it is not the electronic properties of the core but rather the peripheral conformations that determine the quenching rate in such highly congested sensitizers.

Enantiodifferentiating Photoisomerization. The sensitized photoisomerizations of (*Z*)-cyclooctene **1Z** were conducted in the presence of highly bulky and/or electron-donating chiral (ar)alkyl benzene(poly)carboxylates **2–5**. In most runs, pentane solutions containing **1Z** (0.2 M) and sensitizer (1.2–5 mM) were irradiated at 254 nm at temperatures ranging between +25 and −90 °C to give optically active (*E*)-isomer (**1E**) in good to excellent chemical yields. The specific rotations ($[\alpha]^{25}_D$) and op of the isolated photoproduct **1E** are shown in Table III.

The introduction of bulky and/or electron-donating groups in the ester moieties of the sensitizers drastically affects both the product's op and its temperature dependence. The highest op's at ambient temperature are dramatically enhanced by introduction of highly bulky and/or electron-donating substituents, as compared with those reported so far for optically active phthalate **3** (7.6% op)[16b] and benzenetetracarboxylate **5** (11.6% op).[16b] Thus, 8-phenylmenthyl phthalate **3b** and 8-phenylmenthyl or 8-cyclohexylmenthyl benzenetetracarboxylate **5b** or **5c** afford 18.3 and 49.2 or 49.5% op at 25 °C, respectively, the best values reported for these sensitizer categories. At the lower temperatures (ca. −90 °C), several sensitizers, including **5c**, **5f**, **5h**, **5i**, **5l**, and **5n**, readily give very high op's (43–53%). The use of a lower substrate concentration (0.03 M instead of 0.2 M in most runs) further increases the op for **5c** up to 63.5% at −89 °C. These values are impressive in view of the much lower op's (<15%) hitherto reported for the other photosensitized enantiodifferentiating reactions.

In some cases, the substituent effect seems unfavorable judging from the product's op at ambient temperature, as exemplified by **2b**, **4b**, **5g**, **5j**, and **5m** which generally give lower op's than their reference compounds **2a**, **4a**, **5a**, and **5f**. However, the evaluation of a chiral sensitizer solely from the product's op at a specific temperature can be meaningless and even misleading, since the product's op is not only a critical function of the irradiation temperature but also quite frequently inverts its sign at the equipodal temperature.[16] Instead, the differential activation parameters obtained from the temperature dependence of the op are the best and only measure of enantiodifferentiability; this point will be discussed later.

Triplex Formation. It is presumed that the exciplex intermediate, generated through intramolecular charge transfer within the excited donor–acceptor sensitizer, goes on to form a ternary complex upon quenching by the substrate **1**. Unfortunately, the fluorescence quenching study did not afford any spectroscopic evidence for the triplex formation, since no appreciable new emission emerged at longer wavelengths in the exciplex quenching of **5b** by **1E** or **1Z** in both pentane and acetonitrile.

However, a chemical approach using a *hemichiral* sensitizer provided us with indirect but definitive evidence for the intervention of a triplex intermediate in the enantiodifferentiating photosensitization. In *hemichiral* (−)-menthyl 3-phenylpropyl phthalate (**3ao**), an electron-donating phenyl group (D) is introduced at the γ-position of the propyl group in order to mimic the intramolecular [A–D] exciplex formation of **3b** and, simultaneously, create an achiral environment around the open face of the phenyl group introduced. This *hemichiral* donor-acceptor sensitizer **3ao** is useful not only in demonstrating the intervention of the triplex, but also in discriminating between two stacking possibilities of the triplex intermediate, i.e., [A–D···D′] versus [D–A···D′]. This determination is made possible because the [A–D···D′] triplex, lacking direct interaction between the chiral menthyl group attached to A and the substrate D′, must lead to negligible enantiodifferentiation at any temperature, while the [D–A···D′] triplex, in which the menthyl group is located more closely to D′, may afford appreciable op in the product **1E**.

As can be seen from runs 5–11 in Table III, both dimenthyl and bis(8-phenylmenthyl) phthalates **3a** and **3b** give the temperature-dependent op's of 3.8–10% and 8.4–18%, respectively, which are fairly good values for chiral phthalates. By contrast, the *hemichiral* phthalate **3ao** gives an extremely low op of 0.5–1.0% at both 25 and −40 °C, unambiguously indicating that the enantiodifferentiating photosensitization proceeds through the [A–D···D′] triplex shown in Chart II.

Enantiodifferentiation Mechanism. Although the major purpose of this study is not to reconfirm the basic features and mechanism of this enantiodifferentiating photosensitization as proposed in the previous paper,[16b] it is still necessary to perform some experiments to investigate the conversion dependence and solvent effects upon the op, using phenyl-substituted alkyl esters **5b** and **5i**. This is important, since the rationalizations using the previously proposed mechanism[16] become meaningless if the present strategy, utilizing the intramolecular exciplex formation within the sensitizer, alters the enantiodifferentiation step or mechanism.

However, as can be seen from runs 19–21 in Table III, the sensitization with exciplex-forming **5b** gives a high op of 50% even at the initial stages (1% conversion), and the op remains high (44–50%) throughout the photolysis until the photolyzate reaches the photostationary state upon prolonged irradiations. As discussed in detail in the previous paper,[16b] the enantiodifferentiating photoisomerization of **1Z** can be actualized only through one or both of the following mechanisms: (1) kinetic resolution in the enantiodifferentiating excitation of the initially produced racemic **1E** and/or (2) enantiodifferentiating rotational relaxation of the double bond of **1Z** within the exciplex intermediate. The invariant op's over a wide range of conversions unequivocally indicate that, as was the case with the non-electron-donating alkyl esters,[16] only the latter mechanism is operative in this highly efficient enantiodifferentiation sensitized by the phenyl-substituted alkyl esters.

Solvent Effects. As described in the foregoing discussion on fluorescence spectra, the large Stokes shifts

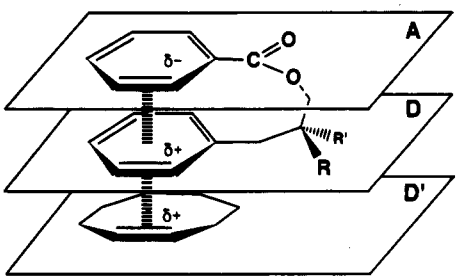
Table III. Enantiodifferentiating Photoisomerization of (*Z*)-Cyclooctene (1Z) Sensitized by Bulky and/or Electron-Donating Chiral Polyalkyl Benzenepolycarboxylates[a]

entry	sensitizer	solvent	temp, °C	irradn time, h	% conversn	% yield[b]	$[\alpha]^{25}_D$ (c, CH_2Cl_2)	% op[c]	ref
1	**2a**	pentane	25	28	21	17	−11.6 (1.1)	−2.72	*d*
2			−25	60	20	15	−12.6 (3.1)	−2.97	*d*
3	**2b**	pentane	25	15[e]	20	6	−2.20 (1.5)	−0.53	*f*
4			−40	44	12	10	−6.39 (1.6)	−1.57	*f*
5	**3a**	pentane	25	23	9	5	16.2 (1.4)	3.80	*d*
6			−60	70	18	9	43.7 (2.1)	10.3	*d*
7	**3ao**	pentane	25	18[e]	4	3	−4.09 (2.6)	−1.07	*f*
8			−40	44	7	5	−2.18 (1.6)	−0.53	*f*
9	**3b**	pentane	25	20[e]	8	2	74.0 (0.9)	18.3	*f*
10			−40	44	5	4	50.3 (2.8)	12.7	*f*
11			−87	64	10	4	35.3 (1.7)	8.45	*f*
12	**4a**	pentane	25	24	25	8	−25.4 (2.6)	−5.96	*d*
13			−40	64	24	18	−34.7 (3.1)	−8.16	*d*
14	**4b**	pentane	25	18[e]	10	5	−12.9 (1.5)	−3.14	*f*
15			−40	44	3	2	−12.0 (2.0)	−2.93	*f*
16	**5a**	pentane	25	29	15	8	−41.0 (1.2)	−9.60	*d*
17			−40	48	23	15	30.0 (1.8)	7.05	*d*
18			−87	64	22	19	123.2 (1.9)	28.9	*d*
19	**5b**	pentane	25	2[g]	1	1	193.9 (1.2)	49.5	*f*
20				6	3	3	183.7 (1.2)	48.0	*f*
21				24[e]	12	4	179.3 (2.0)	44.1	*f*
22			−40	48	10	5	114.5 (1.8)	27.3	*f*
23			−87	64[g]	16	6	65.6 (1.4)	16.1	*f*
24		methylcyclohexane	25	20[e]	8	5	180.1 (1.1)	42.6	*f*
25			−40	40	10	8	146.0 (1.6)	34.4	*f*
26		CH_3CN	25	21[e]	6	5	149.8 (1.2)	42.0	*f*
27			−40[i]	48	12	6	20.9 (1.8)	5.12	*f*
28	**5c**	pentane	25	23[j]	9	*h*	209.7 (2.4)	49.2	*f*
29			−86	48[j]	10	*h*	226.9 (4.7)	53.3	*f*
30			−89	33[k]	*h*	*h*	270.3 (1.4)	63.5	*f*
31	**5d**	pentane	25	21[e]	4	3	57.1 (1.4)	14.3	*f*
32			−87	64	4	2	13.9 (1.4)	4.81	*f*
33	**5e**	pentane	−40	40[j]	14	7	13.8 (2.4)	3.33	*f*
34			−86	40[j]	12	9	−62.0 (1.7)	−14.8	*f*
35	**5f**	pentane	25	29	7	6	49.2 (1.0)	11.5	*d*
36			−40	48	9	8	116.3 (2.2)	27.3	*d*
37			−88	70	*h*	*h*	172.7 (2.3)	40.6	*d*
38			−90	33[k]	*h*	*h*	184.9 (1.7)	43.4	*d,f*
39	**5g**	pentane	25	15[e]	5	2	−23.4 (2.7)	−6.47	*f*
40			−87	64	9	4	−32.6 (1.8)	−7.87	*f*
41	**5h**	pentane	25	15[e]	6	2	85.6 (2.1)	21.5	*f*
42			−40	44	8	6	133.7 (1.2)	32.5	*f*
43			−87	64	11	8	202.8 (1.9)	49.1	*f*
44	**5i**	pentane	25	23[e]	2	2	−28.0 (2.4)	−7.86	*f*
45			−40	40	4	4	−106.4 (1.8)	−26.3	*f*
46			−88	64	7	5	−180.8 (3.2)	−46.0	*f*
47		CH_3CN	25	15[e]	2	1	−27.2 (0.4)	−7.32	*f*
48	**5j**	pentane	25	15[e]	5	2	17.3 (1.2)	4.62	*f*
49			−87	64	4	3	16.9 (1.6)	4.20	*f*
50	**5k**	pentane	25	17[e]	2	2	−78.9 (2.1)	−19.5	*f*
51			−40	44	6	4	−77.2 (1.9)	−18.7	*f*
52	**5l**	pentane	25	15[e]	12	3	54.0 (3.0)	13.1	*f*
53			−40	44	7	6	148.9 (1.1)	35.9	*f*
54			−88	30	12	10	225.3 (1.4)	53.3	*f*
55	**5m**	pentane	25	22[e]	5	2	26.1 (1.0)	6.89	*f*
56			−40	44	6	4	7.48 (1.7)	1.79	*f*
57			−88	29	10	7	−75.7 (1.8)	−18.6	*f*
58	**5n**	pentane	25	15[e]	2	1	92.7 (1.3)	22.9	*f*
59			−40	44	4	2	119.4 (2.0)	30.1	*f*
60			−88	30	3	2	206.4 (1.5)	51.4	*f*

[a] [1Z] = 0.2 M; [sensitizer] = 1.2 mM, unless stated otherwise. [b] Chemical yield determined by GC analysis on the basis of the starting material. [c] Optical purity of isolated 1E, calculated from the specific rotation of the optically pure (−)-1E ($[\alpha]^{25}_D$ −426° (CH_2Cl_2)); corrected for the presence of the remaining pentane (1–5%). [d] Reference 16b. [e] Apparent photostationary state attained. [f] This work. [g] [Sensitizer] = 1.6 mM. [h] Not determined. [i] Partially insoluble; the product's op has been shown to decrease substantially in the presence of precipitated sensitizer (ref 16b). [j] [Sensitizer] = 2.0 mM. [k] [1Z] = 0.03 M; [sensitizer] = 5.0 mM.

observed for the (ar)alkyl esters clearly indicate that these excited donor–acceptor sensitizers gain additional stabilization through the intramolecular CT interaction to form exciplex or radical ion pair, depending upon the solvent polarity. Consequently, the ultimate conformation of the excited sensitizer must differ considerably in pentane and acetonitrile. In this context, it is somewhat unexpected that, even when the donor–acceptor sensitizer **5b** or **5i** is used, the product's op does not suffer any significant solvent effect, at least at ambient temperature; these sensitizers afford almost comparable op's in pentane, methylcyclohexane, and acetonitrile; see runs 21–27 for **5b** and 44 and 47 for **5i** (Table III; only limited data are available in acetonitrile due to the low solubility of these sensitizers at the low temperatures). The comparable op's obtained in solvents of differing polarity suggest that the

Chart II. Schematic Drawing of A-D···D′ Triplex



quenching of the [A–D] sensitizer by 1 affords [A–D···D′] triplex of similar conformation, irrespective of the solvent polarity. It is not unrealistic in such a ternary complex that the positive charge developed originally on the donor site of [A–D] would be delocalized extensively over the two donating components (D and D′) in the [A–D···D′] triplex, greatly reducing its ionic character even in acetonitrile.

Activation Parameters. The relative frequency factor (A_S/A_R), and the differential activation energy (ΔE_{S-R}), enthalpy ($\Delta\Delta H^{\ddagger}_{S-R}$) and entropy ($\Delta\Delta S^{\ddagger}_{S-R}$) for the enantiodifferentiating photoisomerization can be evaluated from the temperature dependence of the op's obtained at various temperatures, according to the Arrhenius and Eyring equations,

$$\ln (k_S/k_R) = -\Delta E_{S-R}/RT + \ln (A_S/A_R)$$

$$= -\Delta\Delta H^{\ddagger}_{S-R}/RT + \Delta\Delta S^{\ddagger}_{S-R}/R$$

where the k_S/k_R ratio, the relative rate of formation for (*S*)- and (*R*)-**1E**, is experimentally equal to the (100 + % op)/(100 − % op) ratio. The activation parameters listed in Table IV are obtained from the plots of ln (k_S/k_R) values against reciprocal temperature, some of which are shown in Figure 2 for **5g–5j**. It is interesting to note that, of four structurally related benzylbornyl esters **5g–5j**, the sensitizers **5g** and **5j** with endo–endo or exo–exo stereochemistry, both of which form highly stabilized intermolecular exciplexes as judged from the larger Stokes shifts shown in Table I, give only poor op's over the temperature range examined. On the other hand, the exciplex-forming but less-stabilized **5h** and **5i** afford much greater op's and temperature dependences. This result indicates that a moderately fixed as opposed to fully rigid excited-state structure of the chiral sensitizer is favorable for efficient enantiodifferentiation.

It should be emphasized that the present photosensitizing system, employing highly bulky and/or electron-donating (ar)alkyl benzenepolycarboxylates, shares the basic features of the apparently curious temperature-switching behavior seen in the previous system using simpler chiral sensitizers.[16] In most cases, the product's chirality is actually inverted at the *equipodal temperature*[2,16b] either within the experimental temperature range or upon extrapolation of the Arrhenius plot. Interestingly, some sensitizers do not show such inversion phenomena and no equipodal temperature is observed. This seems rather natural when the differential entropy of activation is small ($\Delta\Delta S^{\ddagger} < 0.1$ cal/mol K), or similarly when the relative frequency factor is close to unity ($A_S/A_R = 1.00 \pm 0.03$). In these cases, the op's are also small over the entire temperature range examined and a minimal experimental error would affect the extrapolation of the

Table IV. Activation Parameters at 25 °C, Extrapolated Optical Purities (% op) of 1E at −200 and 10^8 °C, and Equipodal Temperatures (T_0) for Enantiodifferentiating Photoisomerization of 1Z Sensitized by Bulky and/or Electron-Donating Chiral Polyalkyl Benzenepolycarboxylates 2–5 in Pentane[a]

sensitizer	data point	$\Delta\Delta H^{\ddagger}_{S-R}$,[b] kcal/mol	$\Delta\Delta S^{\ddagger}_{S-R}$,[c] cal/mol K	A_S/A_R[d]	% op estimated[e] −200 °C	% op estimated[e] 10^8 °C	T_0,[f] °C	ref
2a	3	0.014	−0.027	0.99	−6.5	−1.5	*g*	*h*
2b	2	0.044	0.055	1.03	−12.0	3.2	74	*i*
3a	4	−0.19	−0.22	0.90	49.0	−12.5	112	*h*
3ao	2	−0.023	−0.052	0.97	4.88	−3.01	−81	*i*
3b	3	0.20	0.60	1.35	−31.8	33.4	−131	*i*
4a	4	0.092	0.033	1.02	−28.9	1.9	930	*h*
4b	2	−0.009	−0.067	0.97	−0.8	−3.9	−215	*i*
5a	9	−0.77	−1.30	0.52	95.5	−63.8	−17	*h*
5b	3	0.62	1.70	2.35	−82.1	75.4	−114	*i*
5c	2	−0.104	0.79	1.48	67.0	42.3	*g*	*i*
5d	2	0.19	0.52	1.30	−33.3	29.4	−117	*i*
5e	2	0.69	1.34	1.96	−92.0	65.0	−50	*i*
5f	4	−0.61	−0.67	0.71	93.5	−37.1	118	*h*
5g	2	0.028	−0.071	0.96	−13.6	−4.1	*g*	*i*
5h	3	−0.63	−0.56	0.75	95.1	−31.3	216	*i*
5i	3	0.81	1.05	1.69	−97.5	54.2	64	*i*
5j	2	0.008	0.092	1.05	2.5	5.3	−234	*i*
5k	2	−0.018	−0.35	0.84	−14.1	−19.9	−251	*i*
5l	3	−0.89	−1.06	0.59	98.6	−54.5	95	*i*
5m	3	0.51	0.90	1.57	−84.0	47.8	−28	*i*
5n	3	−0.66	−0.60	0.74	95.8	−33.6	200	*i*

[a] All activation parameters obtained by Eyring and Arrhenius treatments of the product's op. [b] Differential enthalpy of activation: $\Delta H^{\ddagger}_S - \Delta H^{\ddagger}_R$. [c] Differential entropy of activation: $\Delta S^{\ddagger}_S - \Delta S^{\ddagger}_R$. [d] Relative frequency factor. [e] Optical purity of **1E** at −200 and 10^8 °C, calculated by extrapolating the Arrhenius plot. [f] Isoenantiodifferentiating, or equipodal, temperature, at which no appreciable enantiodifferentiation occurs. [g] Does not exist. [h] Reference 16b. [i] This work.

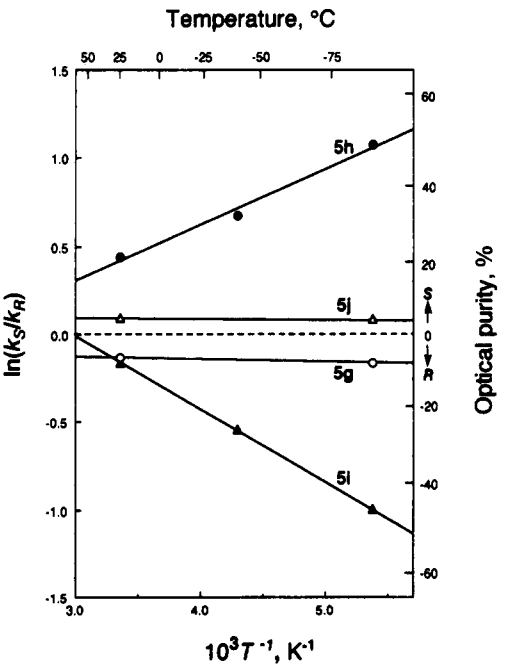


Figure 2. Temperature dependence of the optical purity of product **1E** in the enantiodifferentiating photoisomerization of **1Z** sensitized by **5g** (○) **5h** (●), **5i** (▲), and **5j** (△).

Arrhenius plot. However, the photosensitization with highly bulky 8-cyclohexylmenthyl benzenetetracarboxylate **5c** is an exceptional case. The op remains high over the experimental temperature range (runs 28–30 in Table III), showing little temperature dependence and therefore a small $\Delta\Delta H^{\ddagger}$ value (Table IV), while the differential entropy of activation is significantly high ($\Delta\Delta S^{\ddagger} = 0.79$

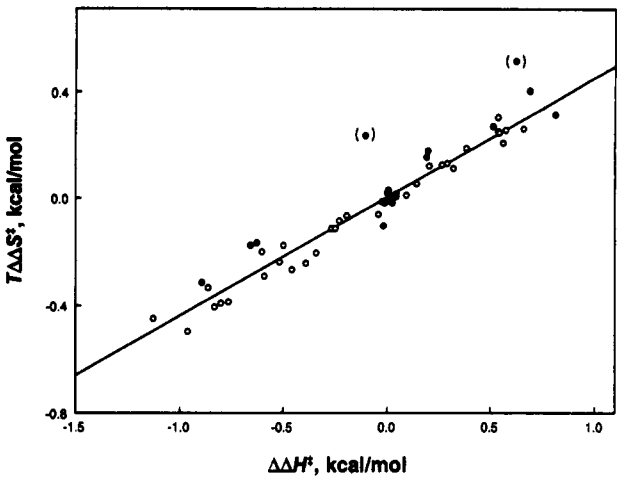


Figure 3. Enthalpy–entropy compensation effect observed in the enantiodifferentiating photoisomerization of cyclooctene sensitized by less-bulky chiral alkyl benzenepolycarboxylates (○, ref 16b) and by highly bulky alkyl or electron-donating aralkyl benzenepolycarboxylates (●, this work); the regression line was drawn without using the two points in the parentheses; see text.

cal/mol K). As a result, this set of thermodynamic data deviates from the regression line in the enthalpy–entropy compensation plot shown below.

The highly bulky and/or electron-donating groups introduced in benzoate **2** and terephthalate **4** slightly enhance the activation parameters, but the relative frequency factors are still very close to unity (A_S/A_R = 1.00 ± 0.03). In contrast, the same groups introduced in the *o*-benzenepolycarboxylates **3** and **5** influence the op and its temperature dependence in a more drastic manner, bringing about both favorable and apparently unfavorable effects in terms of the enantiodifferentiation. However, global examinations of the activation parameters reveal that *any substitution drives the enthalpy and entropy terms compensatorily in the same direction.* Hence, the enthalpy–entropy plot for this enantiodifferentiating photoisomerization gives a good straight line except for the somewhat deviated plots for **5b** and **5c**; see Figure 2:

$$T\Delta\Delta S^{\ddagger} = 0.44\Delta\Delta H^{\ddagger} + 0.03 \quad (r = 0.98)$$

The good linear relationship between $\Delta\Delta H^{\ddagger}$ and $T\Delta\Delta S^{\ddagger}$ indicates that the enantiodifferentiation mechanism is constant for most photosensitizers and solvents, and the obtained slope of 0.44 indicates that up to 56% of the increment in enthalpic gain arising from the change of sensitizer structure, solvent, or any other factors, contributes toward enhancing the product's op. This result implies that further efforts to enhance op will be rewarded.

Conclusions

Both of the newly employed strategies of intra/intermolecular triplex formation and increased steric hindrance in optically active sensitizers have proven successful in giving the highest op not only at low temperatures but also at ambient temperature. These methodologies may provide us with powerful tools applicable to other photochemical enantiodifferentiating reactions which have interested (photo)chemists for a long time.[1,2]

Mechanistically, the enhanced op's arise as a result of dynamic conformational changes in the exciplex/triplex intermediate which are induced by the highly bulky and/or electron-donating (ar)alkyl groups in the ester moieties of the sensitizer. The dynamic structural changes during the enantiodifferentiating rotational relaxation of the substrate in the exciplex/triplex intermediate lead to the anomalously high differential entropy of activation, which plays the major role in determining the product's op and its temperature dependence.

It has also been revealed that the temperature switching behavior of product chirality is not a special but potentially a very general phenomenon which is observed in any photochemical (or thermal) enantiodifferentiating reaction, especially when dynamic structural changes are involved in the enantiodifferentiating step. Further studies on this topic are highly indicated.

Experimental Section

General. Melting points were measured with a YANACO MP-21 apparatus and are uncorrected. Specific rotations of optically active sensitizers and isolated products were determined using a Perkin-Elmer model 243B polarimeter with a temperature-controlled 10-cm cell. Mass spectra were obtained on a JEOL AX-500 instrument by field desorption (FD) or fast-atom bombardment (FAB) ionization with or without potassium iodide added to the sample matrix. ^{1}H NMR spectra were recorded at 400 MHz on a JEOL GX-400 spectrometer, using chloroform-*d* as solvent. Infrared spectra were obtained on a JASCO IR-810 instrument. Electronic absorption and fluorescence spectra were recorded on JASCO Ubest-50 and FP-770 spectrometers, respectively. The fluorescence spectra were not corrected for the instrument response function of the spectrometer. Fluorescence lifetimes were measured by means of the time-correlated single-photon counting method, using a Horiba NAES-550 or 1100 instrument equipped with a pulsed H_2 light source; the radiation from the lamp was made monochromatic (270 nm) by a 10-cm monochrometer, and the emission from the sample solution was filtered with a Toshiba UV-33 or UV-39 filter. Gas chromatographic (GC) analyses of photolyzed samples were performed on a 3-m packed column of 40% β,β′-oxydipropionitrile at 65 °C, which gave satisfactory separation of **1Z**, **1E**, and cyclooctane added as an internal standard. Some benzenepolycarboxylates were purified on a Hitachi HPLC instrument L-6200 over an ODS column with ethanol–water eluent.

Materials. Hydrocarbon solvents were shaken repeatedly with concentrated sulfuric acid until the acid layer no longer turned yellow. The hydrocarbon layer was separated, neutralized with sodium carbonate powder, and then distilled fractionally. Acetonitrile was fractionally distilled from diphosphorous pentoxide. Methanol was refluxed with magnesium turnings and then distilled fractionally. (*Z*)-Cyclooctene (**1Z**) (Nakarai) was purified by treatment with 20% aqueous silver nitrate followed by fractional distillation. The purified sample of **1Z** contained 3–4% cyclooctane as the sole detectable impurity, which was employed as an internal standard in the GC analysis, but was completely free from the (*E*)-isomer and 1,3- and 1,5-cyclooctadienes. (*E*)-Cyclooctene (**1E**) of >99.5% purity was prepared by the singlet-sensitized photoisomerization of **1Z** as reported previously.[16b] The optically active alcohols ROH (**6a–o**; R shown in Chart I) employed as the building blocks of the chiral photosensitizers were commercially available or independently synthesized as described below.

(−)-(1*R*,2*S*,5*R*)-8-Phenylmenthol (**6b**) was prepared from (+)-(5*R*)-pulegone (Nakarai), according to the procedure reported by Corey et al.:[18,19] oil; $[\alpha]^{22}_D$ −24.2° (*c* 1.07, EtOH) (lit.[19] $[\alpha]^{22}_D$ +26.3° (*c* 2.30, EtOH); lit.[20] $[\alpha]^{21}_D$ −29.4° (*c* 0.32, $CHCl_3$)). (−)-(1*R*,2*S*,5*R*)-8-Cyclohexylmenthol (**6c**)[21] was prepared from **6b**

(18) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908.
(19) Ensley, H. E.; Parnell, C. A.; Corey, E. J. *J. Org. Chem.* **1978**, *43*, 1610.
(20) Herzog, H.; Scharf, H.-D. *Synthesis* **1986**, 420.
(21) Whitesell, J. K.; Lawrence, R. M.; Chen, H.-H. *J. Org. Chem.* **1986**, *51*, 4779.

by catalytic hydrogenation over Rh/C: bp 135.0–138.0 °C/3 Torr; $[\alpha]^{20}_D$ −19.6° (c 0.54, C_6H_6).

(+)-(1*R*,2*S*,5*R*)-2-(Diphenylmethyl)-5-methylcyclohexanol (**6d**)[22] was synthesized from (−)-(*R*)-2-benzylidene-5-methylcyclohexanone[23] ($[\alpha]^{20}_D$ −148.9° (c 0.45, MeOH), which was prepared from (+)-(5*R*)-pulegone (Nakarai) via (+)-(*R*)-3-methylcyclohexenone, according to procedures similar to those employed above:[18,19] oil; $[\alpha]^{20}_D$ +3.19° (c 0.97, C_6H_6). (−)-(1*R*,2*S*,5*R*)-2-(Dicyclohexylmethyl)-5-methylcyclohexanol (**6e**) was prepared from **6d** by catalytic hydrogenation over PtO_2: mp 120.0–121.0 °C; $[\alpha]^{20}_D$ −31.5° (c 0.51, C_6H_6).

(−)-(1*S*,2*R*,3*R*)-*endo*-3-Benzyl-*endo*-2-borneol (**6g**) and its three stereoisomers of borneol or isoborneol derivatives were synthesized from (−)-borneol (Aldrich) via (−)-(1*S*)-3-benzylidenecamphor according to the procedures reported by Richer and Rossi: oil; $[\alpha[^{24}_D$ −28.5° (c 1.09, C_6H_6) (lit.[24] $[\alpha]^{24}_D$ +28.2° (c 2.20, C_6H_6)). (−)-(1*S*,2*R*,3*S*)-*exo*-3-Benzyl-*endo*-2-borneol (**6h**):[24] oil; $[\alpha]^{24}_D$ −46.6° (c 0.83, C_6H_6) (lit.[24] $[\alpha]^{24}_D$ +49.4° (c 1.80, C_6H_6)). (−)-(1*S*,2*S*,3*R*)-*endo*-3-Benzyl-*exo*-2-isoborneol (**6i**):[24] oil; $[\alpha]^{24}_D$ −12.8° (c 1.02, C_6H_6) (lit.[24] $[\alpha]^{24}_D$ +10.8° (c 1.33, C_6H_6)). (−)-(1*S*,2*S*,3*S*)-*exo*-3-Benzyl-*exo*-2-isoborneol (**6j**):[24] oil; $[\alpha]^{24}_D$ −26.2° (c 1.03, C_6H_6) (lit.[24] $[\alpha]^{24}_D$ +28.3° (c 1.84, C_6H_6)).

(−)-(1*S*,2*R*,3*R*)-*endo*-3-(Cyclohexylmethyl)-*endo*-2-borneol (**6k**) and its stereoisomers **6l–n** were prepared from the corresponding benzyl derivatives **6g–j** by catalytic hydrogenation over Rh/C. **6k**: mp 53.5–54.0 °C; $[\alpha]^{20}_D$ −13.9° (c 0.79, C_6H_6). (−)-(1*S*,2*R*,3*S*)-*exo*-3-(Cyclohexylmethyl)-*endo*-2-borneol (**6l**): mp 58.0–58.5 °C; $[\alpha]^{20}_D$ −29.1° (c 0.68, C_6H_6). (−)-(1*S*,2*S*,3*R*)-*endo*-3-(Cyclohexylmethyl)-*exo*-2-isoborneol (**6m**): mp 57.0–59.0 °C; $[\alpha]^{20}_D$ −21.5° (c 1.59, C_6H_6). (−)-(1*S*,2*S*,3*S*)-*exo*-3-(Cyclohexylmethyl)-*exo*-2-isoborneol (**6n**): mp 52.0–53.0 °C; $[\alpha]^{20}_D$ −40.1° (c 1.14, C_6H_6).

The chiral alkyl benzoates **2**, phthalates **3**, terephthalates **4**, and 1,2,4,6-benzenetetracarboxylates **5** were prepared from the corresponding acid chlorides and the optically pure alcohols in pyridine, according to the method reported previously, and purified by fractional distillation or repeated recrystallization from ethanol.[16b]

(−)-(1*R*,2*S*,5*R*)-8-Phenylmenthyl benzoate (**2b**): mp 51.0–52.0 °C; $[\alpha]^{20}_D$ −49.6° (c 1.03, C_6H_6). (−)-Bis[(1*R*,2*S*,5*R*)-8-phenylmenthyl]phthalate (**3b**): mp 52.0–54.0 °C; $[\alpha]^{20}_D$ −62.6° (c 0.35, C_6H_6). (−)-(1*R*,2*S*,5*R*)-Menthyl 3-phenylpropyl phthalate (**3ao**): oil; $[\alpha]^{20}_D$ −52.9° (c 0.75, C_6H_6). (−)-Bis[(1*R*,2*S*,5*R*)-8-phenylmenthyl] terephthalate (**4b**): mp 158.0–159.0 °C; $[\alpha]^{20}_D$ −36.6° (c 0.81, C_6H_6).

(−)-Tetrakis[(1*R*,2*S*,5*R*)-8-phenylmenthyl] 1,2,4,5-benzenetetracarboxylate (**5b**): mp 112.0–113.0 °C; $[\alpha]^{20}_D$ −147.8° (c 0.86, C_6H_6). (−)-Tetrakis[(1*R*,2*S*,5*R*)-8-cyclohexylmenthyl] 1,2,4,5-benzenetetracarboxylate (**5c**): mp 97.0–98.0 °C; $[\alpha]^{20}_D$ −69.0° (c 0.53, C_6H_6). (−)-Tetrakis-[(1*R*,2*S*,5*R*)-5-methyl-2-diphenylmethylcyclohexyl] 1,2,4,5-benzenetetracarboxylate (**5d**): mp 119.0–120.5 °C; $[\alpha]^{20}_D$ −147.8° (c 0.88, C_6H_6). (−)-Tetrakis[(1*R*,2*S*,5*R*)-2-(dicyclohexylmethyl)-5-methylcyclohexyl] 1,2,4,5-benzenetetracarboxylate (**5e**): mp 136.0–137.5 °C; $[\alpha]^{20}_D$ −55.0° (c 0.23, C_6H_6). (−)-Tetrakis[(1*S*,2*R*,3*R*)-*endo*-3-benzyl-*endo*-2-bornyl] 1,2,4,5-benzenetetracarboxylate (**5g**): mp 198.5–199.0 °C; $[\alpha]^{20}_D$ −11.8° (c 0.78, C_6H_6). (−)-Tetrakis[(1*S*,2*R*,3*S*)-*exo*-3-benzyl-*endo*-2-bornyl] 1,2,4,5-benzenetetracarboxylate (**5h**): mp 166.5–167.0 °C; $[\alpha]^{20}_D$ −62.8° (c 0.52, C_6H_6). (+)-Tetrakis[(1*S*,2*S*,3*R*)-*endo*-3-benzyl-*exo*-2-isobornyl] 1,2,4,5-benzenetetracarboxylate (**5i**): mp 142.0–143.0 °C; $[\alpha]^{20}_D$ +76.0° (c 0.59, C_6H_6). (+)-Tetrakis-[(1*S*,2*S*,3*S*)-*exo*-3-benzyl-*exo*-2-isobornyl] 1,2,4,5-benzenetetracarboxylate (**5j**): mp 174.0–174.5 °C; $[\alpha]^{20}_D$ +25.7° (c 0.84, C_6H_6). (+)-Tetrakis-[(1*S*,2*R*,3*R*)-*endo*-3-(cyclohexylmethyl)-*endo*-2-bornyl] 1,2,4,5-benzenetetracarboxylate (**5k**): mp 113.0–115.0 °C; $[\alpha]^{20}_D$ +7.87° (c 0.51, C_6H_6). (−)-Tetrakis[(1*S*,2*R*,3*S*)-*exo*-3-(cyclohexylmethyl)-*endo*-2-bornyl] 1,2,4,5-benzenetetracarboxylate (**5l**): mp 138.5–140.0 °C; $[\alpha]^{20}_D$ −7.30° (c 0.81, C_6H_6). (+)-Tetrakis[(1*S*,2*S*,3*R*)-*endo*-3-(cyclohexylmethyl)-*exo*-2-isobornyl] 1,2,4,5-benzenetetracarboxylate (**5m**): mp 96.0–98.0 °C; $[\alpha]^{20}_D$ +14.2° (c 0.56, C_6H_6). (−)-Tetrakis[(1*S*,2*S*,3*S*)-*exo*-3-(cyclohexylmethyl)-*exo*-2-isobornyl] 1,2,4,5-benzenetetracarboxylate (**5n**): mp 108.0–110.0 °C; $[\alpha]^{20}_D$ −3.55° (c 0.56, C_6H_6).

Photolysis. All irradiations were conducted in a temperature-controlled water (25–0 °C) or methanol (−20 to −90 °C) bath. A solution (300 mL) of (*Z*)- or (*E*)-cyclooctene (typically 0.2 M) and an optically active sensitizer (1–5 mM) was irradiated under an argon atmosphere at +25 to −90 °C in an annular quartz vessel, using a 30-W low-pressure mercury lamp fitted with a Vycor sleeve. Only the (*E*)-isomer **1E** was selectively extracted from the photolyzate with three portions of 20% aqueous silver nitrate at <5 °C.[8,25] The combined aqueous extracts were washed with three small portions of pentane and then added dropwise into concentrated ammonium hydroxide at 0 °C to liberate **1E**, which was in turn extracted with three portions of pentane. After evaporating the solvent at a reduced pressure of >150 Torr, the residue obtained was subjected to bulb-to-bulb distillation in vacuo to yield **1E** of sufficient chemical purity (up to 95–99%) as determined by GC analysis. The impurities detected were mostly the solvent pentane (1–5%) and a small amount (<1%) of the starting material **1Z**. ^1H NMR spectra of the isolated products did not show the presence of any trace of the chiral sensitizer used or other byproducts derived therefrom. The optical rotation of isolated **1E** was measured in methylene chloride, and the product's op, corrected for its chemical purity, was determined by comparing the observed specific rotation with that ($[\alpha]^{25}_D$ −426° (CH_2Cl_2)) reported for the optically pure (−)-**1E**.[26]

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Supplementary Material Available: Physical, spectral, and analytical data for the optically active sensitizers synthesized (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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