Enantiodifferentiating Cis–Trans Photoisomerizations of 1,2-Diarylcyclopropanes and 2,3-Diphenyloxirane Sensitized by Chiral Aromatic Esters[1]

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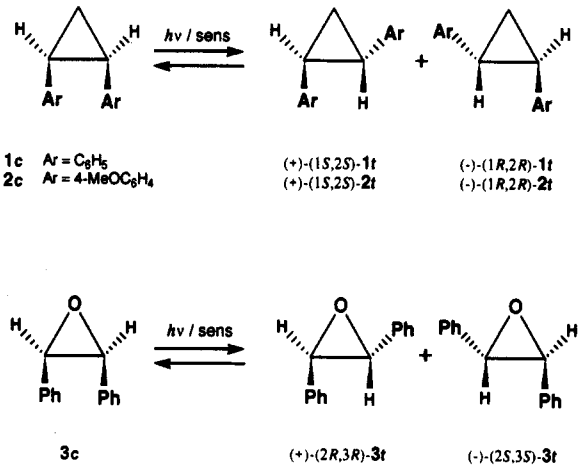
Photosensitized enantiodifferentiating cis–trans isomerizations of 1,2-diphenylcyclopropane (1), 1,2-bis(4-methoxyphenyl)cyclopropane (2), and 2,3-diphenyloxirane (3) were performed in the presence of optically active alkyl arenecarboxylates as electron-accepting photosensitizers. Several photosensitizers possessing different chromophores and chiral groups were examined in polar and nonpolar solvents, and optical purities (op) up to 10% for 1*t* and 1% for 2*t* and 3*t* were obtained. The product's op varied drastically with solvent polarity and, in an extreme case, typical polar and nonpolar solvents gave antipodal products. Mechanistic investigations revealed that the enantiodifferentiation occurs in the quenching of the excited chiral sensitizer by racemic substrates and that full equilibrium is not established between the enantiomeric ambident intermediates, probably owing to their short lifetimes.

Considerable effort has been devoted to the study of enantiodifferentiating photosensitized isomerizations[1-10] ever since the first such isomerization, that of *trans*-1,2-diphenylcyclopropane (1), was reported by Hammond and Cole.[3a] They employed (+)-(*R*)-1-(1-(*N*-acetylamino)-ethyl)naphthalene as a chiral singlet sensitizer[3b] and obtained the optically active trans isomer (1*t*) in an optical purity (op) of 6.7%.[11] Ueno et al.[7] reported an attempted singlet-sensitized photoenantiodifferentiation of 1 using a chiral polypeptide, poly(γ-(1-naphthyl)methyl L-glutamate), but the product did not show any optical activity.[7] Ouannès et al.[4] and Kagan et al.[5] examined the same enantiodifferentiating photoisomerization in the triplet manifold. However, optically active 3-methyl-1-indanone[4] and 3- or 4-methyl-1-tetralone[5] as triplet sensitizers afforded 1*t* in low op's of 3.0 and ca. 1%, respectively. Yet another approach to this photochemical enantiodifferentiation was to effect singlet- or triplet-sensitized photoisomerization in optically active solvents like (−)-isobornyl methyl ether.[12] However, this attempt resulted in low op's (<2.3%).[12]

Recent investigations of the geometrical photoisomerizations of 1,2-diarylcyclopropanes and 2,3-diaryloxiranes through the electron-transfer mechanism[13,14] and the highly efficient enantiodifferentiating photoisomerization of cyclooctene sensitized by chiral benzenepolycarboxylates[10] prompted us to examine these photosensitized enantiodifferentiating photoisomerizations under electron-transfer conditions.

Scheme I



In the present study, we investigated the enantiodifferentiating photoisomerizations of 1,2-diphenylcyclopropane (1), 1,2-bis(4-methoxyphenyl)cyclopropane (2), and 2,3-diphenyloxirane (3) sensitized by chiral arenecarboxylates 4–13 under electron-transfer conditions; we hoped that such conditions would result in better chiral recog-

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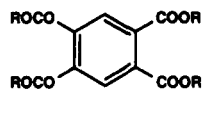
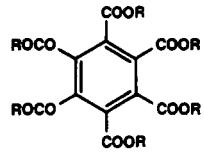
Chart I



4 R = (−)-Menthyl
5 R = (−)-Bornyl
6 R = (−)-8-Phenylmenthyl
7 R = (−)-8-Cyclohexylmenthyl
8 R = (−)-(1*R*,2*S*,5*R*)-2-Diphenylmethyl-5-methylcyclohexyl



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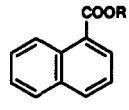

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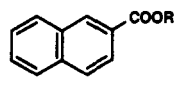

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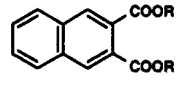

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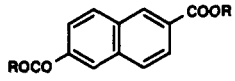
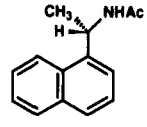


13 R = (−)-Menthyl



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nition in the excited state. From a mechanistic point of view, we expect that the product's op obtained under various conditions would serve as a sensitive probe for the intervening exciplex and/or radical ion pair intermediates.

Results

Diphenylcyclopropane (1). The Effect of the Initial Isomer Composition. Irradiations of various isomer mixtures of 1 were carried out in pentane and acetonitrile at 25 °C in the presence of (−)-tetramenthyl 1,2,4,5-benzenetetracarboxylate (4). The major photoreaction observed was the geometrical isomerization of 1, and the material balance was usually excellent. The isomer compositions of the photolysates and the specific rotations and chemical purities of the isolated products are listed in Table I. Also listed are the product's op's corrected for the chemical pury of the 1*t* isolated.

When the irradiation time was increased, the amount of trans isomer gradually approached the photostationary-state value of 28% in pentane and 34% in acetonitrile, irrespective of the initial isomer composition. The product's op reached a plateau in the early stages of irradiation and then declined to some extent upon prolonged irradiation. Depending upon the initial isomer composition, the highest op's ranged from 8.1 to 10.4% and 2.6 to 2.9% in pentane and acetonitrile, respectively.

The Effect of Solvent and Temperature. Several solvents of different polarities were used in the photoisomerizations with (−)-tetramenthyl or (−)-tetrabornyl benzenetetracarboxylate (4 or 5). The product's op's are listed in Table II. In the photosensitization with 4, increasing the solvent polarity led to a decrease in the highest op from 10% in pentane to 3% in acetonitrile. Interestingly, the photoisomerizations in benzene, which possesses a polarity parameter (E_T = 34.5)[15] comparable to that of ether (E_T = 34.7), afforded the lowest op's (1–2%), whereas *tert*-butylbenzene as a solvent gave an appreciably higher op (3.7%). Similarly, the photosensitization with 5 afforded (+)-(1*S*,2*S*)-1*t* of 3.8% op in pentane and 1.2% in ether. Benzene gave the lowest op (0.8%).

Unexpectedly, the photosensitization with 5 in acetonitrile gave (−)-(1*R*,2*R*)-1*t* (2.4% op), the antipode of the product obtained in the less polar solvents. Thus, by changing the solvent polarity, we were able to obtain a product with inverted chirality without employing the antipodal sensitizer. In order to confirm this unprecedented chirality inversion, the photosensitizations with 5 in pentane and acetonitrile were repeated at a lower temperature (0 °C). Again, (+)-(1*S*,2*S*)-1*t* was produced in 4.7% op in pentane (run 20), and antipode (−)-(1*R*,2*R*)-1*t* (4.1% op) was produced in acetonitrile (run 24).

The Effect of Additives. As shown above, the use of benzene as a solvent for the photosensitizations led to significantly lower op's (Table II), which cannot be rationalized by solvent polarity effect alone. It is likely that benzene molecules act as electron donors that quench the excited sensitizer in competition with the substrate. Hence, biphenyl (5 mM), a stronger electron donor, was added to the system. Comparison of runs 29–31 with runs 17–20 or 21–22 in Table I shows that both the reaction rate and the product's op decreased significantly, owing to preferential quenching of the excited sensitizer by the biphenyl additive.

The effect of added magnesium perchlorate was also investigated, since the salt was known to facilitate the ion separation of exciplexes and contact radical-ion pairs through enforced ion-pairing.[14d,e] In this particular case, however, the addition of magnesium perchlorate did not cause any appreciable changes in the reaction rate or the product's op; see runs 36–40 and 42–44 in Table I.

Sensitizer Structure. Optically active esters 6–8, which have highly bulky ester groups, were prepared from the corresponding alcohols.[16] Photosensitizations with sensitizers 6–8 in pentane and acetonitrile gave the results shown in Table III.

Although these structural modifications of 4 apparently did not improve the product's op, an intriguing solvent effect was observed in the photosensitization with 6. In contrast to the drastic solvent polarity effect observed for 4 and 5 (Table II), no appreciable decrease in op and no inversion of the product chirality were seen for 6, even in acetonitrile. Instead, the op's in acetonitrile were comparable or slightly higher than those in pentane (runs 1–3 and 7–10 in Table III). This result indicates the possible formation of an intramolecular A–D exciplex incorporating an 8-phenyl group of 6 as electron donor. Such a charge-transfer interaction fixes the conformation of the intramolecular exciplex, and the fixed conformation results in analogous exciplex structures and comparable op's in both nonpolar and polar solvents. The lower op obtained in benzene is compatible with this mechanism, since the intramolecular exciplex formation cannot effectively compete with the intermolecular attack of neat benzene (11 M).

Highly congested (−)-hexamenthyl benzenehexacarboxylate (9) also sensitized the photoisomerization, but the op's were lower than those obtained for 4 (see runs 17–19 in Table III). When (−)-menthyl esters 10–13 of 1- and

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Table I. Enantiodifferentiating Cis–Trans Photoisomerizations of *cis*- and Racemic *trans*-1,2-Diphenylcyclopropanes (1*c* and 1*t*) and Their Mixtures of Various Initial Isomer Compositions Sensitized by (–)-Tetramenthyl 1,2,4,5-Benzenetetracarboxylate (4) in Pentane and Acetonitrile at 25 °C[a]

					isolated product		
run	solvent	initial composn (% trans)[b]	irradn time, h	isomer composn (% trans)[c]	$[\alpha]^{20}_D$ (*c*, $CHCl_3$)	purity (% trans)[d]	optical purity,[e] %
1	pentane	0	1.5	6	11.4 (0.31)	80	3.4
2			3	10	19.9 (0.29)	88	5.4
3			5	15	27.0 (0.40)	78	8.3
4			13	17	24.5 (0.40)	80	7.3
5			18	18	22.2 (0.40)	68	7.8
6			36	20	26.4 (0.46)	88	7.2
7			80	25[f]	24.4 (0.40)	90	6.5
8			500	26[f]	16.5 (0.42)	94	4.2
9		40	4	31	25.8 (0.42)	79	7.8
10			8	26[f]	26.5 (0.48)	78	8.2
11			12	27[f]	23.9 (0.40)	73	7.8
12			16	29[f]	24.6 (0.20)	80	7.4
13			24	28[f]	20.9 (0.35)	79	6.3
14			48	26[f]	17.6 (0.36)	81	5.2
15		62	4	49	20.5 (0.40)	83	5.9
16			8	38	32.1 (0.37)	82	9.4
17			12	35	31.6 (0.37)	77	9.8
18			17	31[f]	27.6 (0.39)	77	8.6
19			24	31[f]	30.6 (0.39)	80	9.2
20			48	30[f]	27.5 (0.37)	82	8.0
21		78	13	57	35.2 (0.42)	81	10.4
22			58	23	26.0 (0.47)	95	6.6
23		100	8	84	13.1 (0.36)	93	3.4
24			22	70	20.4 (0.44)	90	6.6
25			36	57	30.3 (0.39)	90	8.1
26			76	44	29.6 (0.40)	88	8.0
27			100	39	26.7 (0.42)	85	7.5
28			148	35	20.3 (0.37)	77	6.3
29	pentane[g]	73	14	67	3.9 (0.31)	78	1.2
30			24	62	10.2 (0.54)	72	3.4
31			64	50	12.3 (0.56)	77	3.8
32	CH_3CN	0	1	8	1.5 (0.33)	54	0.7
33			3	13	1.9 (0.36)	69	0.7
34			6	25	8.8 (0.40)	82	2.6
35			72	34[f]	9.2 (0.40)	96	2.3
36		65	4	54	5.8 (0.48)	91	1.5
37			8	45	9.0 (0.37)	89	2.4
38			12	38	8.1 (0.37)	86	2.2
39			16	35[f]	10.0 (0.42)	83	2.8
40			26	34[f]	8.6 (0.38)	85	2.4
41			30	35[f]	10.0 (0.34)	86	2.7
42	CH_3CN[h]	65	4	58	5.4 (0.46)	94	1.4
43			8	50	7.3 (0.45)	94	1.9
44			20	40	8.3 (0.53)	89	2.2

[a] Irradiation conditions: [1] = 30 mM; [4] = 5 mM; argon atmosphere. [b] Content of trans isomer before irradiation; the balance is cis isomer. [c] Content of trans isomer after irradiation; the balance is cis isomer. [d] Chemical purity of isolated trans isomer, determined by GC analysis. [e] Enantiomeric excess corrected for the chemical purity. [f] Apparent photostationary-state mixture. [g] Biphenyl (5 mM) added. [h] Magnesium perchlorate (5 mM) added.

2-naphthalenecarboxylic and 2,3- and 2,6-naphthalenedicarboxylic acids were employed as chiral sensitizers, only low op (0–2.1%) were obtained (runs 20–24 in Table III).

In experiments using the antipode (14) of Hammond and Cole's chiral aminoethylnaphthalene,[3a] we obtained fairly low op's (0–3.6%) under identical conditions.

Bis(4-methoxyphenyl)cyclopropane (2). Photosensitizations of **2** with **4** and **5** were performed in pentane and acetonitrile under conditions comparable to those used for **1**. Although the major reaction was the cis–trans isomerization, the photosensitization gave racemic **2*t*** in pentane and (–)-(1*R*,2*R*)-**2*t*** of 1.0% op in acetonitrile, as shown in Table IV. It is interesting to note that when chiral sensitizer **5** was used, the enantiomer obtained in excess in the photosensitization of **2** possessed a sign/configuration opposite to that obtained for **1**. On the other hand, **14** as a sensitizer afforded the (+)-(1*S*,2*S*)-enantiomer, as was the case with diphenylcyclopropane.

Diphenyloxirane (3). The enantiodifferentiating geometrical photoisomerization of **3** sensitized by **5** proceeded much slower than that of **1** or **2**, and the photostationary state was not attained between the cis and trans isomers even after prolonged irradiation. The op's of the isolated **3*t*** were generally <1% in the photoisomerizations in pentane and acetonitrile, as shown in Table V.

Fluorescence Quenching. In order to elucidate the excited states involved and the quenching efficiency, fluorescence quenchings of **4** and **10–13** with **1*c*** and **1*t*** were performed in pentane and acetonitrile. The addition of **1*c*** or **1*t*** neither changed the absorption spectra of **4** and **10–13** nor produced a new band ascribable to a ground-

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Table II. Solvent and Temperature Effects on the Product's Optical Purity in Enantiodifferentiating Cis–Trans Photoisomerizations of 1,2-Diphenylcyclopropane (1) Sensitized by (−)-Tetramenthyl or (−)-Tetrabornyl 1,2,4,5-Benzenetetracarboxylate (4 or 5)[a]

						isolated product		
run	sensitizer	solvent	temp °C	irradn time, h	isomer composn (% trans)[b]	$[\alpha]^{20}_D$ (c, $CHCl_3$)	purity (% trans)[c]	optical purity,[d] %
1	4	pentane	25	12	35	31.6 (0.37)	77	9.8
2		cyclohexane	25	18	29	28.5 (0.40)	88	7.7
3		cyclohexane[e]	25	16	30	28.5 (0.35)	80	8.5
4				20	28	24.8 (0.36)	74	8.0
5				24	27	20.1 (0.31)	80	6.0
6		methylcyclohexane	25	22	35	28.5 (0.37)	90	7.6
7		benzene	25	22	56	5.6 (0.43)	95	1.4
8		benzene[e]	25	16	63	7.2 (0.43)	91	1.8
9				20	61	4.4 (0.37)	75	1.4
10				28	60	3.5 (0.42)	93	0.9
11		*tert*-butylbenzene[e]	25	11	60	9.1 (0.36)	95	2.3
12				35	48	14.7 (0.33)	96	3.7
13				50	45	12.4 (0.31)	94	3.2
14		ether	25	20	42	21.2 (0.43)	91	5.6
15		ether[f]	25	16	44	33.2 (0.25)	91	8.7
16				20	43	27.5 (0.43)	92	7.2
17				28	48	26.9 (0.40)	90	7.2
18		CH_3CN	25	16	35	10.0 (0.42)	83	2.9
19	5	pentane	25	21	24	15.3 (0.30)	97	3.8
20			0	25	21	19.2 (0.32)	97	4.7
21		benzene	25	32	38	2.6 (0.20)	75	0.8
22		ether	25	25	27	3.9 (0.22)	81	1.2
23		CH_3CN	25	32	45	−9.8 (0.27)	96	−2.4
24			0	45	51	−16.8 (0.32)	97	−4.1

[a] Irradiation conditions: [1] = 30 mM (initial isomer composition = 65% trans isomer, unless noted otherwise); [4 or 5] = 5 mM; argon atmosphere. [b] Content of trans isomer and after irradiation. [c] Chemical purity of isolated trans isomer, determined by GC analysis. [d] Enantiomeric excess, corrected for the chemical purity, in the same sign as optical rotation. [e] Initial isomer composition = 73% trans. [f] Initial isomer composition = 87% trans.

Table III. Enantiodifferentiating Cis–Trans Photoisomerization of 1,2-Diphenylcyclopropane (1) Sensitized by Chiral Benzenepolycarboxylates 6–9, Naphthalenecarboxylates 10–13, or Aminoethylnaphthalene (14) at 25 °C[a]

						isolated product		
run	sensitizer (mM)	solvent	initial composn (% trans)	irradn time, h	isomer composn (% trans)[b]	$[\alpha]^{20}_D$ (c, $CHCl_3$)	purity (% trans)[c]	optical purity,[d] %
1	6 (2.5)	pentane	73	12	53	31.7 (0.43)	90	8.4
2				24	50	27.8 (0.38)	80	8.3
3				48	43	27.5 (0.40)	81	8.1
4	(2.5)	benzene	73	20	49	11.3 (0.37)	97	2.8
5				40	43	8.1 (0.61)	96	2.0
6				60	42	13.9 (0.47)	97	3.6
7	(5)	CH_3CN	73	16	45	29.4 (0.46)	89	7.9
8				38	44	31.0 (0.36)	79	9.4
9				54	26	32.0 (0.40)	85	9.0
10				68	28	30.3 (0.38)	91	8.0
11	7 (5)	pentane	73	10	27	8.1 (0.45)	85	2.3
12				20	64	10.7 (0.44)	70	3.7
13				40	62	11.4 (0.44)	88	3.0
14	8 (2.5)	CH_3CN	73	30	34	32.0 (0.39)	92	8.3
15				50	30	28.7 (0.24)	93	7.4
16				70	30	21.0 (0.34)	73	6.9
17	9 (5)	pentane	4	100	28	24.4 (0.75)	98	6.0
18			78	48	36	8.8 (0.53)	88	2.4
19		CH_3CN	78	66	53	3.5 (0.48)	80	1.0
20	10 (5)	pentane	86	30	53	7.0 (0.42)	79	2.1
21	11 (5)	pentane	73	96	61	3.4 (0.39)	87	0.9
22	12 (5)	pentane	83	21	79	1.0 (0.50)	80	0.3
23	13 (5)	pentane	0	24	25	5.9 (0.40)	83	1.7
24			73	30	70	*e* (0.42)	*f*	0
25	14 (5)	pentane	73	70	15	*e* (0.42)	*f*	0
26		benzene	0	24	4	*e* (0.34)	*f*	0
27				48	16	−1.7 (0.36)	78	−0.5
28			65	365	57	−7.4 (0.49)	98	−1.8
29			100	264	49	−14.5 (0.53)	96	−3.6

[a] Irradiation conditions: [1] = 30 mM (initial isomer composition = 73% trans); argon atmosphere. [b] Content of trans isomer after irradiation. [c] Chemical purity of isolated trans isomer, determined by GC analysis. [d] Enantiomeric excess, corrected for the chemical purity, in the same sign as optical rotation. [e] $-0.3 < [\alpha]_D < 0.3°$. [f] Not determined.

state charge-transfer complex. The fluorescence lifetimes of 4 and 10–13 were measured under the comparable conditions.

Attempted fluorescence quenching of 4 by 1 was unsuccessful owing to the extremely weak fluorescence intensity and short lifetime of 4.[17] In addition, the

Table IV. Enantiodifferentiating Cis–Trans Photoisomerizations of *cis*- and Racemic *trans*-1,2-Bis(4-methoxyphenyl)cyclopropanes (2*c* and 2*t*) Sensitized by 1,2,4,5-Benzenetetracarboxylate 4 or 5 or Aminoethylnaphthalene (14) in Pentane and Acetonitrile at 25 °C[a]

					isolated product		
compd	sensitizer	solvent	irradn time, h	isomer composn (% trans)[b]	$[\alpha]^{20}_D$ (*c*, $CHCl_3$)	purity (% trans)[c]	optical purity,[d] %
2*c*	4	pentane	53	47	*e* (0.48)	88	0
2*t*	4	pentane	48	46	*e* (0.40)	94	0
	5	CH_3CN	24	95	−3.4 (0.38)	86	−1.0
			48	93	−0.8 (0.41)	88	−0.3
	14	pentane	78	30	+3.6 (0.45)	85	1.1

[a] Irradiation conditions: [2] = 30 mM; [sensitizer] = 5 mM; argon atmosphere. [b] Content of trans isomer after irradiation. [c] Chemical purity of isolated trans isomer, determined by GC analysis. [d] Enantiomeric excess, corrected for the chemical purity, was estimated from the optical rotation of pure (−)-(1*R*,2*R*)-2*t* separated over a Chiralpak column: $[\alpha]^{25}_D$ = −390° (MeOH) (ref 25). [e] $-0.3 < [\alpha]_D < 0.3°$.

Table V. Enantiodifferentiating Cis–Trans Photoisomerizations of *cis*- and Racemic *trans*-2,3-Diphenyloxirane (3*c* and 3*t*) Sensitized by (−)-Tetrabornyl 1,2,4,5-Benzenetetracarboxylate (5) in Pentane and in Acetonitrile at 25 °C[a]

				isolated product		
compd (mM)	solvent	irradn time, h	isomer composn (% trans)[b]	$[\alpha]^{25}_D$ (*c*, C_6H_6)	purity (% trans)[c]	optical purity,[d] %
3*c* (25)	pentane	4	37	3.3 (0.06)	*e*	0.9
		9	75	4.0 (0.05)	*e*	1.1
		18	85	0.9 (0.24)	*e*	0.3
		86	97	3.4 (0.42)	*e*	1.0
3*t* (25)	pentane	9	99	0.6 (0.25)	*e*	0.2
		18	97	0.9 (0.33)	*e*	0.3
(5)	pentane	66	85	3.5 (0.40)	*e*	1.0
(25)	CH_3CN	9	87	0.7 (0.31)	*e*	0.2
(5)	CH_3CN	120	77	0.6 (0.25)	*e*	0.2

[a] Irradiation conditions: [3] = 30 mM; [sensitizer] = 5 mM; argon atmosphere. [b] Content of trans isomer after irradiation. [c] Chemical purity of isolated trans isomer, determined by GC analysis. [d] Enantiomeric excess determined from the optical rotation of pure (−)-3t: $[\alpha]^{ca.15}_D$ = −374° (C_6H_6) (ref 27a). [e] More than 99% pure.

absorption band of 4 overlapped partly with that of 1. However, the fluoresce quenching of the naphthalene-(di)carboxylates gave excellent Stern–Volmer plots, as exemplified in Figure 1, but no new emission ascribable to an exciplex was detected. The Stern–Volmer constant $k_q\tau$ and the quenching rate constant k_q are listed in Table VI.

The trans isomer 1*t*, possessing a lower oxidation potential ($E^{ox}_{1/2}$ = 1.17 V)[18] than 1*c* ($E^{ox}_{1/2}$ = 1.41 V), quenched the fluorescence 2–10 times more efficiently than did 1*c*, although k_q varied widely over a range of 10^7–10^{10} M^{-1} s^{-1}, depending upon the sensitizer and solvent used. In pentane, k_q decreased when the number of alkoxycarbonyl groups increased, whereas that in acetonitrile showed the opposite tendency.

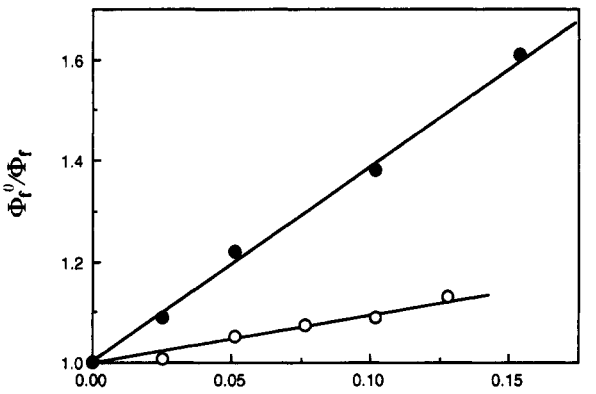

Figure 1. Fluorescence quenching of (−)-menthyl 1-naphthalenecarboxylate (10) with 0–200 mM of *cis*- or *trans*-1,2-diphenylcyclopropanes, 1*c* (○) and 1*t* (●), in aerated pentane solution at 22–23 °C.

Discussion

Isomerization Mechanism. Recent mechanistic investigations[14i,j] have shown that, in polar solvents, the geometrical photoisomerization of 1 sensitized by cyanoaromatics proceeds through a triplet 1,3-biradical ($PhC\dot{H}CH_2\dot{C}HPh$) produced by back-electron transfer within a geminate radical ion pair and that the one-electron-bonded cyclopropane radical cation $1^{\bullet+}$ generated by the initial electron transfer is conformationally stable.[14i] However, the isomerization mechanism and intermediate involved in nonpolar solvents have not been revealed in detail. Singlet photosensitization of 1 is believed to involve an exciplex intermediate with partial charge-transfer character. The exciplex in turn affords a singlet 1,3-biradical as the immediate precursor to isomeric 1,[19] in analogy with the triplet photosensitization where the corresponding triplet 1,3-biradical intervenes.[13a]

The situations differ substantially for 2 and 3. The photoisomerization of 2 sensitized by cyanoaromatics involves a ring-opened radical cation ($ArC\dot{H}$-$CH_2\overset{+}{C}HAr$),[14a,b] and, under certain conditions,[14g] the isomerization proceeds through a quantum chain mechanism, which clearly excludes the biradical mechanism. Furthermore, one-electron-bonded species $2^{\bullet+}$ produced in γ-radiolysis has been known to ring-open upon warming to 100 K or within 1 μs at room temperature.[20] That such

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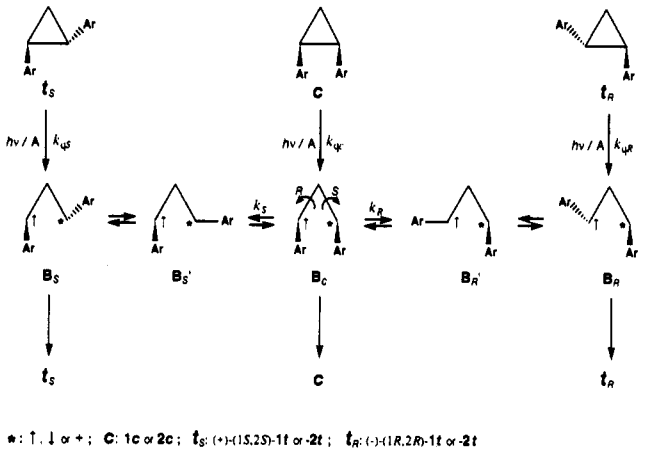
(19) Hixson, S. S.; Boyer, J.; Gallucci, C. *J. Chem. Soc., Chem. Commun.* **1974**, 540.
(20) Toki, S.; Komitsu, S.; Tojo, S.; Takamuku, S.; Ichinose, N.; Mizuno, K.; Otsuji, Y. *Chem. Lett.* **1988**, 433.

Table VI. Fluorescence and Quenching Behavior of Some Sensitizers with *cis*- or *trans*-Diphenylcyclopropane (1*c* or 1*t*) at 22–23 °C[a]

		fluorescence			quenching constant	
compd (mM)	solvent	λ_{max},[b] nm	τ,[c] ns	quencher	$k_q\tau$,[d] M^{-1}	k_q,[e] 10^9 M^{-1} s^{-1}
10 (0.1)	pentane	342	0.8	1*c*	0.89	1.1
				1*t*	4.5	5.6
	CH_3CN	360	1.4	1*c*	7.5	5.4
				1*t*	14.7	10.5
11 (0.1)	pentane	350	8.0 (14.9) [f]	1*c*	<0.2[g]	<0.03
				1*t*	2.5	0.31
	CH_3CN	357	8.0	1*c*	2.4	0.30
				1*t*	7.9	0.99
12 (0.1)	pentane	356	6.6 (9.1) [f]	1*c*	0.46	0.070
				1*t*	4.5	0.68
	CH_3CN	361	6.2	1*c*	4.9	0.79
				1*t*	9.5	1.53
13 (0.01)	pentane	369	9.9 (16.2) [f]	1*c*	0.76	0.077
				1*t*	1.6	0.16
	CH_3CN	376	9.8	1*c*	25.0	2.55
				1*t*	41.0	4.18

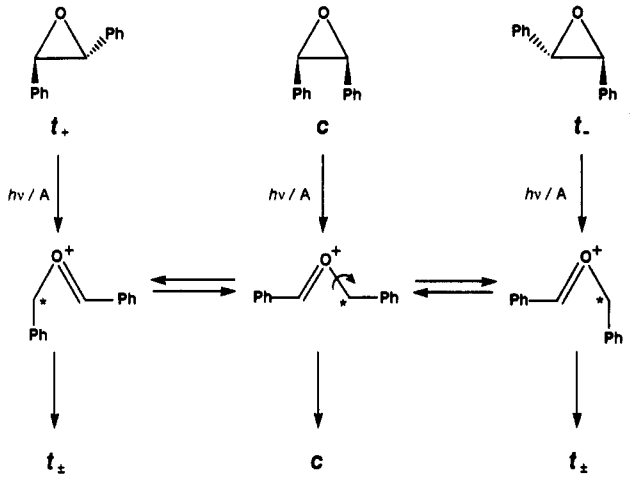
[a] All data taken in aerated solutions, unless noted otherwise. [b] Broad global fluorescence maximum for 4 and apparent 0–0 band maximum for 10–13; the latter band, though broadened more or less in acetonitrile, shows the highest fluorescence intensity for most naphthalene sensitizers except for 13. [c] Fluorescence lifetime under air in the absence of quencher. [d] Stern–Volmer constant. [e] Quenching rate constant, calculated from $k_q\tau$ and τ values. [f] Lifetime under argon atmosphere. [g] No appreciable quenching observed.

Scheme II



*: ↑, ↓ or +; C: 1c or 2c; t_S: (+)-(1S,2S)-1t or -2t; t_R: (-)-(1R,2R)-1t or -2t

Scheme III



*: • or -; C: 3c; t_+: (+)-(2S,3S)-3t; t_-: (-)-(2R,3R)-3t; $t_\pm$: racemic 3t

a spontaneous ring-opening has not been reported for $1^{\bullet+}$ under the comparable conditions[20] is consistent with the results of an earlier CIDNP study.[14i]

In the photosensitized isomerization of 3 with cyanoaromatics, the ring opening of $3^{\bullet+}$ leads to isomeric radical cations of *exo,exo*- and *exo,endo*-carbonyl ylides, which interconvert fairly easily, thus destroying the original stereochemistry.[14f,k] However, the ring closure of *exo,exo*- and *exo,endo*-carbonyl ylides formed upon back-electron transfer is believed to be stereospecific.[14f,k] The intervention of such a stable carbonyl ylide or its radical cation facilitates the ring opening of $3^{\bullet+}$, enforces planar structure, and assures that the ylides will have long lifetimes in the absence of dipolarophiles. These features seem unfavorable for the enantiodifferentiating photoisomerization of 3.

The sensitized photoisomerizations of diarylcyclopropanes 1 and 2 and of diphenyloxirane 3 can be summarized by the general sequences illustrated in Schemes II and III. The irradiation of (+)-(1*S*,2*S*)-1*t* or -2*t* (t_S), (−)-(1*R*,2*R*)-1*t* or -2*t* (t_R), and 1*c* or 2*c* (*c*) in the presence of a chiral sensitizer (A) affords 1,3-ambident species B_S, B_R, or B_c, respectively, as shown in Scheme II. The ambident species is a singlet or triplet biradical or a radical cation (* = ↓, ↑, or +). Successive one-bond rotations of species B_S and B_R, derived from t_S and t_R, yield semiplanar $B_{S'}$ and $B_{R'}$, without loss of the original chirality, and then achiral B_c. In constrast, two types of successive one-bond rotations of B_c afford $B_{S'}$ and $B_{R'}$ and then B_S and B_R, respectively.

In principle, the recognition of sensitizer chirality is possible in the quenching and the subsequent bond rotation. Kinetically, enantiodifferentiation is possible when the quenching of the excited chiral sensitizer (A) by t_S and t_R and/or the one-bond rotation of B_c to $B_{S'}$ and $B_{R'}$ proceed at different rates, i.e., $k_{qS} \neq k_{qR}$ and/or $k_S \neq k_R$. As can be seen from Scheme II, full equilibrium among the species B in the absence of pairing chiral species derived from A leads to a racemic product even if the quenching process is enantiodifferentiating. Thus, the short lifetime of B and/or the pairing of chiral species with B are the conditions for optically active product, and therefore, the rate of back-electron transfer within the radical ion pair is an important factor determining the lifetime of $B^{\bullet+}$.

Enantiodifferentiation Mechanism. Experimentally, the two possible enantiodifferentiation mechanisms described above can be differentiated by performing sensitized photoisomerizations of pure 1*c* and racemic 1*t*. The isomer composition and the product's op obtained in the photoisomerizations of 1*c* and 1*t* sensitized by 4 are plotted as functions of irradiation time in Figure 2.

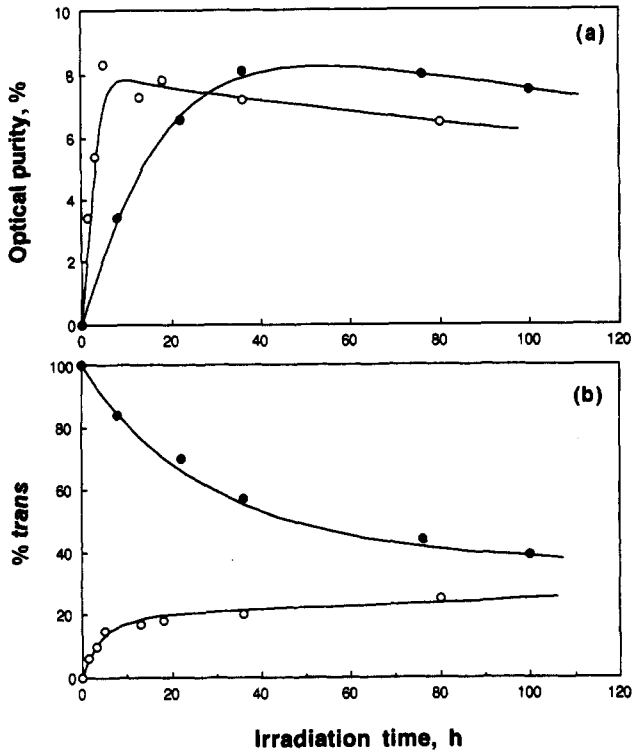


Figure 2. Enantiodifferentiating photoisomerization of *cis*- and racemic *trans*-1,2-diphenylcyclopropanes (30 mM), 1*c* (○), and 1*t* (●), sensitized by (−)-tetramenthyl 1,2,4,5-benzenetetracarboxylate (5 mM) in pentane at 25 °C: (a) optical purity of isolated 1*t* and (b) isomer composition of the reaction mixture as a function of irradiation time.

In the photoisomerization of 1*t*, the product's op increases with the irradiation time and reaches a plateau of ca. 8% at longer irradiation times. The slow increase in op is obviously attributable to the fact that the 1*t* isolated at the early stages of photolysis contains a substantial amount of the original racemic 1*t* along with the photochemically-produced optically active one. In contrast, the photoisomerization starting from 1*c* gives the highest op (8%) after a very short period of irradiation. The rapid development of the product's op indicates that the enantiodifferentiation occurs not in the rotation of **B** but in the quenching of **A** by (+)- and (−)-1*t*. If the rotation process is enantiodifferentiating, the op obtained should remain constant from the initial stage of photolysis. Hence, the rapid development of the product's op further means that species B_S, B_c, and B_R are not fully equilibrated with each other, since the chirality induced upon quenching is maintained in final product 1*t*. The use of polar solvents leads to more or less lower op's in most cases (Tables I–III), owing to the contribution of long-lived radical ion or triplet biradical structure to species **B**.

Curiously, the highest op obtained depends on the initial isomer composition, as shown in Table I. According to the above enantiodifferentiation mechanism, the product's op should reach a common value. Actually, the product's op is a consequence of a critical balance between the generation of optically active 1*t* and its racemization sensitized by achiral byproduct(s). Hence, an initial trans content of 62–78% and an irradiation time of 12–13 h give the optimal op of 9.8–10.4%.

Inversion of Product Chirality by Solvent Polarity. As shown in Table II, (−)-bornyl ester **5** as a sensitizer gives (+)-1*t* of 3.8 and 1.2% op in pentane and ether, respectively. Unexpectedly, the same sensitizer produces the antipode (−)-1*t* of 2.4% op in acetonitrile. The op's obtained at 0 °C exhibit similar chirality inversion: 4.7% op in pentane and −4.1% op in acetonitrile.

Since the presence of a contact ion pair seems impossible in polar solvents, the good op obtained in acetonitrile is attributable to the enantiodifferentiating quenching and the short lifetime of $B^{\bullet+}$, which is probably due to the fast back-electron transfer from $A^{\bullet-}$. It is inferred therefore that the chirality inversion behavior originates from the structural changes that occur in the excited sensitizer. These structural changes are large enough to invert the quenching efficiencies for (+)- and (−)-1*t* in polar and nonpolar solvents, although the detailed structural changes are not known at present.

It is interesting to note that this solvent polarity-driven switching of product chirality is similar to the enantioselectivity inversion caused by changes in solvent hydrophobicity reported recently in the enzyme-catalyzed transesterification of *N*-acylphenylalanine 2-chloroethyl ester by *Aspergillus oryzae* protease in organic solvents.[21] In this transesterification, the critical balance between the hydrophobicities of the solvent and the active center of *A. oryzae* is thought to play a key role.[21]

Chiral Recognition via Triplex. As can be seen from Table II, the product's op's obtained in benzene (runs 7–10) are unexpectedly low, but *tert*-butylbenzene as a solvent gives better op's (runs 11–13). The low op in benzene can be rationalized by the possible intervention of an **A–D–D′** triplex produced in successive stacking of solvent benzene (**D**), 1 (**D′**), and excited sensitizer (**A**). In this context, the higher op's in *tert*-butylbenzene imply that the *tert*-butyl group in **D** is conformationally fixed in the **A–D–D′** triplex and, therefore, the substrate (**D′**) can indirectly recognize the stereochemistry of **A**.

A new strategy for the enantiodifferentiating photosensitization has evolved from the above discussion. The intramolecular donor–acceptor sensitizers **6** and **8** were synthesized as exciplex-forming chiral sensitizers, in which the 8-phenyl group can interact in a face-to-face fashion with the core of benzenetetracarboxylate. In contrast to the photosensitizations with the menthyl esters, the photosensitizations with **6** afford fairly high op's of 8–9% in both pentane and acetonitrile, although benzene as a solvent considerably reduces the op to 2–3% (runs 1–10 in Table III). The high op's with **6** cannot be attributed to the increased steric hindrance of the 8-phenyl group, since the corresponding cyclohexylmenthyl ester (**7**) gives lower op's (around 3%). Diphenyl analog **8** also gives fairly high op's (7–8%) even in acetonitrile (runs 14–16). The facile intramolecular (partial) electron transfer in **6** and **8** leads to the formation of a polarized intramolecular exciplex in nonpolar solvents or a contact radical ion pair in polar solvents, but the local charge-transfer interaction between self-polarizing/ionizing sensitizer (**A–D**) and substrate (**D′**) is rather reduced by charge delocalization. The reduction of the charge-transfer interaction affords short-lived singlet radical(oid) **B** and therefore higher product's op.

Experimental Section

General. Melting points were measured with a YANACO MP-21 apparatus and are uncorrected. Optical rotations were measured in a thermostated cell with a Perkin-Elmer 243B

(21) Tawaki, S.; Klibanov, A. M. *J. Am. Chem. Soc.* **1992**, *114*, 1882.

polarimeter. Infrared spectra were obtained on a JASCO IR-810 instrument. Mass spectra were taken on a JEOL AX-500 instrument by fast-atom bombardment (FAB) ionization with or without KI added to the sample matrix. ^{1}H NMR spectra were recorded in chloroform-*d* at 400 MHz on a JEOL GX-400 spectrometer. Electronic absorption and emission spectra were recorded on JASCO Ubest-50 and FP-770 spectrometers, respectively. Fluorescence lifetimes were measured with a Horiba NAES-550 instrument.

Materials. Saturated hydrocarbon solvents were purified by treatment with concentrated sulfuric acid and subsequent fractional distillation. Benzene and ether were distilled from sodium. Acetonitrile was fractionally distilled from diphosphorus pentaoxide.

1,2-Diarylcyclopropanes 1 and 2 were synthesized in 93–95% yields in thermal decompositions of the corresponding 3,5-diaryl-2-pyrazolines prepared from precursor chalcones and hydrazine hydrate.[22] 1,2-Diphenylcyclopropane (**1**) and 1,2-bis-(4-methoxyphenyl)cyclopropane (**2**) thus obtained were 1:2 cis-trans mixtures and were fractionally distilled.

Isomerically pure **1c** was obtained in 12% yield (from chalcone) by recrystallization from pentane of the initial fraction (80% cis). Pure **1t** was obtained from the last fraction in 4% yield. **1c**: IR (neat) ν 3050, 3010, 1600, 1490, 1450, 1440, 770, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.37 (m, 1 H), 1.47 (m, 1 H), 2.49 (m, 2 H), 6.91–7.11 (m, 10 H); UV (pentane) λ_{max} (ϵ, M^{-1} cm^{-1}) 274 (30), 266 (49), 260 nm (51). **1t**: IR (neat) ν 3050, 3010, 1600, 1500, 1450, 730, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (m, 2 H), 2.17 (m, 2 H), 7.11–7.31 (m, 10 H); UV (pentane) λ_{max} (ϵ) 276 (95), 268 (139), 229 nm (1740).

Isomerically pure *cis*- and *trans*-1,2-bis(4-methoxyphenyl)-cyclopropanes (**2c** and **2t**) were isolated in 10% yield each (from chalcone) by fractional recrystallization from methanol.[23] **2c**: IR (neat) ν 3030, 3000, 2950, 2930, 2900, 2830, 1615, 1520, 1465, 1300, 1250, 1180, 1035, 830, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (q, 1 H), 1.40 (d-t, 1 H), 2.36 (d-d, J = 6.6, 8.3 Hz, 2 H), 6.64 (d, J = 8.1 Hz, 4 H), 6.85 (d, J = 8.1 Hz, 4 H). **2t**: IR (KBr) ν 3030, 3000, 2980, 2940, 2840, 1615, 1520, 1440, 1285, 1250, 1180, 1030, 835, 820, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33 (m, 2 H), 2.05 (m, 2 H), 3.79 (s, 6 H), 6.84 (d, 2 H), 7.07 (d, 2 H).

***trans*-1,2-Diphenyloxirane (3t)** was purchased from Aldrich and used as received. ***cis*-1,2-Diphenyloxirane (3c)** was prepared in 94% yield by the epoxidation of *cis*-stilbene (Nakarai) with 3-chloroperbenzoic acid in dichloromethane and was purified by column chromatography over silica gel with an ethyl acetate/hexane (3/97) eluent. **3c**: IR (KBr) ν 3040, 2960, 1610, 1500, 1460, 1410, 1370, 1180, 1080, 1030, 890, 750, 730, 700, 690, 530, 500 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.37 (s, 2 H), 7.17 (m, 10 H); UV (pentane) λ_{max} (ϵ) 272 (190), 265 (860), 260 (510), 253 nm (530).

(–)-Tetramenthyl and (–)-tetrabornyl 1,2,4,5-benzenetetracarboxylates (4 and 5), (–)-hexamenthylbenzenehexacarboxylate (9), (–)-menthyl 1-naphthalenecarboxylate (10), (–)-menthyl 2-naphthalenecarboxylate (11), (–)-dimenthyl 2,3-naphthalenedicarboxylate (12), and (–)-dimenthyl 2,6-naphthalenedicarboxylate (13) were prepared from the corresponding acid chlorides and optically pure (–)-menthol or (–)-borneol and were purified by repeated recrystallization from ethanol. The spectral data for **4**, **5**, and **9** were reported previously.[10] **10**: $[\alpha]^{20}_D$ –80.3° (*c* 1.06, $CHCl_3$) (lit.[24] –84.5° (*c* 1.59, EtOH)); IR (neat) ν 2950, 2930, 2870, 1710, 1600, 1510, 1460, 1370, 1280, 1240, 1200, 1140, 1010, 960, 780, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (d, J = 7.1 Hz, 3 H), 0.88–1.00 (m, 1 H), 0.94 (d, J = 7.1 Hz, 3 H), 0.97 (d, J = 6.6 Hz, 3 H), 1.12–1.24 (m, 2 H), 1.61 (m, 2 H), 1.76 (m, 2 H), 2.05 (m, 1 H), 2.24 (m, 1 H), 5.07 (d-t, J = 4.4, 10.9 Hz, 1 H), 7.48–7.56 (m, 2 H), 7.61 (m, 1 H), 7.88 (d, 1 H), 8.01 (d, 1 H), 8.15 (d-d, 1 H), 8.91 (d, 1 H); UV (pentane) λ_{max} (ϵ) 297 (15 400), 217 nm (90 800). **11**: mp 73–74 °C; $[\alpha]^{20}_D$ –71.2° (*c* 0.46, $CHCl_3$) (lit.[25] $[\alpha]^{15}_D$ –69.9° (*c* 5, $CHCl_3$)); IR (KBr) ν 2950, 2930, 2860, 1710, 1460, 1350, 1290, 1230, 1200, 1130, 1090, 1040, 960, 830, 780, 760, 470 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (d, J = 7.1 Hz, 3 H), 0.88–1.00 (m, 1 H), 0.94 (d, J = 7.1 Hz, 3 H), 0.95 (d, J = 6.4 Hz, 3 H), 1.16 (m, 2 H), 1.53–1.67 (m, 2 H), 1.76 (m, 2 H), 2.02 (m, 1 H), 2.18 (m, 1 H), 5.01 (d-t, J = 4.4, 10.9 Hz, 1 H), 7.56 (m, 2 H), 7.88 (d, 2 H), 7.97 (d, 1 H), 8.07 (d-d, 1 H), 8.60 (s, 1 H); UV (pentane) λ_{max} (ϵ) 332 (1440), 290 (4530), 279 (6800), 271 (5560), 237 (75 600), 231 nm (65 600). **12**: mp 94.0–94.5°; $[\alpha]^{20}_D$ –84.1° (*c* 0.88, $CHCl_3$); MS (FAB+KI) *m/z* 531 (M^+ + 39); IR (KBr) ν 2950, 2930, 2870, 1720, 1470, 1370, 1290, 1210, 1200, 1120, 1030, 960, 760, 480 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.0 (m, 2 H), 0.85 (d, J = 7.1 Hz, 6 H), 0.92 (d, J = 6.8 Hz, 6 H), 0.96 (d, J = 6.3 Hz, 6 H), 1.08–1.21 (m, 4 H), 1.48–1.64 (m, 4 H), 1.73 (m, 4 H), 2.03 (m, 2 H), 2.26 (m, 2 H), 5.00 (d-t, J = 4.4, 11.0 Hz, 2 H), 7.61 (m, 2 H), 7.93 (m, 2 H), 8.19 (s, 1 H); UV (pentane) λ_{max} (ϵ) 334 (1240), 320 (958), 291 (2890), 280 (5390), 270 (5760), 236 nm (62 000). Anal. Calcd for $C_{32}H_{44}O_4$: C, 78.01; H, 9.00. Found: C, 77.73; H, 9.15. **13**: mp 131–133 °C; $[\alpha]^{20}_D$ –85.8° (*c* 0.43, $CHCl_3$); MS (FAB) *m/z* 492.3224 (calcd for $C_{32}H_{44}O_4$ 492.3239); IR (KBr) ν 2930, 2850, 1710, 1450, 1370, 1330, 1270, 1170, 1120, 1080, 960, 910, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (d, J = 6.8 Hz, 6 H), 0.88–1.01 (m, 2 H), 0.95 (d, J = 6.4 Hz, 6 H), 0.95 (d, J = 7.1 Hz, 6 H), 1.17 (m, 4 H), 1.53–1.70 (m, 4 H), 1.77 (m, 4 H), 2.01 (m, 2 H), 2.18 (m, 2 H), 5.02 (d-t, J = 4.4, 10.9 Hz, 2 H), 8.00 (d, 2 H), 8.12 (m, 2 H), 8.62 (m, 2 H); UV (pentane) λ_{max} (ϵ) 348 (3120), 332 (2390), 294 (14 300), 283 (15 100), 272 (9830), 243 nm (114 000). Anal. Calcd for $C_{32}H_{44}O_4$: C, 78.01; H, 9.00. Found: C, 78.12; H, 9.07.

(–)-Tetrakis(8-phenylmenthyl) and (–)-tetrakis(8-cyclohexylmenthyl) 1,2,4,5-benzenetetracarboxylates (6 and 7) were similarly prepared from optically pure (–)-8-phenylmenthol and (–)-8-cyclohexylmenthol, which were synthesized by the method reported by Corey et al.[16] and subsequent hydrogenation over 5% Rh/C at an H_2 pressure of 5 atm in 1% acetic acid–ethanol at 25 °C.[10c]

(–)-Tetrakis[(1*R*,2*S*,5*R*)-2-(diphenylmethyl)-5-methylcyclohexyl] 1,2,4,5-benzenetetracarboxylate (8) was similarly prepared from optically pure (–)-2-(diphenylmethyl)-5-methylcyclohexanol.[10c]

(–)-(*S*)-1-(1-(*N*-Acetylamino)ethyl)naphthalene (14) was prepared by acetylation of the corresponding optically pure amine with acetic anhydride in triethylamine: mp 158–159 °C; $[\alpha]^{25}_D$ –120° (*c* 2.5, $CHCl_3$); IR (KBr) ν 3290, 3050, 2960, 1630, 1540, 1370, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68 (d, J = 6.6 Hz, 3 H), 1.98 (s, 3 H), 5.64 (m, 1 H), 5.94 (m, 1 H), 7.43–8.13 (m, 7 H); UV (pentane) λ_{max} (ϵ) 313 (3820), 291 (40 000), 281 (56 400), 271 nm (49 900).

Photolyses. In preliminary or preparative-scale irradiations, a solution (3 or 300 mL) of **1**, **2**, or **3** (5–30 mM) containing the aromatic ester or amide (2.5–5 mM) as a chiral photosensitizer and cyclododecane (3 mM) as an internal standard was placed in a Pyrex tube (1-cm i.d.) or annular vessel (330 mL), purged with argon gas at –40 °C, and then irradiated in a thermostated water bath, using a 300-W high-pressure mercury arc fitted with a Pyrex sleeve (Eikosha). The progress of photoisomerization was monitored by periodic GC analyses of the photolysate over a 3-m silicone OV-101 column at 160 and 200 °C for the photolysates of **1** and **2**, respectively, and a 20-cm Apiezon L column at temperatures of 50–100 °C (3 °C/min) for **3**.

Product Isolation. The irradiated solutions of **1** were first subjected to column chromatography over silica gel with an ethyl acetate/hexane (1/99) eluent and then to the preparative GC over an OV-101 column (6 mm × 3 m) at 200 °C to give **1t** of 73–98% chemical purity. No traces of fragments derived from the decomposition of the chiral sensitizer were detected on GC or NMR in the isolated product, and the only impurity detected was achiral **1c**. (The presence of achiral **1c** was corrected for in the op's reported). The specific rotation of isolated **1t** was measured in chloroform and compared with the value reported for the optically pure (+)-(1*S*,2*S*)-trans isomer: $[\alpha]^{20}_D$ +418° (*c* 0.96, $CHCl_3$).[11]

The photolyzed solution of **2** was also subjected to column chromatography followed by preparative GC over OV-101 at 240 °C. The specific rotation of the isolated **2t** was measured in

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chloroform and compared with that for the optically pure (−)-(2*R*,3*R*)-**2***t* resolved by Mizuno et al.:[26] $[\alpha]^{25}_{D}$ −390° (*c* 0.25, MeOH).

Evaporation of the photolyzed solutions of **3** to dryness afforded a white solid, and preparative TLC of the solid over silica gel with an ether/hexane (5/95) eluent gave chemically pure **3***t*. Specific rotation of the isolated **3***t* was measured in benzene and compared with the value reported for the optically pure (−)-**3***t*: $[\alpha]^{ca.15}_{D}$ −374° (*c* 0.50, C_6H_6).[27]

Chromatographic optical resolution of **3** was performed by HPLC employing Daicel Chiralpak OA, OB, OC, and OK (4.6 × 250 mm) and 2-propanol–hexane (5/95) eluent. All of the Chiralpak columns used gave satisfactory separation of (+)- and (−)-**3***t* and -**3***c*; the combination of OC and OB columns in series gave the best result. However, the low op (ca. 1%) obtained in the present study did not allow us to determine op from the integrated area of each enantiomer with satisfactory accuracy, although the enantiomeric excess determined chromatographically roughly agreed with the op calculated from the optical rotation of isolated **3***t*.

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(26) Reference 14l. Optically pure (+)- and (−)-**2***t* was isolated from racemic **2***t* (mp 70.5–71 °C) by means of the preparative HPLC employing a Chiralpak OB-L column with methanol eluent. (+)-**2***t* (98% pure): mp 92.5–93.5 °C; $[\alpha]^{25}_{D}$ +374 ± 3° (*c* 0.25, MeOH). (−)-**2***t* (99% pure): mp 92–93 °C; $[\alpha]^{25}_{D}$ +389 ● 2° (*c* 0.25, MeOH).

(27) (a) Read, J.; Campbell, I. G. M. *J. Chem. Soc.* **1930**, 2377. $[\alpha]^{ca.15}_{D}$ −374° (*c* 0.4985, C_6H_6) for (−)-**3***t*. (b) Berti, G.; Bottari, F.; Ferrarini, P. L.; Macchia, B. *J. Org. Chem.* **1965**, *30*, 4091. $[\alpha]^{20}_{D}$ +357° (*c* 0.590, C_6H_6) for (+)-**3***t* of ca. 95% optical purity.