

Enantiodifferentiating Anti-Markovnikov Photoaddition of Alcohols to 1,1-Diphenylalkenes Sensitized by Chiral Naphthalenecarboxylates

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Received March 22, 1999. Revised Manuscript Received June 28, 1999

Abstract: The photosensitized enantiodifferentiating polar additions of alcohols (R^2OH ; $R^2 = Me, Et, n\text{-}Pr, i\text{-}Pr, t\text{-}Bu$) to 1,1-diphenylalkenes **1–3** ($Ph_2C=CHR^1$; $R^1 = Me, Et, i\text{-}Pr$) were performed over a range of temperatures in the presence of chiral 1-, 2-, 1,4-, 1,8-, 2,3-, and 2,6-naphthalene(di)carboxylate (**7–12**) photosensitizers, giving the chiral anti-Markovnikov adduct (**4a**) with optimized enantiomeric excesses (ee's) of up to 33%. An unusual switching of product chirality was induced simply by changing the irradiation temperature, leading to antipodal products at different temperatures, often affording higher ee's at higher temperatures. The differential activation parameters for the enantiodifferentiation process, which were determined from an Eyring treatment of the temperature-dependent ee values, clearly demonstrate that the unusual temperature-switching behavior of the product chirality is entropic in origin. Factors controlling the product's ee were extensively surveyed, and the steric and/or electronic structures of sensitizer, substrate, and alcohol, the solvent polarity, the alcohol concentration, and the irradiation temperature were all shown to play a crucial role. The detailed reaction mechanism and excited states involved and the origin of enantiodifferentiation, as well as the reaction kinetics and energetics, were fully elucidated for the first time from the fluorescence quenching and lifetime measurement of both sensitizer and exciplex in the presence/absence of added alcohol. We have also developed a new strategy to overcome the normally accepted tradeoff between the chemical and optical yields in this typical radical ion-mediated photoaddition.

Introduction

Recently, much interest has been focused on asymmetric photochemistry.¹ In particular, photosensitized enantiodifferentiating reactions have fascinated (photo)chemists as promising candidates for photochemical *catalytic* asymmetric synthesis. Since the first report on the asymmetric photosensitization of *trans*-1,2-diphenylcyclopropane by Hammond and Cole,² a considerable amount of effort has been devoted to the study of enantiodifferentiating photosensitized isomerizations, but in most cases the optical yields obtained in asymmetric photosensitized reactions rarely exceed 10%.^{2–13} However, we have demon-

strated that the enantiodifferentiating geometrical photoisomerization of (*Z*)-cyclooctene, sensitized by chiral benzenepoly-carboxylates, gives the optically active (*E*)-isomer in exceptionally high ee's (64% at $-89\text{ }^\circ\text{C}$), and interestingly, the product chirality can be inverted by temperature and pressure changes.^{5b,h,k}

In contrast to such relatively widely explored unimolecular enantiodifferentiating photoisomerizations, only a few attempts have been hitherto reported concerning bimolecular enantiodifferentiating reactions. The enantiodifferentiating [2 + 2] photocyclodimerizations of aryl vinyl ether and 4-methoxystyrene have been attempted in acetonitrile in the presence of optically active naphthalenecarboxylate sensitizers, giving the corresponding cyclodimers in good chemical yields but ex-

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tremely low optical yields (<1%).¹⁴ More impressively, Kim and Schuster reported that the [4 + 2] photocycloaddition of trans- β -methylstyrene to 1,3-cyclohexadiene, sensitized by (-)-1,1'-bis(2,4-dicyanonaphthalene) in toluene at -65 °C, gave the cycloadduct in 15% ee.¹⁵

We have shown that the enantiodifferentiating polar addition of methanol to 1,1-diphenylpropene **1** ($R^1 = \text{Me}$) sensitized by various chiral alkyl naphthalene(di)carboxylates gave the adduct 1,1-diphenyl-2-methoxypropane (**4a**, $R^1 = \text{Me}$) in low to moderate optical yields. In that study, the product's optical purity (op) appeared to be a function of position and bulk of the sensitizer's chiral ester moiety.¹⁶ Thus, the product's op was enhanced to 27% by increasing the bulk of the ester group of the sterically congested 1,8-naphthalenedicarboxylate (**10b**), while the increased steric hindrance inevitably led to a drastically diminished chemical yield of <2% and necessitated much longer irradiation periods of up to 200 h. No efficient enantiodifferentiating bimolecular reactions that employ chiral photosensitizers have been reported to date, and the elucidation of the enantiodifferentiation mechanism and the attainment of a good optical yield are still challenging themes in asymmetric photochemistry.

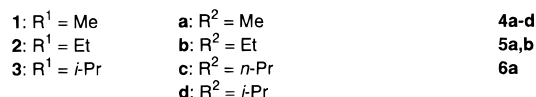
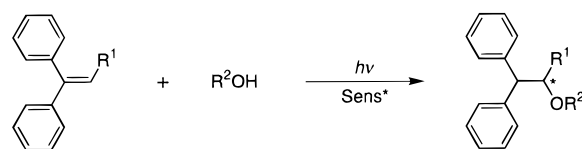
We wish now to report the results of our study that have enabled us to elucidate the detailed mechanism and intermediates involved in this enantiodifferentiating polar photoaddition and also to enhance chemical and optical yields. In this study, we employ series of 1,1-diphenyl-1-alkenes (**1–3**; $R^1 = \text{Me, Et, } i\text{-Pr}$) as substrates and alcohols ($R^2\text{OH}$; $R^2 = \text{Me, Et, } n\text{-Pr, } i\text{-Pr, } t\text{-Bu}$) as nucleophilic reagents, as well as a variety of novel chiral sensitizers in order to overcome the normally encountered tradeoff between chemical and optical yields. On the basis of the unusual effect of temperature upon the optical yields observed in this study, we have demonstrated that the entropy term plays a definitive role in the crucial step that determines the product chirality and optical yield, not only in the unimolecular photoisomerizations,^{5d,e,g} but also in the bimolecular photoaddition reactions. Both of these reactions are governed by weak bi- and termolecular interactions in the exciplex intermediate involving sensitizer, substrate, and/or reagent.

Results and Discussion

Photosensitized Polar Addition of Alcohols to 1,1-Diphenyl-1-alkenes. In the original study by Mizuno et al.,¹⁷ the photochemical polar addition of methanol to 1,1-diphenylpropene (**1**) was effected by 9,10-dicyanoanthracene, which acted as an achiral sensitizer in polar solvents. In the present study, we have employed a variety of optically active (di)alkyl naphthalene(di)carboxylates (**7–12**) as chiral sensitizers for the enantiodifferentiating addition of various alcohols (**a–d**) to a series of 1,1-diphenyl-1-alkenes (**1–3**), as illustrated in Scheme 1.

Although arene(poly)carboxylates have not frequently been used as sensitizers in photoinduced electron-transfer reactions of aromatic alkenes,^{17,18} they are attractive, and probably the

Scheme 1



only, chiral sensitizers for the enantiodifferentiating photoaddition that permit us to examine a wide variety of chiral auxiliaries introduced in the vicinity of chromophore. Fortunately, most of the chiral naphthalene(di)carboxylates employed afforded the alcohol adducts (**4–6**) in good chemical yields of up to 75%, depending on the sensitizer and solvent used, as described below.

One of the most important factors to consider when performing optically and chemically efficient photoenantiodifferentiation in a reaction that involves electron-transfer process and radical ionic species is the choice of solvent. In general, the use of a polar solvent is thought to be an essential condition for high chemical yields, but this often ruins the optical yield of the photoproduct as a result of the intervention of free or solvent-separated radical ion pair between the chiral sensitizer and substrate. Thus, in most cases there is a severe tradeoff relationship between the chemical and optical yield.^{5i,14,15} We therefore began working on the photoaddition of methanol to 1,1-diphenylpropene (**1**) sensitized by electron-accepting aromatics, a process which is known to proceed even in nonpolar solvents such as benzene¹⁷ and pentane.¹⁶ Furthermore, we have developed a new strategy to overcome this apparently inevitable problem concerning the balance between the chemical and optical yield.

Naphthalenecarboxylate Sensitizers. In search of the most effective arenecarboxylate sensitizers for the anti-Markovnikov addition of methanol to **1**, we examined 1-, 2-, 1,4-, 1,8-, 2,3-, and 2,6-naphthalene(di)carboxylates **7–12** with several chiral ester moieties, as illustrated in Chart 1. By using optically active naphthalenecarboxylates (3 mM), we performed the photosensitized addition of methanol to **1** (20 mM) in pentane, methylcyclohexane, or toluene at temperatures ranging from -68 to +60 °C in the presence of 0.5 M methanol, giving the methanol adduct **4a**. The chemical yield and the optical purity (op), calculated from the optical rotation of isolated product) and/or enantiomeric excess (ee, determined by chiral stationary phase gas chromatography) are summarized in Tables 1 and 2, where the sign of the op/ee value represents the direction of product's optical rotation; that is, a negative value indicates the formation of (*S*)-(-)-**4a** as the major product.

In all experiments, the product yield increased gradually over the period of irradiation, ultimately reaching a plateau after prolonged irradiation, which was dependent on the sensitizer and solvent used. In contrast, the product's op/ee remained constant within the experimental error ($\pm 0.5\%$ ee) throughout the irradiation period, as exemplified by runs 49–54 in Table 2 for the methanol addition of **1** sensitized by **9h** in toluene at 25 °C. These results clearly indicate that the photosensitized addition of methanol to **1** is not reversible and that the product, **4a**, is not subjected to any further reactions under the photochemical conditions employed. Since appreciable yields of no other products could be detected by GC analysis, the low

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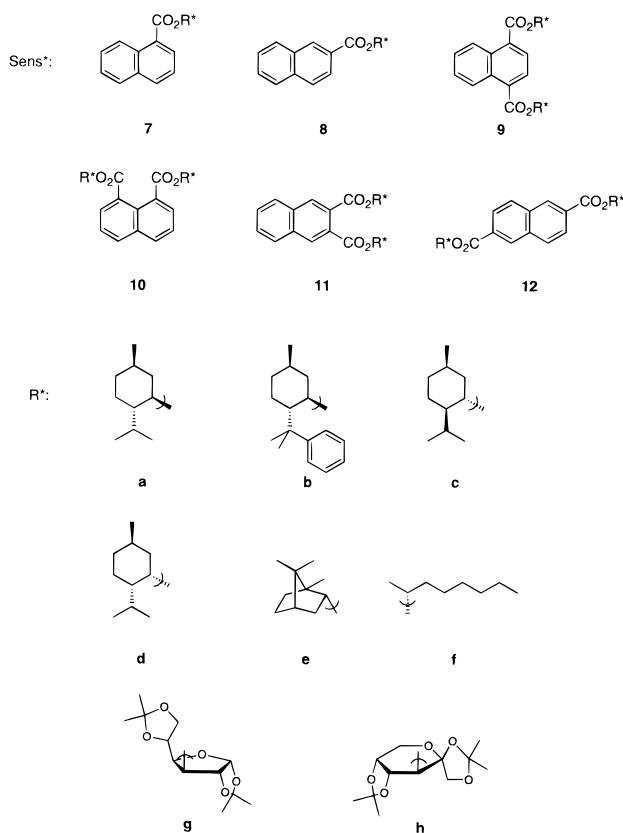
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Chart 1



chemical yields of the methanol adduct **4a**, formed upon sensitization with **7**, **8**, **10**, and **11**, may be attributed to the formation of cross-adducts with the sensitizers,¹⁹ or unidentified oligomeric or polymeric products.

The chemical and optical yields are critical functions of both position and stereochemistry of the alkoxy-carbonyl substituent(s) that are introduced to the naphthalene. The tradeoff relationship between them appears to be unavoidable in this photosensitized enantiodifferentiating polar addition,¹⁶ in which the development of positive charge on the substrate enhances the product yield¹⁷ on one hand, but simultaneously accelerates the spatial separation of the chiral radical ion pair, thus reducing the product's ee. Nevertheless, we prioritized on the chemical, rather than the optical, yield since a high ee value obtained at the expense of good chemical yield is not attractive, even in such an asymmetric photoreaction. Thus, photosensitizations with naphthalene(dicarboxylates) possessing (–)-menthyl and highly bulky (–)-8-phenylmenthyl chiral auxiliaries were conducted at temperatures between –68 and +60 °C for a fixed irradiation period in methylcyclohexane and toluene solutions containing 0.5 M methanol. As shown in Table 1, 1- and 2-naphthalenedicarboxylates **7a,b** and **8a,b** (runs 1–16 and 17–32, respectively) gave only low conversions (4–30%) and very low yields (1–6%), but the ee's obtained (3–9%) were not so poor for this type of bimolecular enantiodifferentiating photosensitization. The use of an aromatic solvent or carrying out the irradiation at low temperature did not improve either the chemical or optical yield. Although 1,8- and 2,3-naphthalenedicarboxylates **10a,b** and **11a,b** (runs 33–49 and 50–66) gave similarly low conversions (3–30%) and yields (1–5%) in both

solvents at all reaction temperatures studied, the product's ee was considerably improved to 13–17% upon sensitization by **10a,b** in methylcyclohexane. Again adjusting the temperature did not appear to affect the product's ee. However, 2,6-naphthalenedicarboxylate sensitizers **12a,b** gave higher conversions (22–66%) and yields (5–31%), as shown in Table 1 (runs 67–82). The obtained ee's were not very high (9–12% at the best) but were found to suffer a dramatic temperature effect, particularly upon sensitization with **12b** in methylcyclohexane. In this case, the absolute configuration of **4a** was inverted from *R* (+1.8% ee) at +60 °C to *S* (–12.0% ee) at –68 °C (runs 75–78). As can be seen from runs 1–22 (Table 2), photosensitizations with 1,4-naphthalenedicarboxylates **9a,b** afforded much higher conversions (50–98%) and yields (15–60%) under comparable conditions. To establish the origin of this difference in reactivity, we calculated the Rehm–Weller free-energy change (ΔG_{et})²⁰ from the oxidation potential of the substrate **1** ($E_{ox} = 1.306$ V) and the reduction potentials (E_{red}) and absorption 0–0 bands (λ_{0-0}) of sensitizers **7a–12a**, all of which are listed in Table 3, along with the quantum yield. Although the photosensitizations were carried out in nonpolar solvents and, therefore, the quantum yields were generally low in the present cases, the observed differences in photoreactivity are well accounted for in terms of the calculated ΔG_{et} values. Apart from 1,8-naphthalenedicarboxylate **10a**,²¹ 1,4-naphthalenedicarboxylate **9a** gave the most negative ΔG_{et} value among the sensitizers examined as well as affording the best chemical and quantum yields. We therefore focused on a series of sensitizers based on 1,4-naphthalenedicarboxylates with various chiral ester auxiliaries and their ability to effect the photosensitized enantiodifferentiating polar addition to **1**.

Effect of the Chiral Auxiliary. To systematically investigate the stereochemical effects of the chiral ester auxiliary upon optical yield, we examined a series of optically active dialkyl 1,4-naphthalenedicarboxylates **9a–f** with cyclic menthyl and its derivatives/isomers (**a–d**), bicyclic bornyl (**e**), and acyclic 1-methylheptyl (**f**) groups. As can be seen from Table 2, the epimeric menthyl esters **9a,c,d** behave entirely differently to one another as chiral sensitizers. The (–)-menthyl ester **9a** afforded (*S*)-(–)-**4a** in 2.3% ee in pentane and 2.5% ee in methylcyclohexane at 25 °C, but the ee was increased to 11.7% at –68 °C in pentane and 12.2% at –40 °C in methylcyclohexane. In contrast, the neo- and isomenthyl esters **9c** and **9d** gave much smaller ee's (<5%) even at low temperatures, but interestingly, the product chirality was switched within the experimental temperature range. Thus, (*R*)-(+)-**4a** was produced preferentially in 1–2% ee in pentane at 25 °C, while antipodal (*S*)-(–)-**4a** was favored in 4–5% ee at –68 °C in the same solvent. Similar temperature switching of product chirality has been reported previously for the enantiodifferentiating photoisomerization of cyclooctene sensitized by chiral benzenepoly-carboxylates.^{5e,g} Such behavior is also observed to occur upon photosensitization with the sensitizers employed in this study, and this phenomenon is reasonably rationalized as a function of the entropy term, as described below.

The above observations indicate that the absolute configuration of the asymmetric carbon (C-1) adjacent to the ester oxygen plays the decisive role in determining the product's stereochemistry and optical yield, although the 8-phenyl group introduced in **9b** does not appreciably affect the asymmetric

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(21) The severe steric hindrance of **10a** caused by the two menthoxy-carbonyl groups at the adjacent peri positions would prevent the intimate electron-transfer interaction between the substrate and the sensitizer, resulting in poor chemical yield.

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Table 1. Enantiodifferentiating Photoaddition of Methanol to 1,1-Diphenylpropene **1** Sensitized by Chiral Naphthalene(di)carboxylates **7**, **8**, and **10–12**^a

entry	sensitizer	solvent	temperature (°C)	irradiation time (h)	conversion ^b (%)	yield ^c (%)	ee ^d (%)
1	7a	methyl-cyclohexane	60	24	11	2	-3.7
2			25	24	10	1	-2.6
3			-40	48	<3	<1	-2.3
4	toluene		-68	48	7	2	-1.5
5			60	24	16	2	-4.2
6			25	24	9	2	-4.0
7			-40	48	17	5	-4.6
8			-68	48	12	<1	-4.1
9			60	24	16	4	-8.6
10	7b	methyl-cyclohexane	25	24	22	4	-6.3
11			-40	48	18	3	-7.2
12			-68	48	10	2	-6.9
13	toluene		60	24	15	1	-2.2
14			25	24	30	6	-4.8
15			-40	48	29	6	-5.9
16			-68	48	14	3	-5.4
17			60	24	8	2	-3.4
18			25	24	<3	1	-5.2
19	8a	methyl-cyclohexane	-40	48	13	3	-4.5
20			-68	48	<3	<1	-4.3
21			60	24	5	<1	-0.1
22	toluene		25	24	<3	<1	-5.3
23			-40	48	9	1	-2.2
24			-68	48	5	<1	-2.0
25			60	24	4	2	-8.2
26			25	24	4	2	-6.7
27			-40	48	5	3	-6.0
28	8b	methyl-cyclohexane	-68	48	4	2	-9.5
29			60	24	<3	2	-5.6
30			25	24	8	2	-7.0
31	toluene		-40	48	12	2	-6.4
32			-68	48	4	1	-7.0
33			60	24	10	3	-12.1
34			40	24	9	3	-12.5
35			25	24	<3	2	-9.4
36			0	48	16	5	-17.2
37	10a	methyl-cyclohexane	-40	48	11	2	-14.2
38			60	24	<3	1	-6.3
39			25	24	<3	<1	-7.3
40	toluene		-40	48	5	<1	-8.4
41			-68	48	4	<1	-5.1
42			60	24	6	3	-13.2
43			25	24	<3	3	-13.6
44			-40	48	<3	1	-10.3
45			-68	48	<3	2	-12.1
46	10b	methyl-cyclohexane	60	24	<3	2	-7.2
47			25	24	5	2	-8.2
48			-40	48	<3	1	-7.0
49	toluene		-68	48	<3	1	-6.9
50			60	24	33	3	-4.6
51			40	24	29	3	-6.3
52			25	24	6	2	-5.5
53			0	48	26	5	-5.8
54			-40	48	30	5	-3.9
55	11a	methyl-cyclohexane	60	24	18	3	-2.9
56			25	24	7	1	-4.2
57			-40	48	19	2	-4.1
58	toluene		-68	48	12	<1	-3.7
59			60	24	11	4	-8.6
60			25	24	15	5	-5.5
61			-40	48	11	4	+5.8
62			-68	48	9	3	-3.3
63			60	24	9	3	-3.3
64	11b	methyl-cyclohexane	25	24	15	4	-1.8
65			-40	48	15	3	-0.3
66			-68	48	6	1	-3.8
67	toluene		60	24	42	13	-4.7
68			25	24	39	12	-9.4
69			0	48	66	23	-7.1
70			-40	48	49	9	-8.6
71			60	24	36	9	0.0
72			25	24	31	11	-3.7
73	12a	methyl-cyclohexane	-40	48	44	19	-3.4
74			-68	48	37	9	-0.6
75			60	24	23	5	+1.8
76	toluene		25	24	42	15	-2.8
77			-40	48	46	16	-8.1
78			-68	48	25	7	-12.0
79			60	24	22	8	-0.9
80			25	24	46	16	-1.6
81			-40	48	62	31	-3.7
82	-68	48	32	15	-5.5		

^a [1] = 20 mM; [Sens*] = 3 mM; [MeOH] = 0.5 M; reaction scale: 4 mL. ^b Loss of starting material determined by GC. ^c Chemical yield determined by GC on the basis of initial concentration of **1**. ^d Enantiomeric excess determined by chiral GC.

Table 2. Enantiodifferentiating Photoaddition of Methanol, Ethanol, 1-Propanol, 2-Propanol, and/or *tert*-Butyl alcohol to 1,1-Diphenylalkenes **1–3** Sensitized by Chiral 1,4-Naphthalenedicarboxylates **9a–h**^e

entry	alkene	alcohol	sensitizer	solvent	temperature (°C)	irradiation time (h)	conversion ^e (%)	yield ^d (%)	op ^e (%)	ee ^f (%)
1	1	MeOH	9a	pentane	25	24	98	26	-0.2 ^b	-2.3
2					-40	48	64	14	-6.5 ^b	-5.4
3					-68	48	54	13	-11.5 ^b	-11.7
4				methyl-	60	24	93	61		-2.5
5				cyclohexane	25	24	82	53		-4.0
6					0	48	87	56		-6.2
7					-40	48	60	25		-12.2
8				toluene	60	24	77	41		-1.7
9					25	24	80	52		-2.2
10					-40	48	54	26		-3.4
11					-68	48	44	16		-5.5
12			9b	pentane	25	24	91	31	+5.0 ^b	+5.1
13					-40	48	61	13	+1.3 ^b	+2.6
14					-68	48	61	13	-2.2 ^b	-5.6
15				methyl-	60	24	83	46		-1.4
16				cyclohexane	25	24	74	44		-1.0
17					-40	48	55	22		-12.5
18					-68	48	46	15		-17.9
19				toluene	60	24	71	36		-3.8
20					25	24	68	34		-3.7
21					-40	48	65	31		-5.2
22					-68	48	52	21		-3.8
23			9c	pentane	25	24	>99	54	-0.7 ^b	
24					-40	48	43	11	+2.2 ^b	
25					-68	48	39	13	+4.7 ^b	
26			9d	pentane	25	24	83	30	-1.8 ^b	
27					-40	48	46	22	+1.9 ^b	
28					-68	48	38	4	+3.8 ^b	
29			9e	pentane	25	24	>99	26		-1.5
30					-40	48	69	13		-0.5
31					-68	48	58	14		-1.6
32			9f	pentane	25	24	95	13		-0.6
33					-40	48	62	16		-1.1
34					-68	48	65	11		-2.9
35			9g	methyl-	60	24	89	60		-7.7
36				cyclohexane	40	24	82	52		-8.0
37					25	24	85	59		-8.7
38					0	48	76	46		-6.8
39				toluene	60	24	89	55	-11.2 ^b	-11.3
40					25	24	81	57	-9.6 ^b	-10.6
41					-40	48	61	28		-6.3
42					-68	48	48	19		-6.5
43			9h	methyl-	60	24	95	66		-10.2
44				cyclohexane	40	24	88	59		-8.2
45					25	24	82	54		-4.7
46					0 ^g	48	78	53		+1.1
47					-40 ^g	48	17	3		+11.2
48				toluene	60	24	86	54		-16.0
49					25	0.5	33	18		-15.6
50						1	48	28		-14.6
51						2	62	40		-16.1
52						4	72	45		-16.3
53						8	73	47		-16.0
54						24	75	47		-15.7
55					-40	48	56	24		-8.8
56					-68	48	44	17		-7.2
57				acetonitrile	60	24	>99	75		-0.3
58					25	24	>99	73		-0.4
59					-40	48	>99	73		-0.2
60	1	EtOH	9h	methyl-	95	9	62	36		-21.0
61				cyclohexane	60	7	84	70		-17.4
62					25	14	96	68		-8.6
63				toluene	95	9	72	35		-21.7
64					60	10	90	35		-22.3
65					25	31	72	47		-18.9
66	1	1-PrOH		methyl-	95	9	82	38		-20.0
67				cyclohexane	60	7	96	52		-17.4
68					25	14	>99	59		-7.8
69				toluene	95	9	66	22		-20.4
70					60	12	68	32		-23.7
71					25	16	78	40		-21.4

Table 2 (Continued)

entry	alkene	alcohol	sensitizer	solvent	temperature (°C)	irradiation time (h)	conversion ^c (%)	yield ^d (%)	op ^e (%)	ee ^f (%)
72	1	2-PrOH		toluene	60	10	63	3		+32.0 ^h
73					25	31	36	4		+33.4 ^h
74	1	<i>t</i> -BuOH		toluene	60	10	38	0		—
75					25	31	51	0		—
76	2	MeOH	9h	methyl-	60	12	97	43		-19.7
77				cyclohexane	25	20	98	24		-12.6
78				toluene	60	10	66	18		-23.4
79					25	18	60	29		-24.5
80	2	EtOH	9h	methyl-	95	6	25	11		+30.6
81				cyclohexane	60	6	51	27		+27.8
82					25	17	83	39		+24.4
83				toluene	95	9	30	7		+26.1
84					60	7	80	12		+28.6
85					25	22	64	34		+25.7
86	3	MeOH		toluene	60	10	32	8		+3.8
87					25	18	43	16		+5.8

^a [1] = 20 mM; [Sens*] = 3 mM; [MeOH] = 0.5 M; reaction scale: 4 mL, unless noted otherwise. ^b Reaction scale: 300 mL. ^c Loss of starting material determined by GC. ^d Chemical yield determined by GC on the basis of the initial concentration of **1**. ^e Optical purity of isolated **4a**, calculated from the specific rotation of optical pure (–)-(*S*)-**4a** ([α]_D²⁰ = –52.5° (CHCl₃)). ^f Enantiomeric excess determined by chiral GC. ^g [Sens*] < 3 mM due to low solubility. ^h Incomplete separation on chiral GC.

Table 3. Reduction Potentials and Calculated Free-Energy Change (ΔG_{et}) for Electron-Transfer Process to Singlet Excited State of Chiral Naphthalene(di)carboxylates **7–12a** and Quantum Yields for Photoaddition of Methanol to 1,1-Diphenylpropene **1**

sensitizer	E _{red} ^a (V)	λ _{0–0} ^b (nm)	ΔG _{et} ^c (kcal mol ⁻¹)	Φ _{4a} ^d
7a	–2.30	334	–1.15	1.2 × 10 ⁻⁴
8a	–2.39	339	2.19	2.5 × 10 ⁻⁵
9a	–1.84	371	–3.22	1.4 × 10 ⁻²
10a	–2.22	334	–2.99	2.5 × 10 ⁻⁴
11a	–2.30	341	0.61	1.1 × 10 ⁻⁴
12a	–2.02	357	–2.09	1.8 × 10 ⁻³

^a Reduction potentials estimated as half-wave potential measured at a platinum electrode, relative to the Ag/AgCl electrode using 0.1 M tetrabutylammonium perchlorate as the electrolyte in acetonitrile. ^b Fluorescence maxima of highest energy emission in frozen EPA (diethyl ether: isopentane: ethanol = 5:5:2) Glass at 77 K. ^c Based on Weller equation: ΔG_{et} = 23.06(E_{ox}(D⁺/D) – E_{red}(A/A⁻)) – ΔG_{0–0} – w_p; oxidation potential of **1** (E_{ox} = 1.306 V) estimated as 0.028 V before the peak potential; Coulombic attraction term (w_p) taken to be –1.3 kcal mol⁻¹. ^d Quantum yield of **4a** upon photosensitization of **1** with **7a–12a** in pentane containing 0.5 M methanol.

photochemical behavior. It is likely that the favored enantiomer at the low-temperature limit, where the effect of entropy is minimized, can be related to the absolute configuration at C-1; i.e., (*S*)-(–)-**4a** from (1*R*)-(–)-menthyl esters **9a,b** and (*R*)-(+)–**4a** from (1*S*)-(–)-isomenthyl and neomenthyl esters **9c,d**. This empirical rule can be extended to photosensitizations with the other chiral alkyl esters **9e,f** and saccharide derivatives **9g,h**, in which all (1*S*)-sensitizers give the (*R*)-(+)–product.

In sharp contrast to the *normal* temperature dependence of ee observed for alkyl esters **9a–9f** (runs 1–34 in Table 2), the saccharide ester **9h** (runs 43–56) displays an *unusual* temperature dependence as well as a dramatic switching of product chirality within the experimental temperature range, although **9g** (runs 35–42) shows more moderate temperature dependence. In the case of **9h**, the product's ee is increased to 16% not by lowering but by raising the temperature to 60 °C (runs 48–54), and either of the enantiomers of **4a** can be produced predominantly simply by changing the irradiation temperature. These apparently *extraordinary* observations are rationalized in terms of the nonzero differential entropy factor for the enantiodifferentiation process(es), as described below.

Activation Parameters. Recently, we have found analogous temperature-switching behavior in the enantiodifferentiating *Z*-to-*E* photoisomerization of cyclooctene sensitized by a wide variety of chiral benzenepolycarboxylates.^{5d,e,g} The Eyring-type analysis of the ee values of (*E*)-cyclooctene produced at various temperatures has revealed that the product's ee, which is determined exclusively by the differential free energy of activation (ΔΔG[‡]) for the enantiodifferentiating photoisomerization, is governed not only by the differential enthalpy change of activation (ΔΔH[‡]), according to conventional reasoning, but also by the differential entropy change of activation (ΔΔS[‡]). The most important finding arising from this study was that the ΔΔS[‡] is not always negligible and often plays the key role in determining the product chirality particularly at ambient and higher temperatures.^{1b,c}

In the present study, the activation parameters for the enantiodifferentiating photoaddition from the temperature dependence of the ee values obtained at various temperatures were also determined, according to modified Arrhenius and Eyring equations:

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

$$= \frac{-\Delta\Delta H_{R-S}^{\ddagger}}{RT} + \frac{\Delta\Delta S_{R-S}^{\ddagger}}{R} \quad (1)$$

where *k_R* and *k_S* are the apparent rates of formation of (*R*)-(+)– and (*S*)-(–)-**4a**, *A_R/A_S* represents the relative frequency factor, and ΔΔH[‡]_{R-S} and ΔΔS[‡]_{R-S} are the differential enthalpy and entropy changes of activation, respectively. The relative rate constant (*k_R/k_S*) is experimentally equivalent to the (100 + %ee)/(100 – %ee) ratio, and the entity of the rate constants will be discussed in more detail later.

According to eq 1, we plotted the ln(*k_R/k_S*) values obtained for each sensitizer as a function of reciprocal temperature. This gave good to excellent straight lines, as exemplified in Figure 1, for the photosensitization with **9a** and **9h** in methylcyclohexane and toluene. The relative frequency factor (*A_R/A_S*) and the differential activation enthalpy and entropy (ΔΔH[‡]_{R-S} and ΔΔS[‡]_{R-S}) are listed in Table 4, along with the equipodal temperature (*T*₀), at which the product chirality is (expected to be) switched. It should be emphasized that none of the sensitizers

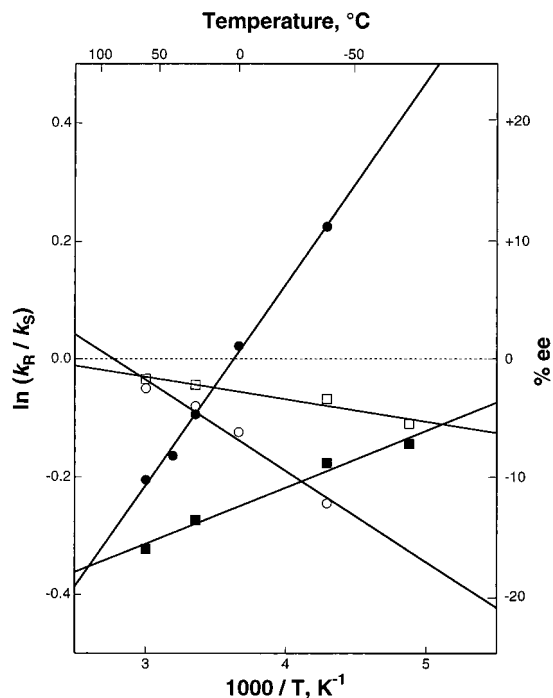


Figure 1. Temperature dependence of the enantiomeric excess (ee): the logarithm of relative rate constant (k_R/k_S) as a function of reciprocal temperature in enantiodifferentiating photosensitized methanol addition to **1** sensitized by **9a** in methycyclohexane (○) and toluene (□) and by **9h** in methycyclohexane (●) and toluene (■).

Table 4. Activation Parameters (at 25 °C) and Equipodal Temperatures (T_0) for Enantiodifferentiating Photoaddition of Methanol to 1,1-Diphenylpropene **1** Sensitized by Some Chiral 1,4-Naphthalenedicarboxylates^a

sensitizer	solvent	data point	$\Delta\Delta H_{R-S}^{\ddagger b}$ (kcal mol ⁻¹)	$\Delta\Delta S_{R-S}^{\ddagger c}$ (cal mol ⁻¹ K ⁻¹)	A_R/A_S^d	T_0^e (°C)
9a	pentane	3	+0.24	+0.73	1.44	51
	methycyclohexane	4	+0.31	+0.85	1.53	89
		4	+0.08	+0.17	1.09	178
9b	pentane	3	+0.26	+1.12	1.76	-39
	methycyclohexane	3	+0.45	+1.46	2.08	35
9c	pentane	3	-0.14	-0.50	0.78	6
9d	pentane	3	-0.15	-0.56	0.75	-12
9g	methycyclohexane	3	-0.22	-1.09	0.58	-70
	toluene	4	-0.12	-0.80	0.67	-127
9h	methycyclohexane	5	-0.68	-2.47	0.29	3
	toluene	4	-0.19	-1.19	0.55	-114

^a All activation parameters obtained by Arrhenius treatment of the optical yields. ^b Differential enthalpy of activation: $\Delta H_R^{\ddagger} - \Delta H_S^{\ddagger}$. ^c Differential entropy of activation: $\Delta S_R^{\ddagger} - \Delta S_S^{\ddagger}$. ^d Relative frequency factor. ^e Equipodal temperature, at which no appreciable enantiodifferentiation occurs.

employed give null $\Delta\Delta S_{R-S}^{\ddagger}$ values, or unit A_R/A_S , which is the origin of the unusual temperature-switching phenomena observed. Again, the widespread hypothesis that "lowering temperature leads to higher optical yield" is demonstrated not to be true in the photosensitized photoaddition reaction as well as in photoisomerization reactions.⁵ These phenomena are attributable solely to the contribution of the entropic factor in the photochemical, and probably thermal, enantiodifferentiation processes.

Effect of Methanol Concentration. As expected from the radical ionic nature of the intermediate involved, a change in

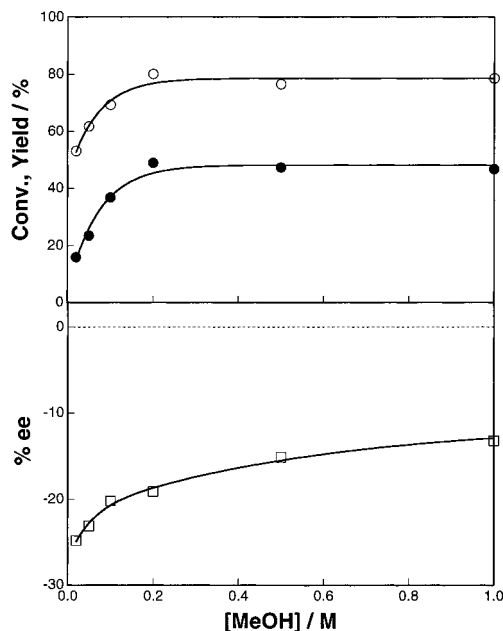


Figure 2. Conversion (○), chemical yield (●), and enantiomeric excess (ee, □) as a function of methanol content in enantiodifferentiating photosensitized methanol addition to **1** (20 mM) photosensitized by **9h** (3 mM) at 25 °C.

the solvent polarity significantly affected the product's ee. An extreme case is observed for highly polar solvents, such as acetonitrile. As shown in Table 2 (runs 57–59), the photosensitization of **1** by **9h** in acetonitrile containing 0.5 M methanol leads to the formation of racemic product **4a** in high yield at all temperatures examined, while the same photoreaction in toluene containing 0.5 M methanol affords (*S*)-(–)**4a** in 7–16% ee under comparable irradiation conditions (runs 48–56).

In this context, it is crucial to investigate the effect of methanol content on the product's chemical and optical yields. The photosensitization of **1** by **9h** was conducted at 25 °C for a fixed irradiation period (24 h) in toluene with methanol concentrations ranging from 0.02 to 1.0 M, giving the results shown in Figure 2. The conversion and chemical yield rapidly increased with increasing methanol concentration up to 0.2 M, reaching a plateau of 80% conversion and 50% yield. These results seem quite encouraging in the sense that the photoaddition occurs in lower, but appreciable, conversions and yields even in a less polar solvent that contains extremely low methanol content (0.02 M). The constant levels of conversion and yield obtained with higher methanol concentrations indicate that a methanol concentration of 0.2 M is sufficient to generate and trap the radical cationic substrate ($1^{\cdot+}$ or $1^{\delta+}$).

In contrast, the ee of (*S*)-(–)**4a** produced was almost halved from 25% to 13% by increasing the methanol from 0.02 to 1.0 M, as shown in Figure 2 (bottom). Taking into account the extremely low ee in acetonitrile, this result clearly indicates that the use of a more polar solvent, or high methanol content, accelerates the separation of the excited sensitizer–substrate complex which has radical ionic character. This generates a solvent-separated or free radical ion pair, in which the enantiodifferentiating interaction between substrate and chiral sensitizer should be much reduced. Fortunately, the high ee's obtained at low methanol concentrations are applicable to practical photochemical asymmetric synthesis, since the low product yield is expected to improve by extending the irradiation time.

Effect of the Alcohol's Bulk. Since the present photochemical polar addition involves the enantiofacially selective nucleo-

philic attack of an alcohol, the bulk of the alcohol should affect the product yield and ee. Thus, the photoaddition of more bulky alcohols to **1**, sensitized by **9h**, was performed in methylcyclohexane or toluene. The results for the photoaddition of ethanol, 1-propanol, 2-propanol, and *tert*-butyl alcohol are summarized in Table 2 (entries 60–75). The adducts **4a–d** were all isolated from the photolyzed solutions on a preparative scale, and their structures were confirmed spectroscopically.

As shown in Table 2, the primary alcohols, that is, ethanol and 1-propanol (runs 60–65 and 66–71, respectively), afforded the corresponding adducts **4b** and **4c** in good chemical yields (up to 70%). These yields are comparable or slightly higher than those obtained for methanol, probably as a result of the lower polarity of ethanol (E_T 51.9)²² or 1-propanol (E_T 50.7)²² as compared to that of methanol (E_T 55.5).²² In contrast, the use of 2-propanol (runs 72 and 73) dramatically lowered the yield of adduct **4d** to 3–4%, and *tert*-butyl alcohol (runs 74 and 75) afforded none of the desired product. These much lower yields are largely attributed to the increased steric hindrance during the nucleophilic attack of the alcohol on the radical cationic substrate **1**^{δ+} in the exciplex or contact ion pair intermediate, although the lower polarity of 2-propanol (E_T 48.6)²² and *tert*-butyl alcohol (E_T 43.9)²² may also be responsible to some extent.

Interestingly, the product's ee behaved quite differently to the chemical yield. By using the higher primary alcohols, we obtained much improved ee's for adducts **4b** and **4c** in both methylcyclohexane and toluene at all temperatures investigated. For example, the ee of adduct **4** obtained in methylcyclohexane at 60 °C was increased from –10% for **4a** (run 43) to –17% for both **4b** and **4c** (runs 61 and 67), ultimately affording –20% ee at 95 °C (runs 60 and 66), while the photoreactions in toluene give almost constant ee's of ca. –22% for both **4b** and **4c** at 25–95 °C (runs 63–65 and 69–71). By using the more bulky 2-propanol nucleophile, we further increased the ee of product **4d** to 33% (runs 72 and 73), although the chemical yields are substantially lower. We may conclude that the bulk and probably polarity of the alcohol can be used as a convenient and effective tool for enhancing the product ee in this enantiodifferentiating photoaddition that involves a charge-transfer exciplex or a contact ion pair.

Effects of Substrate Structure. Since the bulk of the alcohol was demonstrated to dramatically affect the product yield and ee, we decided to explore the photosensitization of higher homologues of **1**, that is, 1,1-diphenyl-1-butene (**2**) and 1,1-diphenyl-3-methyl-1-butene (**3**), which possess more bulky ethyl and isopropyl substituents on the carbon at which the nucleophilic attack occurs. Photoadditions of methanol to **2** and **3** sensitized by **9h** were performed in methylcyclohexane or toluene over a range of temperature, and the adducts **5a** and **6a**, produced from **2** and **3**, respectively, were isolated and characterized spectroscopically. The results are summarized in Table 2 (runs 76–79 and 86–87).

The product's ee obtained in methylcyclohexane at 60 °C was significantly increased from –10% for **4a** (run 43 in Table 2) to –20% for **5a** (run 76), accompanied by an appreciable decrease of the chemical yield from 66% to 43%. In toluene solution at 60 °C, the ee was also improved from –16% for **4a** (run 48) to –23% for **5a** (run 78), but the yield decreased. Similar tendencies were also observed at 25 °C.

The introduction of a more bulky isopropyl group at the olefinic carbon, C-2, led to a considerable decrease in chemical

Table 5. Fluorescence Quenching of Chiral Sensitizers by 1,1-Diphenylpropene **1**^a

sensitizer	solvent	[MeOH] (M)	$k_Q\tau^0$ (M ⁻¹)	τ^0 ^b (ns)	$k_Q/10^9$ (M ⁻¹ s ⁻¹)	λ_{\max} (nm) (kcal mol ⁻¹)	
						sensitizer	exciplex ^c
9a	pentane	0	28.3	3.6	7.9	388 (73.7)	434 (65.9)
		0.5	37.1	3.0	12.0	391 (73.1)	458 (62.4)
	methylcyclohexane	0	16.3	4.4	3.7	389 (73.5)	438 (65.3)
		0.5	13.6	2.9	4.8	393 (72.7)	459 (62.3)
	toluene	0	6.2	8.5	0.73	408 (70.1)	<i>d</i>
		0.5	7.9	7.8	1.0	411 (69.6)	<i>d</i>
9h	pentane	0	57.2	6.3	9.1	394 (72.6)	457 (62.6)
		0.5	35.7	3.9	9.2	397 (72.0)	465 (61.5)
	methylcyclohexane	0	30.5	5.6	5.4	396 (72.2)	459 (62.3)
		0.5	22.1	3.9	5.6	400 (71.5)	467 (61.2)
	toluene	0	10.8	11.6	0.94	420 (68.1)	462 (61.9)
		0.5	12.6	11.5	1.1	423 (67.6)	472 (60.6)

^a Measured with 0.01 mM aerated solution of sensitizer **9** at 25 °C.

^b Fluorescence lifetime of sensitizers in aerated solution at 25 °C.

^c Exciplex fluorescence obtained by the spectrum subtraction. ^d Exciplex emission not observed.

and optical yields of product **6a** in toluene at 25 and 60 °C (runs 86 and 87). These results may be rationalized if it is assumed that the bulky substituent in substrate **3** prevents the formation of a close exciplex with the chiral sensitizer. This must inevitably reduce both steric and electronic interactions within the exciplex, leading to low chemical and optical yields.

Optimization of Ee. Using the knowledge obtained from the examinations of a variety of chiral sensitizers, substrates, and alcohols, we attempted to optimize the conditions for the photosensitized enantiodifferentiating polar addition reaction in order to maximize the product's ee. Although the use of bulky 2-propanol instead of methanol or ethanol in the photoaddition to **1** gave **4a** in up to 33% ee (runs 72 and 73 in Table 2), the chemical yield is unsatisfactory (3–4%), and we therefore decided to employ a combination of moderately bulky substrate and nucleophile, that is, **2** and ethanol. The photoaddition of ethanol to **2** sensitized by **9h** was performed in methylcyclohexane or toluene at 25–95 °C, and the results are summarized in Table 2 (runs 80–85). The chemical yield was good in both solvents with the highest ee of 30.6% in methylcyclohexane at 95 °C. As well as having a chemical yield of 44% based on consumed substrate, this reaction represents the highest ee value for a bimolecular enantiodifferentiating photoreaction ever reported.^{14–16}

Quenching of Sensitizer Fluorescence. To elucidate the excited state involved and also to evaluate the rate constants for the relevant processes in the photosensitized polar addition, we performed fluorescence quenching experiments with two representative sensitizers **9a** and **9h** in nondegassed pentane, methylcyclohexane, and toluene. The fluorescence spectra of **9a** and **9h** in these solvents were first examined in the presence or absence of methanol (0.5 M). As can be seen from Table 5, the fluorescence maxima of **9a** and **9h** show significant bathochromic shifts of 20–26 nm in toluene as compared with

(22) Dimroth and Reichardt's E_T value; for reviews, see: (a) Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, Germany, 1979. (b) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

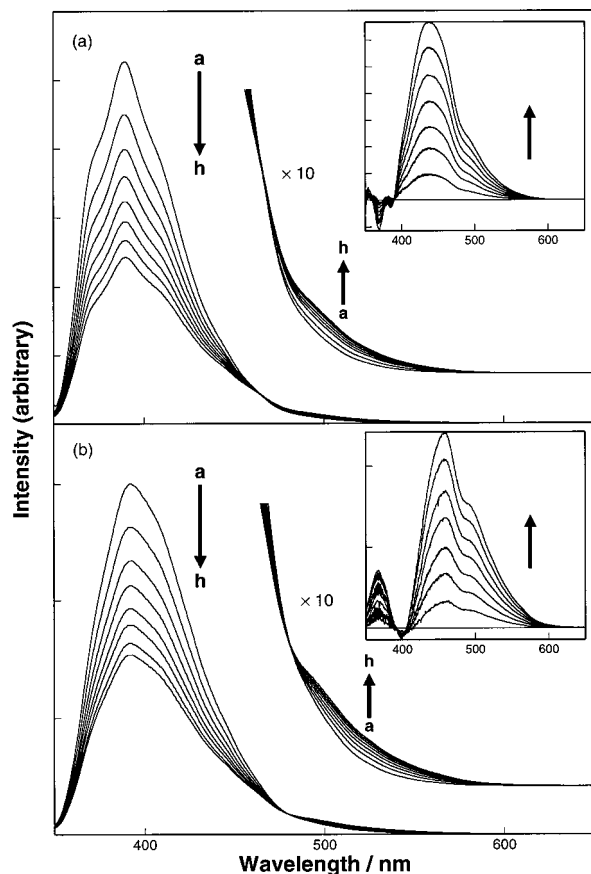


Figure 3. Fluorescence spectra of **9a** excited at 340 nm in methylcyclohexane in the presence (lower traces) and absence (upper traces) of methanol (0.5 M) with varying concentrations of **1**: (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, (g) 60, (h) 70 mM.

those in pentane, whereas the added methanol or the use of methylcyclohexane induces only trivial red shifts of 1–3 nm. Since the excitation spectra in all three solvents coincide each other, this specific shift in toluene clearly indicates a charge-transfer interaction between the sensitizer and solvent.

The sensitizer fluorescence was quenched efficiently by adding up to 70 mM substrate **1** in the presence or absence of 0.5 M methanol. Representative quenching behavior of **9a** and **9h** in methylcyclohexane is illustrated in Figures 3 and 4. As the fluorescence intensity gradually decreased with increasing concentrations of **1**, a new weak emission attributable to an exciplex intermediate emerged at longer wavelengths except for **9a** in toluene, accompanying the isoemissive point at 464 and 467 nm for **9a** and **9h**, respectively. As shown in the insets of Figures 3 and 4 and summarized in Table 5, the exciplex fluorescence peaks, obtained by the spectrum subtraction, occur at 438 and 459 nm for **9a** and **9h**, respectively. The finding that exciplex fluorescence of **9h** appears at longer wavelengths (by 21–23 nm) as compared to that of **9a** may be attributed to an extra stabilization of the exciplex by a higher microenvironmental polarity induced by the polar saccharide moiety. In this context, a similar but less extensive bathochromic shift (6–12 nm, depending on the solvent used) of sensitizer fluorescence of **9h** as compared to that of **9a** may also be rationalized by the increased microenvironmental polarity, as the sensitizer fluorescence of **9a** and **9h** shows a bathochromic shift of 3–4 nm by adding 0.5 M methanol to each solvent.

Upon addition of 0.5 M methanol to each solution, the sensitizer fluorescence shifted only slightly to longer wavelengths (3 nm), irrespective of the solvent used. In contrast, the

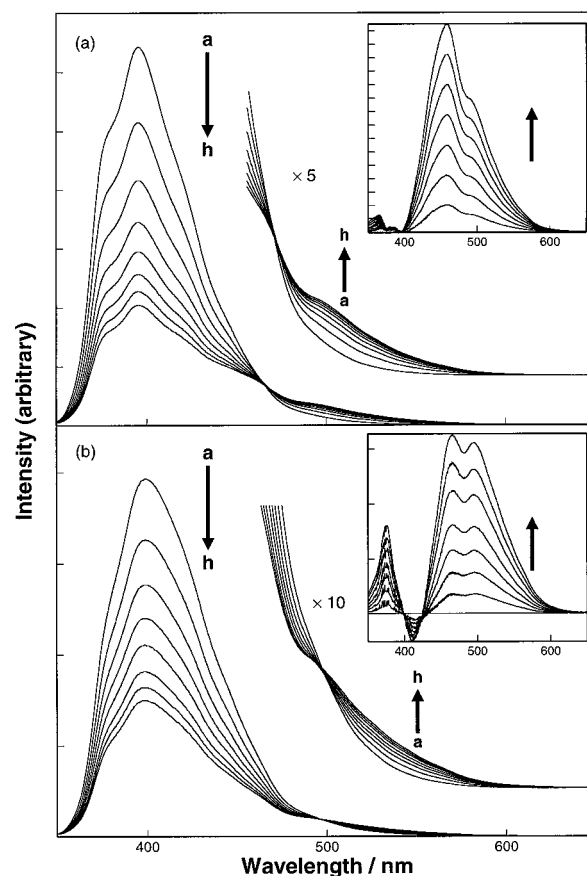


Figure 4. Fluorescence spectra of **9h** excited at 340 nm in methylcyclohexane in the presence (lower traces) and absence (upper traces) of methanol (0.5 M) with varying concentrations of **1**: (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, (g) 60, (h) 70 mM.

exciplex fluorescence showed much larger bathochromic shifts of 21–24 nm for **9a** and 8–10 nm for **9h** in both pentane and methylcyclohexane, indicating that the exciplex formed between excited **1** and **9** has a strong charge-transfer character. It is also interesting to note that the peak of exciplex fluorescence observed for **9h** in pentane or methylcyclohexane coincides with that observed for **9a** in the same solvent containing 0.5 M methanol. This may indicate that the microenvironmental polarity around the exciplex of **9h** is comparable to the bulk polarity of pentane or methylcyclohexane containing 0.5 M methanol. In the presence of methanol, similar fluorescence quenching behavior was observed for both **9a** and **9h** in all three solvents employed, as exemplified in Figures 3b and 4b.

By using a conventional Stern–Volmer treatment of these quenching data (eq 2), we plotted the relative fluorescence

$$I_F/I_F^0 = 1 + k_Q\tau^0[Q] \quad (2)$$

intensity (I_F/I_F^0) in the presence and absence of substrate as a function of the concentration of added **1**, affording an excellent straight line for all combinations of the sensitizers and solvents examined, as shown in Figure 5. From the Stern–Volmer constant ($k_Q\tau^0$) obtained as the slope of the plot and the fluorescence lifetime (τ^0) determined independently by a single photon-counting technique, we can calculate the apparent quenching rate constant (k_Q) for each sensitizer. The results are summarized in Table 5.

Quenching of Exciplex Fluorescence. To reveal the kinetic details of the nucleophilic addition step, we also performed the quenching of exciplex fluorescence by methanol with **9a** and

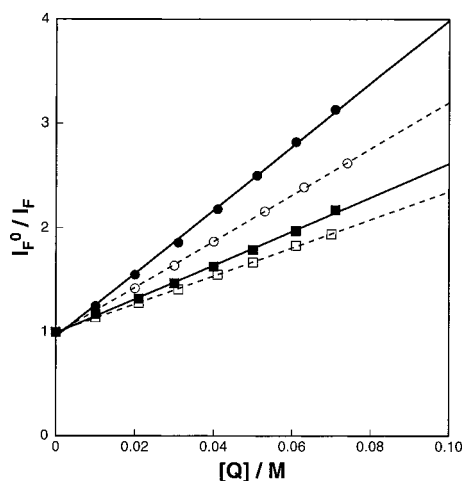


Figure 5. Stern–Volmer plots for fluorescence quenching of **9a** by **1** in the presence (□)/absence (■) of 0.5 M methanol and of **9h** by **1** in the presence (○)/absence (●) of 0.5 M methanol in methylcyclohexane.

Table 6. Fluorescence Lifetime in Nanoseconds of Chiral Sensitizer (τ) and Exciplex (τ_{ex}) and the Apparent Rate Constant (k_A) for the Quenching of Exciplex Determined by Stern–Volmer Analysis of τ_{ex} at Varying Methanol Content in Some Solvents^a

[MeOH] (M)	pentane		methylcyclohexane				toluene			
	9a	9h	9a	9h	9a	9h	τ	τ_{ex}		
0	1.1	4.9	2.0	10.9	2.0	4.9	2.3	11.4	4.7	12.7
0.05	1.3	4.8	1.9	10.7	1.9	4.8	2.2	10.7	4.7	12.0
0.1	1.2	4.7	1.7	9.6	1.8	4.6	2.3	10.2	4.5	11.1
0.2	1.2	4.5	1.5	8.0	1.7	4.2	2.3	9.0	4.4	10.2
0.3	1.3	4.4	1.3	6.9	1.8	4.2	2.3	8.1	4.2	8.9
0.4	1.2	4.3	1.4	6.2	1.8	4.1	2.3	7.5	4.2	8.5
0.5	1.2	4.1	1.4	5.9	1.8	3.7	2.2	7.0	3.8	7.5
1.0	1.2	3.4	1.3	3.9	1.7	3.1	2.3	4.3	3.7	6.3
k_A (M ⁻¹)	0.43		1.8		0.60		1.6		1.1	

^a Measured with nondegassed pentane solutions containing **1** (20 mM), **9** (0.01 mM), and varying amounts of methanol using a time-correlated single-photon-counting method at 25 °C. The decay profile was fitted to a double-exponential curve ($\chi^2 = 0.5\text{--}1.5$), and the shorter lifetime obtained was assigned to the sensitizer fluorescence in each case.

9h in pentane, methylcyclohexane, and toluene. Since the exciplex fluorescence was fairly weak and overlapped with the sensitizer fluorescence, the fluorescence lifetime, instead of intensity, was measured in the presence of methanol at concentrations of up to 1.0 M. The time profile of the whole fluorescence was successfully analyzed in each case as a double-exponential decay with fast and slow components, which correspond to the sensitizer and exciplex fluorescence, respectively. As can be seen from Table 6, the sensitizer lifetime (τ) suffered little or no effects upon the addition of methanol up to 1.0 M, while the exciplex lifetime (τ_{ex}) was significantly shortened. According to the modified Stern–Volmer equation (eq 3), the relative fluorescence lifetime was plotted as a function

$$\tau_{\text{ex}}^0/\tau_{\text{ex}} = 1 + k_A[\text{MeOH}] \quad (3)$$

of the methanol concentration, giving a good to excellent straight line for each sensitizer–solvent combination, as demonstrated in Figure 6. The Stern–Volmer constant (k_A) for each sensitizer is obtained as the slope of the plot.

Mechanism. All of the results obtained above are compatible with the mechanism proposed previously by Mizuno et al. for the achiral photoaddition of methanol to **1** sensitized by 9,10-

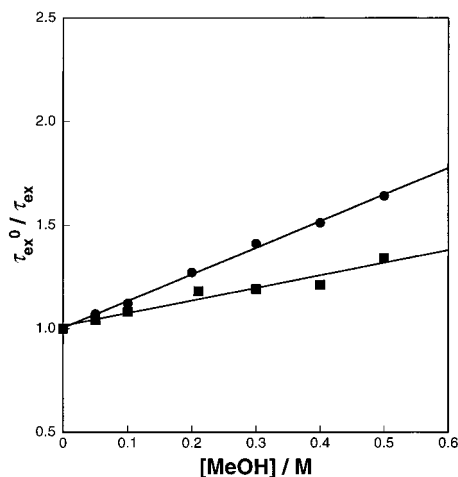
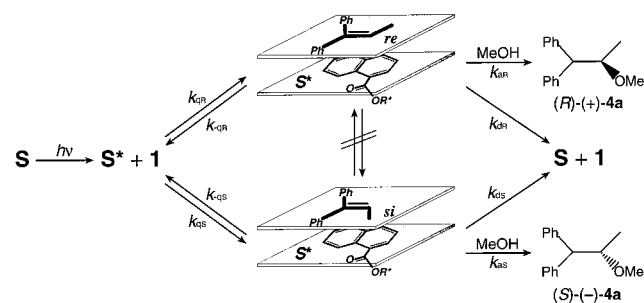


Figure 6. Stern–Volmer plots for the fluorescence lifetime of the exciplex between **1** and **9a** (■) or **9h** (●) in the presence of varying amounts of methanol in methylcyclohexane.

Scheme 2



dicyanoanthracene.¹⁷ In the present study, the use of a chiral sensitizer leads to the formation of a pair of diastereomeric exciplexes upon quenching of the excited singlet state of the enantiomerically pure sensitizer **9** by the prochiral substrate **1**. We therefore propose a chirally modified mechanism that involves a diastereomeric exciplex pair, which is equilibrated with the excited sensitizer and is simultaneously subjected to an enantiofacially selective nucleophilic attack by the alcohol. Scheme 2 illustrates the detailed mechanism of the enantio-differentiating photoaddition of methanol sensitized by chiral sensitizer (**S**) and the rate constants for the relevant processes, that is, k_q and k_{-q} for the formation and dissociation of exciplex, k_d for the radiative and nonradiative decay from the exciplex, and k_a for the addition of alcohol to the exciplex (the subscripts R and S refer to the absolute configurations of the product **4a**).

In principle, if these two diastereomeric exciplexes possess distinctly different fluorescence maxima and lifetimes, we can discriminate them spectroscopically as independent species. However, the decay profile of the exciplex fluorescence at longer wavelength does not appear to contain two components in addition to the sensitizer fluorescence, and the two peaks with ~ 30 nm (1200–1300 cm^{-1}) separation, observed in the exciplex fluorescence (insets in Figures 3 and 4), are more likely to be assigned to vibronic fine structure than to two independent species. This seems quite reasonable, because an energy difference of even 0.4 kcal/mol in the stability or activation energy, which corresponds to a wavelength difference of 2–3 nm in this region, is capable of affording the highest ee's (30–33%) obtained in this study.

Kinetics and Energetics. The specific rate constants, which are assigned to the processes indicated in Scheme 2, are related to the apparent quenching constants k_Q and k_A that have been

Table 7. Rate Constants for the Photoaddition of Methanol to **1** Sensitized by Chiral Sensitizers **9a** and **9h**^a

sensitizer	solvent	k_q (10^9 $M^{-1} s^{-1}$)	k_{-q} (10^7 s^{-1})	k_a (10^7 $M^{-1} s^{-1}$)	k_d (10^7 s^{-1})	K_{ex}^b (M^{-1})	ΔG_{ex}^c (kcal mol^{-1})
9a	pentane	33.0	16.0	8.8	4.9	210	-3.2
	methyl- cyclo- hexane	8.2	11.4	12.3	8.8	72	-2.3
9h	pentane	9.2	0.17	17.0	9.0	5400	-5.1
	methyl- cyclo- hexane	5.9	0.92	11.3	7.9	640	-3.5
	toluene	1.4	2.7	8.5	5.2	52	-2.4

^a The kinetic parameters calculated from the quenching rate constants k_Q and k_A using eqs 4 and 5. ^b Equilibrium constant for the exciplex formation: $K_{ex} = k_q/k_{-q}$. ^c Free-energy change for the exciplex formation calculated from K_{ex} .

determined in the Stern–Volmer analyses described above. The calculated rate constants are listed in Table 7.

$$k_Q = k_q \left(1 - \frac{k_{-q}}{(k_{-q} + k_d + k_a[\text{MeOH}])} \right) \quad (4)$$

$$k_A = \frac{k_a}{(k_{-q} + k_d)} \quad (5)$$

As expected from the highly negative ΔG_{et} obtained for **9** (Table 3), the quenching of the sensitizer singlet by substrate **1** proceeds at a rate of $0.6\text{--}3.3 \times 10^{10} M^{-1} s^{-1}$, which is almost comparable to diffusion-controlled rates in pentane ($k_{diff} 4.4 \times 10^{10} M^{-1} s^{-1}$)²³ and methylcyclohexane ($k_{diff} 1.4 \times 10^{10} M^{-1} s^{-1}$).²³ In toluene ($k_{diff} 1.8 \times 10^{10} M^{-1} s^{-1}$),²³ the k_q value falls considerably to $1.4 \times 10^9 M^{-1} s^{-1}$, probably due to the electron-donating solvation of the excited sensitizer, as demonstrated by the bathochromic shift of sensitizer fluorescence in the aromatic solvent (Table 4).

In sharp contrast to the comparable k_q 's for **9a** and **9h** in pentane and methylcyclohexane, the rate of the reverse reaction (k_{-q}) differs by almost 2 orders of magnitude between these two sensitizers, with much greater equilibrium constants (K_{ex}) and stabilization energies (ΔG_{ex}) obtained for **9h** than for **9a**. The large K_{ex} ($640\text{--}5400 M^{-1}$) and highly negative ΔG_{ex} (-3.5 to -5.1 kcal/mol) render the exciplex formation of **9h** with **1** practically irreversible in nonpolar solvents. From the fluorescence maxima of the sensitizer and exciplex (λ_{max} and λ_{max}^{ex} in Table 5) and the free-energy change upon exciplex formation (ΔG_{ex} in Table 7), we can draw detailed energy diagrams for the sensitizers **9a** and **9h** and their exciplexes with substrate **1** in pentane at 25 °C, as illustrated in Figure 7a (this has been energy normalized to the ground-state sensitizers). In pentane solution, the exciplex [**9h*** \cdots **1**] (67.5 kcal/mol) is more stabilized than [**9a*** \cdots **1**] (70.5 kcal/mol), although the excited singlets of **9a** and **9h** do not differ appreciably in energy (73.7 and 72.6 kcal/mol). As shown in Figure 7b, the excited singlet of **9h** is more stabilized in toluene (68.1 kcal/mol) than in pentane (72.6 kcal/mol) through the electron-donating interaction with the aromatic solvent, although this extra stabilization is less effective upon exciplex formation with **1**, affording a smaller energy difference (67.5 and 65.7 kcal/mol in pentane and toluene, respectively).

From a kinetic point of view, the formation of the exciplex proceeds at a rate comparable to diffusion, while the subsequent

nucleophilic attack of methanol on the electron-deficient substrate **1** contained in the exciplex is much slower ($k_a[\text{MeOH}] = 4.3\text{--}8.5 \times 10^7 s^{-1}$). This attack is in comparison with exciplex decay ($k_d = 4.9\text{--}9.1 \times 10^7 s^{-1}$) and also with exciplex dissociation ($k_{-q} = 0.17\text{--}16 \times 10^7 s^{-1}$). We may conclude, therefore, that the addition of methanol is the rate-determining step in the overall reaction sequence to the adduct **4**.

Judging from the greater bathochromic shifts, longer lifetimes, and larger equilibrium constants observed, the exciplex of **9h** with **1** is obviously more polarized, stabilized, and tightly bound than that of **9a** with **1**. This is probably a result of the increased microenvironmental polarity around the saccharide substituents, and the formation of the more polarized exciplex enhances the enantiofacial selectivity upon formation of the diastereomeric exciplex pair and accelerates the subsequent attack of methanol.

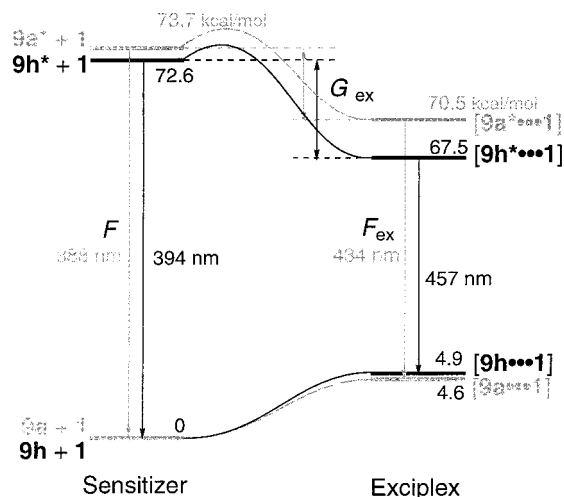
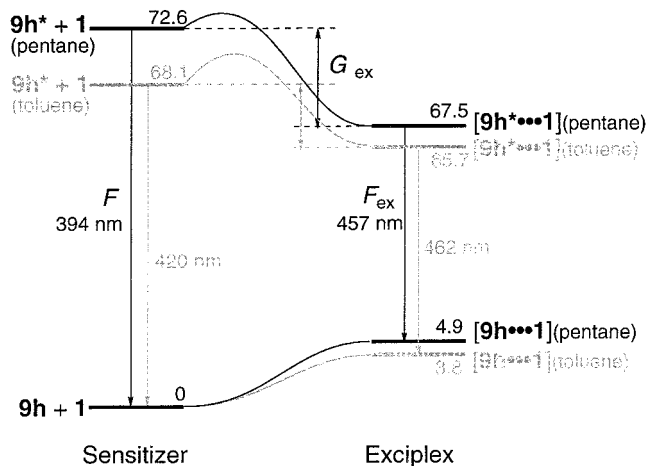
Origin of Enantioselectivity. In the mechanism shown in Scheme 2, the product's ee can be determined either *thermodynamically* by the stability difference between the diastereomeric exciplex pair, or *kinetically* by the difference in the rate of subsequent methanol addition, and this depends critically on the relative rates of the excited-state equilibrium and the subsequent processes. According to the proposed mechanism and the experimental data obtained above, the apparent enantioselectivity (k_R/k_S) used in eq 1 is expressed in further detail as a combination of relevant rate constants (eq 6).

$$\frac{k_R}{k_S} = \frac{\left[\left(\frac{k_{qR}}{k_{-qR}} \right) k_{aR} \right]}{\left[\left(\frac{k_{qS}}{k_{-qS}} \right) k_{aS} \right]} = \frac{(K_{exR} k_{aR})}{(K_{exS} k_{aS})} = \left(\frac{K_{exR}}{K_{exS}} \right) \left(\frac{k_{aR}}{k_{aS}} \right) \quad (6)$$

It is now apparent that the product's ee is not a simple function of a single pair of rate constants for an enantiodifferentiating process that gives the (*R*)- and (*S*)-adducts but instead is controlled, in principle at least, by both the relative stability of the diastereomeric exciplexes (K_{exR}/K_{exS}) and the relative rate of the subsequent addition of methanol (k_{aR}/k_{aS}). The final form of eq 6 clearly indicates that the apparent enantioselectivity (k_R/k_S), that is, the R/S ratio of adduct, is a product of the relative stability (K_{exR}/K_{exS}) and reactivity (k_{aR}/k_{aS}) of the diastereomeric exciplex intermediates.

At this point of our discussion, it should be emphasized that the $\ln(k_R/k_S)$ vs T^{-1} plot gives a single straight line in most cases, as exemplified in Figure 1. This clearly indicates that the product's ee is determined in a single enantiodifferentiating step, since it is unlikely that the two enantiodifferentiating processes (equilibrium or rate) incidentally possess very close thermodynamic or activation parameters over the entire temperature range in all cases examined. Consequently, either the relative stability (K_{exR}/K_{exS}) or reactivity (k_{aR}/k_{aS}) must be responsible for the good enantiodifferentiation observed in the polar photoaddition of alcohol to **1**. A comparison of the rate constants for methanol addition (k_a), obtained from reactions photosensitized with **9a** and **9h**, leads to the conclusion that the observed enantioselectivity originates from the different thermodynamic stabilities between the diastereomeric exciplexes. As can be seen from the data shown in Tables 5 and 7 or illustrated in Figure 7, the exciplex [**9h** $\delta^- \cdots$ **1** δ^+] is 3.0–3.1 kcal/mol more stabilized in energy in nonpolar solvents than [**9a** $\delta^- \cdots$ **1** δ^+], which clearly indicates a more polarized, charge-transferred structure for [**9h** $\delta^- \cdots$ **1** δ^+]. Despite the higher positive

(23) Murov, S. L.; *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 207.

(a) **9a** (grey) and **9h** (black) in pentane(b) **9h** in pentane (black) and toluene (grey)**Figure 7.** Energy diagram for sensitizers **9a** and **9h** and their exciplexes with **1** in pentane and toluene at 25 °C.

charge developed on the substrate moiety, the rate of methanol addition (k_a) to $[9h^{\delta-}\cdots 1^{\delta+}]$ is accelerated only by a factor of 1.2–1.9 as compared to $[9a^{\delta-}\cdots 1^{\delta+}]$. In this context, the minimal differences in stability and polarity between the diastereomeric exciplex pair are not expected to be able to differentiate the rate of methanol attack on each of the diastereomers. We may therefore conclude that the relative stability (K_{exR}/K_{exS}) is the major source of the observed enantioselectivity in the present asymmetric photoaddition.

Conclusions

In this comprehensive study on the enantiodifferentiating photochemical polar addition of alcohols to 1,1-diphenyl-1-alkenes sensitized by chiral naphthalene(di)carboxylates, we have revealed several novel mechanistic and synthetic findings of general significance and applicability in discussing and designing uni- and bimolecular asymmetric photochemical reactions, as outlined below.

(1) The “unusual” temperature dependence, giving higher op/ee 's at elevated temperatures, and the “unprecedented” switching of product chirality by temperature in a bimolecular process, both of which were reported originally for the enantiodifferen-

tiating geometrical photoisomerizations of cyclooctenes, are neither strange, uncommon behavior nor specific to the unimolecular photoreactions, but are natural consequences of the entropic contribution to the enantiodifferentiating processes in uni- and bimolecular asymmetric photochemical reactions. This enables us to use the entropic term as a convenient, versatile tool for controlling a wide variety of asymmetric photochemical reactions which are governed by the weak interactions in the exciplex intermediates.

(2) The tradeoff relationship between chemical and optical yields, which was frequently observed in previous work and thought to be unavoidable, can be overcome by optimizing the internal and external factors such as sensitizer's chromophore and chiral auxiliary, substrate and reagent structures, solvent polarity, and reaction temperature. In particular, the use of saccharides as chiral auxiliaries enhances the chemical and optical yields through the increased microenvironmental polarity, as proven by the increased exciplex fluorescence shift.

(3) The detailed reaction and enantiodifferentiation mechanism and the intermediates involved in the enantiodifferentiating polar photoaddition have been elucidated by extensive fluorescence quenching experiments. The kinetics and energetics, as well as the origin of enantiodifferentiation, that have been revealed for the first time for such a bimolecular asymmetric photochemical reaction are a good basis for the future development of this relatively unexplored area of photochemistry.

Experimental Section

General. Melting points were measured with a YANACO MP-300 apparatus and are uncorrected. 1H NMR spectra were obtained on a JEOL GX-400 spectrometer in chloroform-*d*. Infrared spectra were obtained on a JASCO Report-100 instrument. Electronic absorption and fluorescence spectra were recorded on JASCO V-550 and FP-777 instruments, respectively. Optical rotations were determined at 589 nm in a thermostated conventional 10 cm cell, using a JASCO DIP-1000 polarimeter.

Fluorescence lifetimes were measured with a 0.01 mM solution of sensitizers in nondegassed pentane, methylcyclohexane, or toluene by means of the time-correlated single-photon-counting method on a Horiba NAES-1100 instrument equipped with a pulsed H_2 light source. The radiation from the lamp was made monochromatic by a 10 cm monochromator, and the emission from sample solution was detected through a Toshiba UV-37 or L-42 filter.

Quantum yields for the product **4a**, formed upon sensitization with **7a–12a**, were determined at 313 nm using a 2-hexanone actinometer.^{23,24} A pentane solution of 2-hexanone, the concentration of which was varied from 0.4 to 4.0 M in order to match the absorbance of the relevant sensitizer at 313 nm, and a pentane solution of **1a** (20 mM) containing **7a–12a** (3 mM) and methanol (0.5 M) were prepared, divided into several portions, degassed with argon, and irradiated at 313 nm at 25 °C for several different periods in a merry-go-round apparatus. The quantum yield of **4a** was determined by assuming the quantum yield for the formation of acetone from 2-hexanone to be 0.22, as reported in the literature.^{23,24}

Optical purities of **4a** were determined by the comparison of specific rotation with that of the authentic sample prepared independently.²⁵ Enantiomeric excesses of **4a–d**, **5a, b**, and **6a** were determined by gas chromatography over a 15 m chiral capillary column (TCI Chiraldex B-DA) at 145 °C, using a Shimadzu GC-14B instrument. All GC peaks were integrated with a Shimadzu C-R6A integrator connected to the GC instrument.

Materials. Pentane and methylcyclohexane used as solvents were stirred over concentrated sulfuric acid until the acid layer no longer turned yellow, washed with water, neutralized with aqueous sodium

(24) Wagner, P. J., *Tetrahedron Lett.* **1968**, 5385.

(25) Haller, R.; Schneider, H. J. *Arch. Pharm. (Weinheim, Ger.)* **1973**, *306*, 846.

hydrogen carbonate, dried over sodium sulfate, and then distilled fractionally. Toluene and alcohols were fractionally distilled from melting sodium and magnesium turnings, respectively.

1,1-Diphenyl-1-alkenes **1–3** were synthesized by dehydration of the corresponding 1,1-diphenyl-1-alkanols, which were prepared by the Grignard reactions of the corresponding ketones with the appropriate alkyl bromides. 1,1-Diphenylpropene (**1**): mp 48.0–48.5 °C (lit.²⁶ 48.5–49.0 °C); ¹H NMR (CDCl₃) δ 1.76 (d, *J* = 6.8 Hz, 3H), 6.17 (q, *J* = 7.3 Hz, 1H), 7.17–7.39 (m, 10H). 1,1-Diphenyl-1-butene (**2**): ¹H NMR (CDCl₃) δ 1.02 (t, *J* = 7.4 Hz, 3H), 1.99–2.17 (m, 2H), 6.06 (t, *J* = 7.3 Hz, 1H), 7.00–7.52 (m, 10H). 1,1-Diphenyl-3-methyl-1-butene (**3**): ¹H NMR (CDCl₃) δ 1.02 (d, *J* = 6.6 Hz, 6H), 2.44–2.49 (m, 1H), 5.90 (d, *J* = 9.9 Hz, 1H), 7.11–7.50 (m, 10H).

Most optically active alcohols employed were commercially available: (–)-menthol, (+)-isomenthol, and (–)-borneol from TCI; (+)-neomenthol from Aldrich; and (–)-2-octanol from Nakarai. Optically pure (–)-8-phenylmenthol was synthesized from (+)-(*5R*)-pulegone according to the procedures reported by Corey et al.:²⁷ [α]_D²⁵ –22.5° (c 1.92, EtOH) (lit.^{27b} [α]_D²⁵ –26.3° (c 2.30, EtOH)).

Sugar derivatives were prepared from D-glucose and D-fructose according to the procedures reported by Glen et al.²⁸ and Kang et al.,²⁹ respectively. 1,2:5,6-Di-*O*-isopropylidene-α-D-glucopyranose: [α]_D²⁵ –17.2° (c 0.80, H₂O); ¹H NMR (CDCl₃) δ 1.32 (s, 3H), 1.37 (s, 3H), 1.45 (s, 3H), 1.50 (s, 3H), 2.50 (d, *J* = 3.9 Hz, 1H), 3.98 (dd, *J* = 3.4, 5.4 Hz, 1H), 4.07 (dd, *J* = 2.4, 4.8 Hz, 1H), 4.18 (dd, *J* = 2.4, 6.4 Hz, 1H), 4.26–4.37 (m, 2H), 4.54 (d, *J* = 3.4 Hz, 1H), 5.94 (d, *J* = 3.9 Hz, 1H). 1,2:4,5-Di-*O*-isopropylidene-β-D-fructopyranose: [α]_D²⁵ –154.6° (c 1.10, acetone) (lit.²⁹ [α]_D²⁸ –156.6° (c 1.00, acetone)); mp 112–113 °C (lit.²⁹ 117.5–118 °C); ¹H NMR (CDCl₃) δ 1.34 (s, 3H), 1.42 (s, 3H), 1.49 (s, 3H), 1.51 (s, 3H), 3.64 (d, *J* = 6.8 Hz, 1H), 3.97 (t, *J* = 8.8 Hz, 1H), 4.06–4.21 (m, 4H).

Optically active naphthalenedicarboxylates employed as chiral sensitizers were prepared from the corresponding alcohols and acid chloride in pyridine; see Supporting Information for the relevant physical properties and spectral data.

Photolysis. All irradiations were carried out in a temperature-controlled water (25 °C), methanol/2-propanol (–40 °C), and methanol/ethanol (–68 °C) bath. The light sources employed were a conventional 300 W high-pressure mercury lamp for irradiations at 25 °C and an equivalent lamp fitted with a transparent Pyrex vacuum sleeve designed for low-temperature irradiation (Eikosha). A solution (4 or 300 mL), containing 1,1-diphenylalkene **1–3** (20 mM), alcohol (0.5 mM), optically active sensitizer **7–12** (3 mM), and cyclododecane (3 mM) added as an internal standard, was irradiated at >300 nm under an argon atmosphere in a Pyrex tube (1 cm i.d.) placed near the lamp surface or in an annular Pyrex vessel surrounding the lamp, the whole system being immersed in the cooling bath.

Product Isolation. In preparative runs using an annular vessel (300 mL), the photolyzed solutions of **1–3** were first subjected to column chromatography over silica gel with an ethyl acetate/hexane (3:97)

(26) Serijan, K. T.; Wise, P. H. *J. Am. Chem. Soc.* **1951**, *73*, 4766.

(27) (a) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908. (b) Ensley, H. E.; Parnell, C. A.; Corey, E. J. *J. Org. Chem.* **1978**, *43*, 1610.

(28) Glen, W. L.; Gordon, S. M.; Barber, R. J.; Grant, G. A. *Am. Horne. Product. Corp.* **1955**, Aug, 9.

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eluent and then to the preparative GC over SE-30 to give chemically pure adducts **4a–d**, **5a,b**, and **6a**. No traces of fragments derived from the decomposition of the chiral sensitizer were detected on GC or NMR in the isolated products.

1,1-Diphenyl-2-methoxypropane (**4a**): ¹H NMR (CDCl₃) δ 1.11 (d, *J* = 5.9 Hz, 3H), 3.27 (s, 3H), 3.88 (d, *J* = 8.3 Hz, 1H), 3.92–4.19 (m, 1H), 7.11–7.36 (m, 10H) (lit.¹⁷ δ 1.08 (d, *J* = 6.0 Hz, 3H), 3.23 (s, 3H), 3.87 (d, *J* = 8.5 Hz, 1H), 4.01 (dq, 1H), 7.1–7.4 (m, 10H)).

1,1-Diphenyl-2-ethoxypropane (**4b**): ¹H NMR (CDCl₃) δ 0.86 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H), 3.04 (m, 1H), 3.35 (m, 1H), 3.75–3.86 (m, 1H), 3.92 (d, *J* = 8.1 Hz, 1H), 7.03–7.39 (m, 10H); IR (neat) ν 3060, 3030, 2970, 2930, 2860, 1600, 1580, 1490, 1450, 1370, 1130, 1080, 1030, 960, 760, 740, 700 cm^{–1}. HRMS Calcd for C₁₇H₂₀O (M⁺): 240.1513. Found: 240.1514.

1,1-Diphenyl-2-propoxypropane (**4c**): ¹H NMR (CDCl₃) δ 0.67 (t, *J* = 7.7 Hz, 3H), 1.06 (d, *J* = 5.9 Hz, 3H), 1.37 (m, 2H), 3.07 (m, 1H), 3.43 (m, 1H), 3.83 (d, *J* = 8.8 Hz, 1H), 4.04 (m, 1H), 7.05–7.36 (m, 10H); IR (neat) ν 3070, 3030, 2970, 2930, 2870, 1660, 1600, 1580, 1490, 1450, 1370, 1330, 1280, 1250, 1130, 1100, 1030, 1000, 940, 910, 760, 740, 700 cm^{–1}. HRMS calcd for C₁₈H₂₂O (M⁺): 254.1670. Found: 254.1675.

1,1-Diphenyl-2-isopropoxypropane (**4d**): ¹H NMR (CDCl₃) δ 0.73 (d, *J* = 6.2 Hz, 3H), 1.02 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H), 3.31 (m, 1H), 3.79 (d, *J* = 8.8 Hz, 1H), 4.07 (m, 1H), 7.05–7.40 (m, 10H); IR (neat) ν 3060, 3030, 2970, 2930, 2900, 1600, 1580, 1490, 1450, 1370, 1320, 1180, 1120, 1090, 1030, 990, 940, 900, 760, 740, 700 cm^{–1}. HRMS calcd for C₁₈H₂₂O (M⁺): 254.1670. Found: 254.1677.

1,1-Diphenyl-2-methoxybutane (**5a**): ¹H NMR (CDCl₃) δ 0.85 (t, *J* = 7.3 Hz, 3H), 1.25–1.60 (m, 2H), 3.12 (s, 3H), 3.79 (m, 1H), 3.94 (d, *J* = 8.4 Hz, 1H), 7.05–7.36 (m, 10H); IR (neat) ν 3060, 3030, 2960, 2940, 2880, 2820, 1600, 1580, 1490, 1450, 1370, 1270, 1190, 1130, 1100, 1080, 1030, 940, 750, 740, 700 cm^{–1}. HRMS calcd for C₁₇H₂₀O (M⁺): 240.1513. Found: 240.1517.

1,1-Diphenyl-2-ethoxybutane (**5b**): ¹H NMR (CDCl₃) δ 0.90 (t, *J* = 7.3 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H), 1.27–1.60 (m, 2H), 3.08 (m, 1H), 3.39 (m, 1H), 3.86 (m, 1H), 3.96 (d, *J* = 8.1 Hz, 1H), 7.08–7.42 (m, 10H); IR (neat) ν 3060, 3030, 2970, 2940, 2880, 1600, 1580, 1490, 1450, 1370, 1100, 1080, 1030, 980, 760, 740, 700 cm^{–1}. HRMS calcd for C₁₈H₂₂O (M⁺): 254.1670. Found: 254.1666.

1,1-Diphenyl-2-methoxy-3-methylbutane (**6a**): ¹H NMR (CDCl₃) δ 0.87 (d, *J* = 6.2 Hz, 6H), 1.09 (d, *J* = 7.0 Hz, 1H), 2.98 (s, 3H), 3.54 (dd, *J* = 4.4, 8.4 Hz, 1H), 4.00 (d, *J* = 8.1 Hz, 1H), 7.03–7.51 (m, 10H).

Acknowledgment. We are grateful to Dr. Simon Everitt for discussion, corrections, and improvements arising from preliminary reading of this manuscript.

Supporting Information Available: Melting points, specific rotations, ¹H NMR, UV, IR, MS spectra, and the elemental analysis data of all photosensitizers and the fluorescence excitation spectra of **9a** and **9h** in the presence/absence of 1,1-diphenylpropene (**1**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA9909374