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Microenvironmental Polarity Control of Electron-Transfer Photochirogenesis. Enantiodifferentiating Polar Addition of 1,1-Diphenyl-1-alkenes Photosensitized by Saccharide Naphthalenecarboxylates

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Abstract: Enantiodifferentiating polar photoaddition of alcohol to 1,1-diphenylpropene and 1,1-diphenyl-1-butene sensitized by saccharide naphthalene(di)carboxylates was performed in nonpolar to polar solvents containing methanol, ethanol, or 2-propanol as the nucleophile to give the corresponding anti-Markovnikov alcohol adduct, that is, 1,1-diphenyl-2-alkoxy-propane and -butane in low-to-good chemical yields, depending on the sensitizer, chiral auxiliary, alcohol, solvent, and temperature employed. The excited state and intermediate involved, the reaction and enantiodifferentiation mechanism operating, and the factors controlling chemical and optical yields were elucidated from the photochemical and stereochemical outcomes under various conditions and also from the sensitizer and exciplex fluorescence quenching experiments and the molecular orbital calculations. A new strategy was developed to overcome the normally accepted tradeoff between the chemical and optical yields. This is made possible by employing protected saccharides as chiral auxiliaries and running the photoreactions not in a nonpolar but in a low-polarity solvent such as diethyl ether, which jointly enhance the "microenvironmental" polarity around the sensitizer to facilitate electron transfer, keeping the intimate interactions between the chiral sensitizer and substrate within the exciplex intermediate. By optimizing these factors, we obtained the photoadduct in enantiomeric excesses of up to 58%, which is the highest ever reported for a photosensitized bimolecular enantiodifferentiating reaction.

Introduction

Among various photochirogenesis methodologies, asymmetric photosensitization provides us with the most convenient, versatile, and chirogen-efficient route to the transfer and multiplication of molecular chirality through the electronically excited state[1] and has therefore been attracting significant attention from mechanistic and synthetic (photo)chemists.[1−13] This is remarkable considering that it has only been a relatively short time since the enantiodifferentiating photoisomerization of (*Z*)-cyclooctene sensitized by chiral benzenecarboxylates was found to afford the chiral (*E*)-isomer in an enantiomeric excess (ee) of up to 40%,[5e] not only exceeding the original 7% ee reported by Hammond and Cole[2] but also demonstrating that significant enantiodifferentiation can be achieved in the excited state. We have also revealed that the product chirality can be inverted simply by changing temperature,[5d−j] pressure,[5k] or solvent polarity.[5m] Analogous photosensitization of (*Z*)-cyclo-

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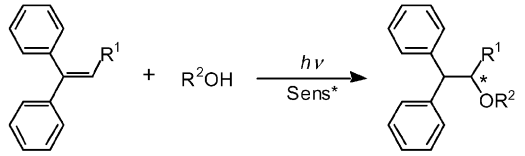
Scheme 1



1: R^1 = Me **a**: R^2 = Me **3a-c**
2: R^1 = Et **b**: R^2 = Et **4a-c**
c: R^2 = *i*Pr

heptene affords the chiral (*E*)-isomer, which is trapped by 1,3-diphenylisobenzofuran, in high ee's of up to 77%.[5l]

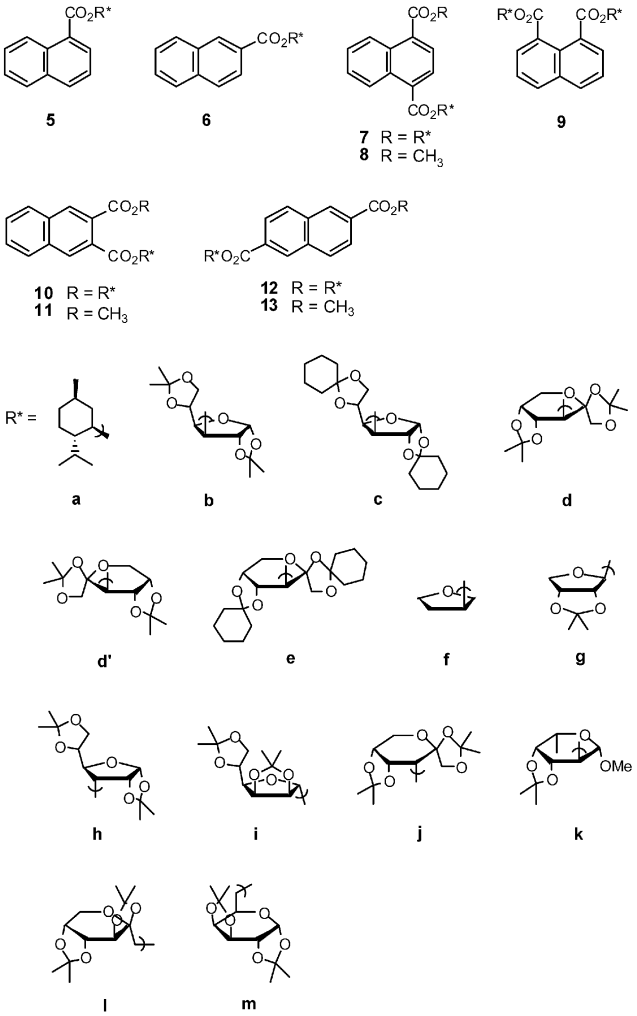
In sharp contrast to the rapidly growing interest and insight, as well as obtained ee, in enantiodifferentiating photosensitization of unimolecular isomerization processes, the investigation and knowledge of bimolecular photoaddition processes are lacking in both depth and variety, which renders our understanding and control of such photoenantiodifferentiation insufficient. In light of this, the enantiodifferentiating [2 + 2] photocyclodimerizations of aryl vinyl ethers and 4-methoxystyrene were examined in the presence of chiral naphthalene-(di)carboxylates, giving the corresponding cyclodimers in extremely low ee's (<1%).[14a] However, Kim and Schuster reported product ee's of up to 15% for 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.[15]

More recently, we have reported the enantiodifferentiating photocyclodimerization of cyclohexene sensitized by chiral benzene(poly)carboxylates.[14b] Of the two chiral cyclodimers obtained, only the *trans*−*anti*−*trans* isomer was optically active with good-to-high ee's of up to 68% at −68 °C. However, it has turned out that this photocyclodimerization is a stepwise photo/thermal process, which involves the initial enantiodifferentiating photoisomerization of the (*Z*)- to optically active (*E*)-cyclohexene, followed by the concerted thermal cycloaddition to the (*Z*)-isomer.[14b]

The "real" enantiodifferentiating bimolecular photocycloaddition, which involves the termolecular sensitizer−substrate−reagent interaction in the excited state, was observed in the enantiodifferentiating competitive [4 + 2] and [2 + 2] photocyclodimerization of 1,3-cyclohexadiene sensitized by chiral arene(poly)carboxylates.[14c] Among the three chiral cyclodimers obtained, only *exo*-[4 + 2] cyclodimer was optically active, with 8% being the best ee obtained at −41 °C.

Apart from the photocycloaddition reactions mentioned above, the enantiodifferentiating polar addition of alcohols to 1,1-diphenyl-1-alkenes (**1** and **2**) (Scheme 1) sensitized by chiral naphthalene(di)carboxylates (**5**−**7**, **9**, **10**, and **12**; **a**, **b**, and **d**)

Chart 1. Chiral Sensitizers



(Chart 1) was also investigated.[16] As is the case with the enantiodifferentiating photoisomerization of cycloalkenes,[5] unusual switching of product chirality was induced by changing the irradiation temperature, affording the antipodal products, often with higher ee's at higher temperatures. Furthermore, an essentially new strategy was developed to overcome the tradeoff between the chemical and optical yields, which is a commonly encountered drawback in asymmetric photoreactions via electron transfer.[14a,16a] This was accomplished by introducing polar chiral auxiliaries in the sensitizer molecule, which enhance the "microenvironmental polarity" around the chromophore without increasing the bulk polarity of solvent. The enhanced local polarity around the sensitizer molecule facilitates electron transfer from the substrate to give a chiral radical ion pair, dissociation of which is, however, discouraged by the low bulk polarity, and hence the chiral information is effectively transferred from the sensitizer to substrate within the confined radical ion pair. For that purpose, two protected saccharides, diisopropylideneglucose and diisopropylidenefructose (**b** and **d** in Chart 1), were employed as polar chiral auxiliaries, affording improved ee's of 29−33% in good chemical yields.[16b] However, the scope and limitations of this novel and potentially versatile strategy

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have not been extensively explored, and only a limited search for better chiral saccharide auxiliaries has been made.[14c]

In the present study, we wish to demonstrate more clearly the roles of the polar chiral auxiliaries incorporated in various naphthalene sensitizers, elucidate the factors and mechanisms controlling the enantiodifferentiating photoaddition to 1,1-diphenyl-1-alkenes (**1**), and eventually optimize the product ee by expanding the range of the chiral saccharide auxiliaries and their protective groups as well as the sensitizer structures (Chart 1). The detailed reaction mechanism and the origin of the enantiodifferentiation were fully elucidated from steady-state and time-resolved fluorescence quenching experiments, and the vital role of the "microenvironmental polarity" around the chromophore on the enantiodifferentiating mechanism, as well as the chemical and optical yields, was unequivocally proved by investigating the effect of solvent polarity and alcohol concentration.

Results and Discussion

Naphthalenecarboxylate Sensitizers. We synthesized a wide variety of new naphthalene(di)carboxylates **5**−**13** with menthyl (**a**) and protected saccharide auxiliaries (**b**−**m**), illustrated in Chart 1. The photosensitized enantiodifferentiating addition of methanol to 1,1-diphenylpropene **1** (20 mM) was performed in methylcyclohexane and diethyl ether, containing 0.5 M methanol, at temperatures ranging from −68 to +60 °C. The anti-Markovnikov adduct **3a** was obtained as the sole detectable product in moderate-to-good yields with varying ee's. The product ee remained constant throughout the irradiation period in all cases examined; this indicates that the photosensitized addition of methanol to **1** is irreversible and the product (**3a**) is not subject to any further reactions under the conditions employed. Hence, the irradiation period was fixed at 4, 24, or 48 h in most runs. The chemical and optical yields of the photoproduct, determined by chiral stationary-phase gas chromatography, are summarized in Table 1. The sign of the ee value represents the direction of the product's optical rotation; that is, a negative value indicates the formation of (*S*)-(−)-**3a** as the major enantiomer.

As can be seen from Table 1, the chemical yield is a critical function of the position and number of ester group(s) introduced to sensitizing naphthalene. Sensitizations with 1-, 2-, 1,8-, and 2,3-naphthalene(di)carboxylates **5**, **6**, **9**, and **10**/**11** (entries 1−76 and 214−301) give only low-to-moderate conversions (mostly <50%) even after 48 h with low chemical yields (mostly <10%), irrespective of the alcohol residue (**a**−**e**) employed; the low mass balance, particularly in ether solution, may be attributable to the formation of cross-adduct with sensitizers or unidentified oligomeric products, as no volatile monomeric products could be detected by GC. In contrast, 1,4- and 2,6-naphthalenedicarboxylates **7**/**8** and **12**/**13** with chiral auxiliaries **a**−**m** (entries 77−213 and 302−399) afforded the adduct in high conversions (mostly 50−99%) and moderate-to-good yields (mostly 20−86%). The critical difference in chemical yield is reasonably accounted for in terms of the Rehm−Weller's free-energy change (ΔG_{et})[17] for the electron transfer, except for the 1,8-naphthalenedicarboxylates. The ΔG_{et} values, determined from the oxidation potential of **1**, the reduction potentials (E_{red}), and fluorescence 0−0 bands (λ_{0-0}) of the relevant sensitizers (Table 2), are less negative or even positive for 1-, 2-, and 2,3-naphthalene(di)carboxylates **5**, **6**, and **10** ($\Delta G_{et} = -3.87$ to 2.14 kcal/mol), but are moderately-to-highly negative for 1,4- and 2,6-naphthalenedicarboxylates **7** and **12** ($\Delta G_{et} = -7.06$ to −2.06 kcal/mol), which more greatly facilitate the electron transfer.

The chemical yield is also affected by the structure of chiral auxiliary. The naphthalenedicarboxylate sensitizers with saccharide moieties **b**−**e** afford the adducts in yields appreciably higher than the corresponding menthyl ester (**a**), particularly in less polar solvents. This observation is rationalized by the more negative ΔG_{et} (by 1.2−3.0 kcal/mol) of the saccharide esters (**b** and **d**) in comparison to the corresponding menthyl ester (**a**) with higher E_{red}. This clearly indicates that the saccharide auxiliaries enhance the "microenvironmental polarity" around the sensitizer, lower the E_{red}, and eventually facilitate the electron transfer from substrate to excited sensitizer.

Similar sensitizations with highly congested 1,8-naphthalenedicarboxylates **9a**−**e** lead to much lower conversions and yields (Table 1, runs 214−247), despite the highly negative ΔG_{et} values (Table 2). In particular, the sensitizers with fructopyranose (**9d**/**e**) rather than glucofranose moieties (**9b**/**c**) consistently afford significantly lower conversions and chemical yields. Probably, the steric hindrance of the dual peri-substitution and the bulky saccharide moiety (in particular, the tertiary substitution at the C-1 of fructopyranose) jointly prevent the close approach of substrate to the naphthalene chromophore, which is indispensable for efficient electron transfer needed to generate the substrate radical cation. It is thus revealed that the photoreactivity is significantly enhanced by increased "microenvironmental polarity" around the saccharide moieties, facilitating the electron transfer and therefore adduct formation. Conversely, too bulky chiral auxiliaries introduced to the sensitizer decelerate the electron transfer to give low conversions and yields, although the product ee's are moderately high (25−30%), particularly for **9b**,**c** (Table 1).

The product ee's obtained in the present study are relatively good for such a polar photoaddition reaction involving a radical ionic intermediate and are highly dependent on the position and structure of the chiral ester moieties introduced to naphthalene. The saccharide, rather than menthyl esters, give better ee's in most cases. In contrast to the poor performance of chiral benzoate sensitizers in the enantiodifferentiating photoisomerization of cyclooctene,[5] even the simple monoesters **5** and **6** give moderate ee's of up to 16−24%. The use of diesters **7**−**13** leads to better ee's in most cases; thus, the enantiodifferentiating photosensitization with 2,6-naphthalenedicarboxylate **12d** affords the methanol adduct **3a** with the highest ee of 35% in diethyl ether at 0 °C (entry 332). Except for the 1,8-naphthalenedicarboxylate cases (**9b**−**e**), the fructose (**d** and **e**) esters give better ee's than do the corresponding glucose (**b** and **c**) esters. In contrast, for the 1,8-naphthalenedicarboxylate cases, the fructose esters **9d**,**e** give only poor ee's (mostly 0−5%) with low conversions and yields, while the glucose esters **9b**,**c** afford much higher ee's of up to 25−30% in better yields. The steric hindrance of the bulky fructose auxiliaries in **9d**,**e** may prevent the intimate interaction between substrate and sensitizer, giving

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Table 1. Enantiodifferentiating Photoaddition of Methanol to 1,1-Diphenylpropene **1** Sensitized by Chiral Naphthalene(di)carboxylates **5**−**10**[a]

entry	solvent	temp/°C	*t*/h[b]	conv[c]/%	yield[d]/%	ee[e]/%	entry	solvent	temp/°C	*t*/h[b]	conv[c]/%	yield[d]/%	ee[e]/%
						5a							
1	methylcyclohexane[f]	25	24	10	1	−2.6	4	diethyl ether	0	48	40	4	−7.4
2	methylcyclohexane	−68	48	7	2	−1.5	5	diethyl ether	−40	48	44	5	−7.5
3	diethyl ether	25	24	40	3	−9.1	6	diethyl ether	−68	48	35	4	−12.0
						5b							
7	methylcyclohexane	60	24	36	10	−9.7	11	diethyl ether	25	24	55	9	−12.9
8	methylcyclohexane	25	24	15	5	−7.1	12	diethyl ether	0	48	51	9	−12.7
9	methylcyclohexane	−40	48	16	3	−3.2	13	diethyl ether	−40	48	53	8	−11.4
10	methylcyclohexane	−68	48	11	2	−2.3	14	diethyl ether	−68	48	39	7	−11.9
						5c							
15	methylcyclohexane	60	24	33	11	−7.7	19	diethyl ether	25	24	34	7	−7.6
16	methylcyclohexane	25	24	35	13	−6.3	20	diethyl ether	0	48	47	7	−6.1
17	methylcyclohexane	−40	48	40	14	−5.4	21	diethyl ether	−40	48	32	8	−5.5
18	methylcyclohexane	−68	48	23	5	−1.5	22	diethyl ether	−68	48	25	6	−3.2
						5d							
23	methylcyclohexane	60	24	31	5	−8.6	27	diethyl ether	25	24	41	6	−16.0
24	methylcyclohexane	25	24	13	3	−6.3	28	diethyl ether	0	48	40	7	−16.1
25	methylcyclohexane	−40	48	5	2	−1.2	29	diethyl ether	−40	48	48	7	−8.1
26	methylcyclohexane	−68	48	5	<1	+0.7	30	diethyl ether	−68	48	39	6	+0.1
						5e							
31	methylcyclohexane	60	24	22	5	−8.5	35	diethyl ether	25	24	46	5	−15.5
32	methylcyclohexane	25	24	14	3	−4.3	36	diethyl ether	0	48	45	6	−13.8
33	methylcyclohexane	−40	48	12	1	−2.4	37	diethyl ether	−40	48	43	7	−7.1
34	methylcyclohexane	−68	48	<3	<1	−2.2	38	diethyl ether	−68	48	42	6	+5.2
						6a							
39	methylcyclohexane[f]	25	24	<3	1	−5.2	42	diethyl ether	0	48	32	2	−7.9
40	methylcyclohexane	−68	48	<3	<1	−4.3	43	diethyl ether	−40	48	29	2	−6.5
41	diethyl ether	25	24	21	2	−4.0	44	diethyl ether	−68	48	30	2	−9.3
						6b							
45	methylcyclohexane	60	24	25	7	−15.9	49	diethyl ether	25	24	34	3	−12.5
46	methylcyclohexane	25	24	17	4	−17.1	50	diethyl ether	0	48	35	4	−14.2
47	methylcyclohexane	−40	48	31	4	−8.6	51	diethyl ether	−40	48	37	4	−22.6
48	methylcyclohexane	−68	48	23	2	−7.2	52	diethyl ether	−68	48	41	5	−22.3
						6c							
53	methylcyclohexane	60	24	15	3	−20.1	57	diethyl ether	25	24	8	2	−14.2
54	methylcyclohexane	25	24	22	4	−19.5	58	diethyl ether	0	48	12	2	−18.0
55	methylcyclohexane	−40	48	27	5	−17.8	59	diethyl ether	−40	48	16	2	−23.0
56	methylcyclohexane	−68	48	22	2	−8.5	60	diethyl ether	−68	48	21	3	−23.8
						6d							
61	methylcyclohexane	60	24	18	4	−13.7	65	diethyl ether	25	24	34	2	−16.4
62	methylcyclohexane	25	24	11	3	−13.4	66	diethyl ether	0	48	38	3	−19.9
63	methylcyclohexane	−40	48	25	5	+0.9	67	diethyl ether	−40	48	35	3	−23.1
64	methylcyclohexane	−68	48	13	2	+6.8	68	diethyl ether	−68	48	35	4	−16.9
						6e							
69	methylcyclohexane	60	24	16	4	−13.4	73	diethyl ether	25	24	30	2	−16.1
70	methylcyclohexane	25	24	10	2	−12.0	74	diethyl ether	0	48	39	3	−18.0
71	methylcyclohexane	−40	48	25	4	+4.4	75	diethyl ether	−40	48	38	3	−18.8
72	methylcyclohexane	−68	48	10	2	+11.4	76	diethyl ether	−68	48	38	4	−11.1
						7a							
77	methylcyclohexane[f]	25	24	82	53	−4.0	91	*t*-butyl methyl ether	50	24	70	15	−2.0
78	methylcyclohexane	−40	48	60	25	−12.2	92	*t*-butyl methyl ether	25	24	67	15	−2.2
79	diethyl ether	25	24	80	21	−4.1	93	*t*-butyl methyl ether	−40	48	71	14	−2.2
80	diethyl ether	0	48	71	22	−4.9	94	*t*-butyl methyl ether	−68	48	64	14	−6.1
81	diethyl ether	−40	48	70	17	−7.1	95	ethyl acetate	60	24	75	21	−2.8
82	diethyl ether	−68	48	88	21	−10.5	96	ethyl acetate	25	24	73	24	−2.2
83	diisopropyl ether	60	24	57	14	−3.8	97	ethyl acetate	−40	48	78	29	−3.3
84	diisopropyl ether	25	24	58	14	−3.3	98	ethyl acetate	−68	48	62	20	−7.1
85	diisopropyl ether	−40	48	49	13	−9.7	99	butyl acetate	60	24	74	25	−3.0
86	diisopropyl ether	−68	48	45	13	−16.5	100	butyl acetate	25	24	74	29	−2.0
87	dibutyl ether	60	24	71	33	−3.7	101	butyl acetate	−40	48	80	36	−6.9
88	dibutyl ether	25	24	66	32	−4.3	102	butyl acetate	−68	48	38	16	−7.2
89	dibutyl ether	−40	48	60	26	−14.0	103	acetonitrile	25	24	>99	71	−0.3
90	dibutyl ether	−68	48	40	14	−16.7	104	acetonitrile	−40	48	>99	76	−0.9
						7b							
105	methylcyclohexane[f]	25	24	85	59	−8.7	108	diethyl ether	0	48	83	22	−15.5
106	methylcyclohexane	−40[g]	48	49	20	−3.5	109	diethyl ether	−40	48	82	17	−12.1
107	diethyl ether	25	24	80	27	−14.9	110	diethyl ether	−68	48	86	24	−9.8

Table 1. (Continued)

entry	solvent	temp/°C	t/h[b]	conv[c]/%	yield[d]/%	ee[e]/%	entry	solvent	temp/°C	t/h[b]	conv[c]/%	yield[d]/%	ee[e]/%
						7c							
111	methylcyclohexane	60	24	94	64	−8.4	115	diethyl ether	25	24	80	24	−11.3
112	methylcyclohexane	25	24	86	58	−7.7	116	diethyl ether	0	48	80	24	−10.3
113	methylcyclohexane	0	48	81	48	−7.1	117	diethyl ether	−40	48	77	13	−6.4
114	methylcyclohexane	−40	48	57	23	−3.3	118	diethyl ether	−68	48	74	12	−5.3
						7d							
119	methylcyclohexane[f]	25	24	82	54	−4.7	136	*t*-butyl methyl ether	25	24	81	29	−22.6
120	methylcyclohexane	−40[g]	48	17	3	+11.2	137	*t*-butyl methyl ether	−40	48	76	21	−14.9
121	diethyl ether	25	24	82	32	−27.0	138	*t*-butyl methyl ether	−68	48	61	21	−9.1
122	diethyl ether	25[h]	2	72	21	−21.7	139	ethyl acetate	60	24	98	45	−18.5
123	diethyl ether	25[i]	2	72	26	−23.0	140	ethyl acetate	25	24	97	49	−20.7
124	diethyl ether	0	48	82	30	−23.8	141	ethyl acetate	−40	48	96	49	−14.3
125	diethyl ether	−40	48	78	23	−18.9	142	ethyl acetate	−68	48	66	26	−6.4
126	diethyl ether	−68	48	79	27	−12.7	143	butyl acetate	60	24	99	53	−19.0
127	diisopropyl ether	60	24	68	33	−22.3	144	butyl acetate	25	24	>99	60	−18.7
128	diisopropyl ether	25	24	62	35	−21.3	145	butyl acetate	−40	48	89	58	−9.2
129	diisopropyl ether	−40	48	55	21	−7.8	146	butyl acetate	−68	48	36	20	−3.9
130	diisopropyl ether	−68	48	51	15	−1.1	147	acetonitrile[f]	25	24	>99	73	−0.4
131	dibutyl ether	60	24	90	61	−19.0	148	acetonitrile	−40	48	>99	73	−0.2
132	dibutyl ether	25	24	86	54	−17.2	149	methanol[j]	60	24	>99	74	−4.6
133	dibutyl ether	−40	48	66	34	+0.5	150	methanol[j]	25	24	>99	76	−4.4
134	dibutyl ether	−68	48	40	18	+0.7	151	methanol[j]	−40	48	>99	86	−4.5
135	*t*-butyl methyl ether	60	24	85	34	−22.4	152	methanol[j]	−68	48	>99	77	−6.6
						7d′							
153	diethyl ether	25	4	95	16	+21.2	155	diethyl ether	−40	24	80	20	+13.7
154	diethyl ether	0	24	82	21	+20.0	156	diethyl ether	−68	24	81	29	+6.9
						7e							
157	methylcyclohexane	60	24	99	70	−9.8	162	diethyl ether	25	24	83	28	−25.7
158	methylcyclohexane	40	24	93	64	−8.3	163	diethyl ether	0	48	84	31	−22.9
159	methylcyclohexane	25	24	95	71	−4.7	164	diethyl ether	−40	48	85	33	−16.0
160	methylcyclohexane	0[g]	48	83	58	+2.7	165	diethyl ether	−68	48	78	33	−9.2
161	methylcyclohexane	−40[g]	48	45	12	+11.7							
						7f							
166	diethyl ether	25	4	82	21	−0.6	168	diethyl ether	−40	24	96	43	−1.7
167	diethyl ether	0	24	85	27	−0.9	169	diethyl ether	−68	24	88	43	−2.7
						7g							
170	diethyl ether	25	4	78	17	−9.0	172	diethyl ether	−40	24	75	30	−12.4
171	diethyl ether	0	24	82	31	−8.3	173	diethyl ether	−68	24	79	24	−10.4
						7h							
174	diethyl ether	25	4	80	25	−6.1	176	diethyl ether	−40	24	76	39	−5.2
175	diethyl ether	0	24	92	47	−6.3	177	diethyl ether	−68	24	53	19	−0.7
						7i							
178	diethyl ether	25	4	81	21	−12.9	180	diethyl ether	−40	24	75	23	−16.8
179	diethyl ether	0	24	81	28	−13.9	181	diethyl ether	−68	24	73	29	−15.2
						7j							
182	diethyl ether	25	4	89	34	+7.0	184	diethyl ether	−40	24	97	26	+10.4
183	diethyl ether	0	24	>99	52	+8.8	185	diethyl ether	−68	24	73	37	+10.5
						7k							
186	diethyl ether	25	4	80	27	−11.4	188	diethyl ether	−40	24	68	24	−6.4
187	diethyl ether	0	24	86	41	−10.8	189	diethyl ether	−68	24	59	19	−2.9
						7l							
190	diethyl ether	25	4	80	30	+2.0	192	diethyl ether	−40	24	68	22	+1.1
191	diethyl ether	0	24	78	22	+2.4	193	diethyl ether	−68	24	68	26	+1.7
						7m							
194	diethyl ether	25	4	70	10	+1.7	196	diethyl ether	−40	24	53	11	+1.6
195	diethyl ether	0	24	70	17	+2.2	197	diethyl ether	−68	24	47	8	+1.6
						8b							
198	methylcyclohexane	60	24	90	59	−7.0	202	diethyl ether	25	24	78	26	−10.4
199	methylcyclohexane	25	24	86	53	−6.8	203	diethyl ether	0	48	77	26	−10.2
200	methylcyclohexane	−40	48	52	20	−3.8	204	diethyl ether	−40	48	72	23	−7.5
201	methylcyclohexane	−68[g]	48	40	17	−3.4	205	diethyl ether	−68	48	77	22	−7.9
						8d							
206	methylcyclohexane	60	24	85	57	−9.5	210	diethyl ether	25	24	74	28	−13.9
207	methylcyclohexane	25	24	89	64	−7.9	211	diethyl ether	0	48	73	22	−15.1
208	methylcyclohexane	−40	48	56	21	+3.8	212	diethyl ether	−40	48	76	23	−12.8
209	methylcyclohexane	−68[g]	48	42	16	+4.1	213	diethyl ether	−68	48	67	24	−11.3

Table 1. (Continued)

entry	solvent	temp/°C	*t*/h[b]	conv[c]/%	yield[d]/%	ee[e]/%	entry	solvent	temp/°C	*t*/h[b]	conv[c]/%	yield[d]/%	ee[e]/%
						9a							
214	methylcyclohexane[f]	25	24	<3	2	−9.4	217	diethyl ether	0	48	30	3	−14.9
215	methylcyclohexane	−40	48	11	2	−14.2	218	diethyl ether	−40	48	29	2	−16.6
216	diethyl ether	25	24	23	3	−14.5	219	diethyl ether	−68	48	20	2	−14.5
						9b							
220	methylcyclohexane	60	24	25	12	−25.7	224	diethyl ether	25	24	46	8	−15.4
221	methylcyclohexane	25	24	12	5	−24.6	225	diethyl ether	0	48	42	9	−14.4
222	methylcyclohexane	0	48	35	14	−29.9	226	diethyl ether	−40	48	43	7	−16.5
223	methylcyclohexane	−40[g]	48	22	8	−20.9	227	diethyl ether	−68	48	15	4	−9.4
						9c							
228	methylcyclohexane	60	24	27	9	−17.0	232	diethyl ether	25	24	22	5	−13.4
229	methylcyclohexane	25	24	28	9	−22.0	233	diethyl ether	0	48	28	6	−16.0
230	methylcyclohexane	0	48	32	10	−25.7	234	diethyl ether	−40	48	19	4	−15.9
231	methylcyclohexane	−40	48	10	4	−22.3	235	diethyl ether	−68	48	<3	1	−11.4
						9d							
236	methylcyclohexane	60	24	8	4	−2.2	239	methylcyclohexane	−40	48	<3	1	−1.4
237	methylcyclohexane	25	24	8	3	+0.1	240	diethyl ether	25	24	*k*	2	+2.7
238	methylcyclohexane	0	48	4	3	−2.5	241	diethyl ether	0	48	*k*	2	+9.5
						9e							
242	methylcyclohexane	60	24	6	3	−3.1	245	methylcyclohexane	−40	48	<3	<1	+4.2
243	methylcyclohexane	25	24	5	2	+0.3	246	diethyl ether	25	24	*k*	2	+5.4
244	methylcyclohexane	0	48	<3	2	+1.9	247	diethyl ether	0	48	*k*	2	+4.7
						10a							
248	methylcyclohexane[f]	25	24	6	2	−5.5	251	diethyl ether	0	48	38	2	−9.0
249	methylcyclohexane	−40	48	30	5	−3.9	252	diethyl ether	−40	48	39	3	−7.7
250	diethyl ether	25	24	34	3	−11.4	253	diethyl ether	−68	48	35	3	−8.1
						10b							
254	methylcyclohexane	60	24	43	16	−14.1	258	diethyl ether	25	24	53	10	−15.9
255	methylcyclohexane	25	24	26	11	−14.4	259	diethyl ether	0	48	35	4	−11.9
256	methylcyclohexane	0	48	57	22	−11.2	260	diethyl ether	−40	48	50	8	−12.3
257	methylcyclohexane	−40[g]	48	40	11	−7.4	261	diethyl ether	−68	48	54	9	−14.9
						10c							
262	methylcyclohexane	60	24	24	8	−9.5	266	diethyl ether	25	24	35	7	−13.4
263	methylcyclohexane	25	24	43	15	−7.6	267	diethyl ether	0	48	42	8	−12.8
264	methylcyclohexane	0	48	48	14	−8.2	268	diethyl ether	−40	48	33	5	−10.6
265	methylcyclohexane	−40	48	32	7	−5.2	269	diethyl ether	−68	48	18	3	−7.0
						10d							
270	methylcyclohexane	60	24	32	9	−10.3	274	diethyl ether	25	24	39	4	−12.5
271	methylcyclohexane	25	24	17	5	−8.9	275	diethyl ether	0	48	28	3	−9.9
272	methylcyclohexane	0	48	41	12	−7.3	276	diethyl ether	−40	48	38	3	−14.3
273	methylcyclohexane	−40[g]	48	28	5	−4.9	277	diethyl ether	−68	48	37	3	−13.0
						10e							
278	methylcyclohexane	60	24	20	6	−6.4	282	diethyl ether	25	24	*k*	2	−3.0
279	methylcyclohexane	25	24	19	5	−4.7	283	diethyl ether	0	48	*k*	2	−5.9
280	methylcyclohexane	0	48	20	5	−7.4	284	diethyl ether	−40	48	*k*	2	0.0
281	methylcyclohexane	−40	48	12	2	−6.5	285	diethyl ether	−68	48	*k*	1	+6.1
						11b							
286	methylcyclohexane	60	24	44	12	−16.9	290	diethyl ether	25	24	43	4	−15.4
287	methylcyclohexane	25	24	46	11	−16.8	291	diethyl ether	0	48	43	4	−17.4
288	methylcyclohexane	−40	48	34	4	−12.9	292	diethyl ether	−40	48	38	3	−16.9
289	methylcyclohexane	−68	48	25	2	−9.2	293	diethyl ether	−68	48	37	2	−11.3
						11d							
294	methylcyclohexane	60	24	33	6	−13.4	298	diethyl ether	25	24	38	2	−10.3
295	methylcyclohexane	25	24	40	8	−10.2	299	diethyl ether	0	48	37	2	−13.0
296	methylcyclohexane	−40	48	34	5	−7.3	300	diethyl ether	−40	48	33	2	−11.8
297	methylcyclohexane	−68	48	27	2	−2.5	301	diethyl ether	−68	48	28	2	−6.1
						12a							
302	methylcyclohexane[f]	25	24	39	12	−9.4	305	diethyl ether	0	48	58	9	−6.3
303	methylcyclohexane	−40	48	49	9	−8.6	306	diethyl ether	−40	48	59	9	−3.2
304	diethyl ether	25	24	54	7	−2.8	307	diethyl ether	−68	48	55	11	−2.8
						12b							
308	methylcyclohexane	60	24	67	23	−20.2	312	diethyl ether	25	24	55	13	−19.8
309	methylcyclohexane	25	24	50	18	−20.9	313	diethyl ether	0	48	58	13	−19.3
310	methylcyclohexane	0	48	59	16	−18.2	314	diethyl ether	−40	48	53	10	−13.2
311	methylcyclohexane	−40[g]	48	34	5	−12.2	315	diethyl ether	−68	48	51	12	−11.6

Table 1. (Continued)

entry	solvent	temp/°C	t/h[b]	conv[c]/%	yield[d]/%	ee[e]/%	entry	solvent	temp/°C	t/h[b]	conv[c]/%	yield[d]/%	ee[e]/%
						12c							
316	methylcyclohexane	60	24	62	21	−15.1	320	diethyl ether	25	24	55	8	−15.5
317	methylcyclohexane	25	24	59	22	−14.0	321	diethyl ether	0	48	56	9	−13.8
318	methylcyclohexane	0	48	58	19	−12.6	322	diethyl ether	−40	48	56	8	−8.6
319	methylcyclohexane	−40	48	44	8	−8.8	323	diethyl ether	−68	48	56	9	−5.3
						12d							
324	methylcyclohexane	60	24	58	19	−24.9	336	diisopropyl ether	25	24	27	5	−33.8
325	methylcyclohexane	40	24	52	18	−25.1	337	diisopropyl ether	−40	48	39	12	−23.8
326	methylcyclohexane	25	24	46	15	−26.2	338	diisopropyl ether	−68	48	34	12	−20.3
327	methylcyclohexane	0	48	68	25	−18.2	339	dibutyl ether	60	24	42	9	−28.8
328	methylcyclohexane	−40[g]	48	45	11	−12.6	340	dibutyl ether	25	24	48	14	−29.6
329	diethyl ether	25	24	54	12	−33.8	341	dibutyl ether	−40	48	67	33	−16.7
330	diethyl ether	25[h]	2	31	5	−34.1	342	dibutyl ether	−68	48	46	24	−8.6
331	diethyl ether	25[i]	2	33	4	−33.1	343	*t*-butyl methyl ether	60	24	46	6	−30.2
332	diethyl ether	0	48	57	15	−35.1	344	*t*-butyl methyl ether	25	24	47	7	−31.9
333	diethyl ether	−40	48	64	22	−32.6	345	*t*-butyl methyl ether	−40	48	52	11	−26.9
334	diethyl ether	−68	48	71	32	−28.5	346	*t*-butyl methyl ether	−68	48	50	18	−23.6
335	diisopropyl ether	60	24	23	3	−33.8							
						12d′							
347	diethyl ether	25	24	54	6	+30.5	349	diethyl ether	−40	48	64	9	+26.5
348	diethyl ether	0	48	61	6	+31.7	350	diethyl ether	−68	48	68	19	+22.7
						12e							
351	methylcyclohexane	60	24	49	14	−25.5	355	diethyl ether	25	24	54	9	−29.7
352	methylcyclohexane	25	24	44	17	−21.5	356	diethyl ether	0	48	52	12	−33.0
353	methylcyclohexane	0	48	68	23	−16.6	357	diethyl ether	−40	48	72	29	−24.9
354	methylcyclohexane	−40	48	47	11	−9.8	358	diethyl ether	−68	48	60	21	−23.5
						12f							
359	diethyl ether	25	24	43	5	−1.4	361	diethyl ether	−40	24	50	12	−6.1
360	diethyl ether	0	24	40	9	−2.4							
						12h							
362	diethyl ether	25	24	45	8	−13.5	364	diethyl ether	−40	24	53	16	−15.5
363	diethyl ether	0	24	47	9	−20.2	365	diethyl ether	−68	24	65	27	−9.1
						12i							
366	diethyl ether	25	24	58	5	−19.6	368	diethyl ether	−40[g]	24	38	1	−12.6
367	diethyl ether	0[g]	24	54	2	−17.9							
						12j							
369	diethyl ether	25	24	47	11	−12.5	371	diethyl ether	−40	24	54	16	−8.6
370	diethyl ether	0	24	45	11	−14.0	372	diethyl ether	−68	24	65	27	−7.2
						12k							
373	diethyl ether	25	24	41	5	−29.6	375	diethyl ether	−40	24	49	10	−26.0
374	diethyl ether	0	24	40	6	−33.0	376	diethyl ether	−68	24	52	14	−19.9
						12l							
377	diethyl ether	25	24	50	3	−0.3	379	diethyl ether	−40	24	56	4	+0.2
378	diethyl ether	0	24	52	4	+1.5	380	diethyl ether	−68	24	54	7	−1.2
						12m							
381	diethyl ether	25	24	38	5	−0.8	383	diethyl ether	−68	24	40	10	−2.5
382	diethyl ether	0	24	41	5	−0.1							
						13b							
384	methylcyclohexane	60	24	52	14	−18.3	388	diethyl ether	25	24	42	7	−19.6
385	methylcyclohexane	25	24	59	21	−17.2	389	diethyl ether	0	48	48	8	−17.7
386	methylcyclohexane	0[g]	48	39	6	−7.3	390	diethyl ether	−40	48	60	6	−14.3
387	methylcyclohexane	−40[g]	48	29	5	−4.8	391	diethyl ether	−68	48	49	9	−12.0
						13d							
392	methylcyclohexane	60	24	51	18	−18.1	396	diethyl ether	25	24	46	5	−19.0
393	methylcyclohexane	25	24	62	28	−16.8	397	diethyl ether	0	48	52	5	−20.4
394	methylcyclohexane	0	48	46	11	−7.7	398	diethyl ether	−40	48	57	13	−16.5
395	methylcyclohexane	−40[g]	48	41	11	−6.2	399	diethyl ether	−68	48	53	7	−18.2

[a] [**1**] = 20 mM; [sens*] = 3 mM; [MeOH] = 0.5 M, unless noted otherwise. [b] Irradiation time. [c] Loss of starting material determined by GC. [d] Chemical yield determined by GC on the basis of the initial concentration of **1**. [e] Enantiomeric excess determined by chiral GC. [f] Reference 16b. [g] [sens*] < 3 mM due to low solubility. [h] Irradiated under a 0 T magnetic field. [i] Under a 8 T magnetic field. [j] In neat methanol ([MeOH] ≈ 24.7 M). [k] Not determined by GC.

the low chemical and optical yields for **9d**,**e**. However, the more bulky cyclohexylidene protecting groups introduced to glucose or fructose (**9c**,**e**) do not appear to affect significantly the product ee, probably because the peripheral modification of the saccharide, which is distant from the chromophore, cannot influence the enantiodifferentiating process.

Hemichiral Sensitizers. For further insights into the "microenvironmental polarity" effect induced by the saccharide auxiliary, we performed the photosensitization with methyl, saccharide-mixed esters **8**, **11**, and **13** in methylcyclohexane and in ether. As can be seen from the results obtained for **8b**,**d** versus **7b**,**d**, **11b**,**d** versus **10b**,**d**, and **13b**,**d** versus **12b**,**d** (Table 1),

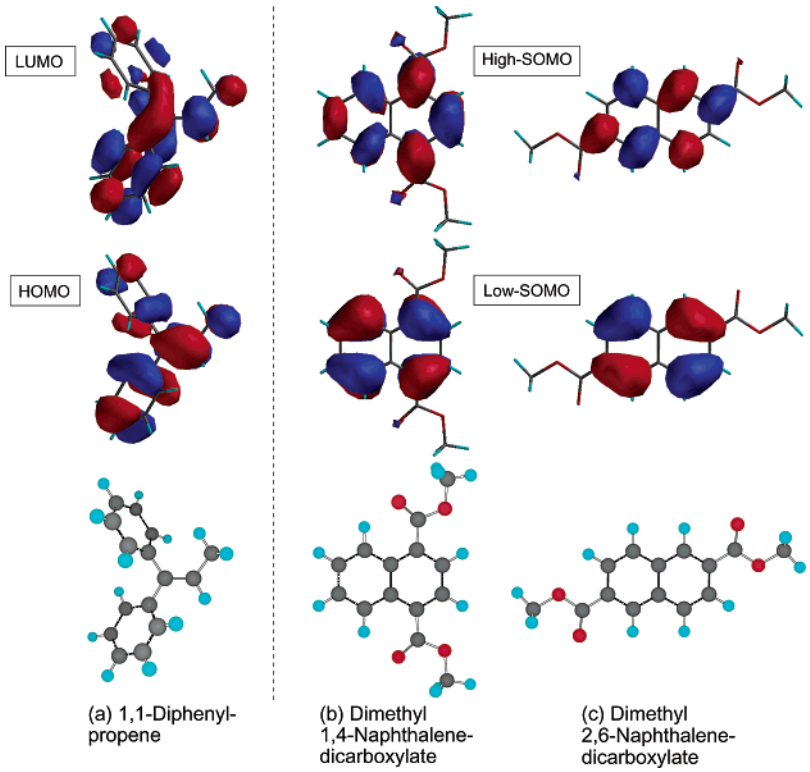


Figure 1. AM1-optimized structures and molecular orbitals: (a) HOMO and LUMO of 1,1-diphenylpropene **1** in the ground state, (b) low and high SOMOs of dimethyl 1,4-naphthalenedicarboxylate in the excited singlet state, and (c) low and high SOMOs of dimethyl 2,6-naphthalenedicarboxylate in the excited singlet state.

Table 2. Reduction Potentials and 0−0 Absorption Bands of Chiral Naphthalene(di)carboxylates **5**−**12** and Free-Energy Changes (ΔG_{et}) upon Electron Transfer from 1,1-Diphenylpropene **1** to the Excited Singlet Sensitizer

sensitizer	E_{red}[a]/V	λ_{0-0}[b]/nm	ΔG_{et}[c]/kcal mol^{-1}
5a	−2.30	334	−1.12
5b	−2.18	334	−3.87
5d	−2.19	335	−3.50
6a	−2.39	339	2.14
6b	−2.28	340	−0.18
6d	−2.30	343	0.92
7a	−1.84	371	−3.18
7b	−1.67	372	−7.06
7d	−1.68	374	−6.23
9a	−2.22	334	−3.11
9b	−2.03	333	−7.84
9d	−2.07	333	−6.65
10a	−2.30	341	0.64
10b	−2.12	344	−2.78
10d	−2.18	343	−1.86
12a	−2.02	357	−2.08
12b	−1.88	359	−5.07
12d	−1.90	361	−4.14

[a] Reduction potentials estimated as half-wave potential measured with a platinum electrode, relative to a Ag/AgCl electrode using a 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 the Weller equation: $\Delta G_{et} = 23.06(E_{ox}(D^+/D) - E_{red}(A/A^-)) - \Delta G_{0-0} - w_p$; oxidation potential of **1** (E_{ox} = 1.306 V) estimated by subtracting 0.028 V from the peak potential; Coulombic attraction term (w_p) taken as −1.3 kcal mol^{-1}.

the product yield of **3a** is not significantly affected by the methyl replacement, particularly in methylcyclohexane. This somewhat unexpected result indicates that the microenvironmental polarity around the mixed ester sensitizers is still high enough to appreciably facilitate the electron transfer.

Interestingly, the use of these mixed esters as "hemichiral" sensitizers does not simply reduce the product ee to one-half of the original value obtained with the corresponding "fully chiral" sensitizers, but only leads to an insignificant reduction of the original ee, particularly in the case of 2,3-naphthalene-dicarboxylate (**11** versus **10**). This observation clearly indicates that the two ester moieties do not behave as independent (chiral) auxiliaries, but rather work cooperatively to discriminate between the *re*/*si* faces of the substrate in the intervening radical ionic sensitizer−substrate complex, for which extensive π overlap and intimate interaction between chiral sensitizer and substrate should certainly be required.

Molecular Orbital Calculations. To elucidate the structural features of the sensitizer−substrate interaction, semiempirical molecular orbital calculations using AM1 were carried out with 1,1-diphenylpropene (**1**) in the ground state and dimethyl 1,4- and 2,6-naphthalenedicarboxylates (**8** and **13**; R* = CH_3) in the excited singlet state. The optimized structure and the HOMO and LUMO of **1** in the ground state are illustrated in Figure 1a. The two phenyls are obviously not equivalent in either geometry or in the molecular orbital. Thus, one phenyl, located cis to the methyl, is rotated by 59° from the olefin plane, while the other is much less twisted (40°), and the HOMO and LUMO orbital lobes are more developed for both the *trans*-phenyl and the olefinic double bond.

The AM1-optimized structures and the low and high singly occupied MOs (SOMOs) of dimethyl 1,4- and 2,6-naphthalene-dicarboxylates in the excited singlet state are illustrated in Figure 1b and c, respectively. The sign and contribution of each atomic orbital to the low SOMO are essentially the same for all of the naphthalene(di)carboxylates **5**−**13**, irrespective of the substitu-

tion pattern, whilst the high SOMO shows significantly different patterns in each case, as exemplified for 1,4- and 2,6-naphthalenedicarboxylates in Figure 1b and c (top). Because the single electron transfer occurs from the HOMO of the substrate to the low-SOMO of the sensitizer, the interaction between the two MOs is considered to be most important in determining the sensitizer−substrate interaction in the excited state. Judging from the orbital signs and patterns of both components, we find it is reasonable to assume that the less twisted *trans*-phenyl group of substrate **1** lays over the substituted aromatic ring of the naphthalene sensitizers and the olefinic C-1 and C-2 carbons of **1** over the α- and β-carbons of another aromatic ring of naphthalene with an almost full match of the orbital signs. This is also the sterically least-hindered complex structure. In this model, the prochiral C-2 of **1** is located right over the naphthalene's β-carbon, and therefore the chiral auxiliary introduced to the β-, rather than α-, position is anticipated to be more effective in inducing chirality in the product through a better enantioface selectivity upon diastereomeric exciplex formation.[16b] Indeed, the present results are generally in good agreement with this hypothesis, exhibiting higher ee's for 2-naphthalenecarboxylates **6a**−**e** than for the 1-analogues **5a**−**e**, and also for 2,6-naphthalenedicarboxylates **12b**−**k** than for the 1,4-analogues **7b**−**k**. The relatively low ee's (<15%) obtained with 2,3-naphthalenedicarboxylates **10a**−**e** are reasonable, because the chiral auxiliaries are located at the end of one aromatic ring and thus inefficiently discriminate between the enantiofaces of **1**. It is unlikely that the same interaction mechanism and complex structure can be applied to the 1,8-naphthalenedicarboxylate sensitization because of the severe steric hindrance caused by dual peri-substitution.

Temperature Dependence of Product ee. Irradiation temperature significantly affected the product ee. In extreme cases, the product chirality was switched just by changing the temperature, as in the case with the enantiodifferentiating photoisomerization of cyclooctene.[5]

The (−)-menthyl naphthalene(di)carboxylates consistently gave (−)-(*S*)-**3a** as the dominant enantiomer at all temperatures examined, and the ee increased with lowering temperature, irrespective of the sensitizer's structure. In contrast, the saccharide esters exhibited an entirely different temperature dependence. Upon sensitization with 1,4-naphthalenedicarboxylate **7d**, the product ee was enhanced at higher temperatures with an accompanying dramatic switching of the product chirality within the experimental temperature range, as shown in Figure 2. Such unusual temperature dependence was observed also for the other saccharide esters, such as **5d**, **5e**, **6d**, **6e**, **7e**, and **10e** (entries 23−30, 35−38, 61−64, 69−72, 157−161, and 282−285). As shown in Table 1 and Figure 2, many of the saccharide sensitizers give maximum ee's at high temperatures. Intriguingly, the temperature dependence of the ee was inverted by changing the solvent upon sensitization with glucose 2-naphthalenecarboxylates **6b** and **6c**. Thus, the product ee can be increased either by increasing the temperature in methylcyclohexane (entries 45−48 and 53−56) or by lowering it in diethyl ether (entries 49−52 and 57−60), for which the preferential solvation by the ether of the saccharide moiety would be responsible.[16b]

These apparently extraordinary observations are rationalized in terms of the nonzero entropy factor in the enantiodifferentiating process. Differential activation parameters for the enantiodifferentiating photoaddition can be determined from the product ee's obtained at various temperatures, according to the modified Arrhenius and Eyring equations:[16b]

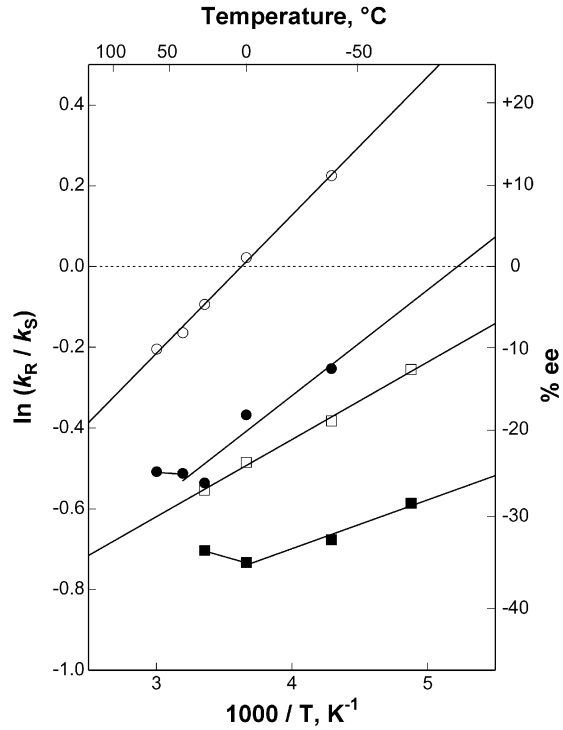


Figure 2. Temperature dependence of the enantiomeric excess (ee): the logarithm of the relative rate constant (k_R/k_S) as a function of reciprocal temperature in enantiodifferentiating photosensitized methanol addition to **1** sensitized by **7d** in methylcyclohexane (○) and ether (□) and by **12d** in methylcyclohexane (●) and ether (■).

$$\ln(k_R/k_S) = -\Delta E_{R-S}/RT + \ln(A_R/A_S)$$
$$= -\Delta\Delta H_{R-S}^{\ddagger}/RT + \Delta\Delta S_{R-S}^{\ddagger}/R \qquad (1)$$

where k_R and k_S represent the apparent rates of formation of (*R*)-(+)- and (*S*)-(−)-**3a**, A_R/A_S is the relative frequency factor, and $\Delta\Delta H_{R-S}^{\ddagger}$ and $\Delta\Delta S_{R-S}^{\ddagger}$ are the differential enthalpy and entropy changes of activation, respectively. The relative rate constant (k_R/k_S) is equivalent to the (100 + %ee)/(100 − %ee) ratio. As shown in Figure 2, the plot of $\ln(k_R/k_S)$ against the reciprocal temperature (eq 1) gave a straight line for most of the sensitizers examined within the experimental temperature range. The relative frequency factors (A_R/A_S), the equipodal temperatures (T_0) at which the product chirality is switched, and the differential activation enthalpies and entropies ($\Delta\Delta H_{R-S}^{\ddagger}$ and $\Delta\Delta S_{R-S}^{\ddagger}$) obtained from these linear plots are listed in Table 3. Theoretically, the unusual temperature switching of product chirality is expected to occur from eq 1, whenever the $\Delta\Delta H_{R-S}^{\ddagger}$ and $\Delta\Delta S_{R-S}^{\ddagger}$ values are not zero and possess the same sign. Such phenomena have been amply demonstrated for the unimolecular enantiodifferentiating photoisomerization of cycloalkenes.[5] However, this is the first extensive, unequivocal experimental verification of this theory for bimolecular enantiodifferentiating polar photoadditions.

As discussed later in the Mechanism and Kinetics section,[16b] the observed enantioselectivity, k_R/k_S, is governed in principle by the thermodynamics (stability difference) of the intervening

Table 3. Activation Parameters (at 25 °C) and Equipodal Temperatures (T_0) for Enantiodifferentiating Photoaddition of Methanol to 1,1-Diphenylpropene **1** Sensitized by Chiral Naphthalene(di)carboxylates **5**−**13**[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
5b	methylcyclohexane	4	−0.16	−0.83	0.66	−58
	diethyl ether	4	−0.032	−0.62	0.73	−222
5d	methylcyclohexane	4	−0.20	−0.93	0.63	−84
6b	methylcyclohexane	3	−0.27	−1.58	0.45	−100
	diethyl ether	3	+0.46	+1.06	1.70	158
6d	methylcyclohexane	3	−0.54	−2.32	0.31	−41
	diethyl ether	3	+0.29	+0.28	1.15	757
6e	methylcyclohexane	3	−0.62	−2.54	0.28	−29
7b	methylcyclohexane[f]	3	−0.22	−1.09	0.58	−70
	diethyl ether	3	−0.19	−1.31	0.52	−128
7c	methylcyclohexane	4	−0.16	−0.83	0.66	−82
	diethyl ether	4	−0.17	−1.01	0.60	−107
7d	methylcyclohexane[f]	5	−0.68	−2.47	0.29	3
	diethyl ether	4	−0.38	−2.37	0.30	−113
7e	methylcyclohexane	5	−0.70	−2.51	0.28	5
	diethyl ether	4	−0.45	−2.56	0.28	−98
8b	methylcyclohexane	4	−0.086	−0.54	0.76	−114
8d	methylcyclohexane	3	−0.43	−1.70	0.43	−21
9c	methylcyclohexane	3	+0.55	+0.97	1.63	295
10b	methylcyclohexane	3	−0.29	−1.55	0.46	−83
10d	methylcyclohexane	4	−0.21	−1.07	0.58	−80
10e	diethyl ether	3	−0.39	−1.68	0.43	−39
11b	methylcyclohexane	4	−0.17	−1.21	0.54	−134
11d	methylcyclohexane	4	−0.21	−1.15	0.56	−90
12b	methylcyclohexane	4	−0.43	−2.31	0.31	−88
	diethyl ether	4	−0.24	−1.63	0.44	−123
12c	methylcyclohexane	4	−0.20	−1.23	0.54	−109
	diethyl ether	4	−0.28	−1.56	0.46	−94
12d	methylcyclohexane	4	−0.52	−2.72	0.26	−82
	diethyl ether	3	−0.24	−2.35	0.31	−171
12e	methylcyclohexane	5	−0.51	−2.54	0.28	−75
13b	methylcyclohexane	4	−0.32	−1.71	0.42	−87
13d	methylcyclohexane	4	−0.28	−1.58	0.45	−95

[a] All activation parameters obtained by the 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. [f] Reference 16b.

diastereomeric exciplex pair and/or by the kinetics (relative rate) of the subsequent methanol addition to the radical cationic substrate $\mathbf{1}^{+\bullet}$ resulting from the electron transfer. As exemplified in Figure 2, the ee data obtained at the highest temperature employed sometimes deviate appreciably from the regression line fitted to the majority of the data at lower temperatures. However, such deviations are found only infrequently and for a limited number of sensitizers; for the large majority of cases, the ee data fall on the regression line over the examined temperature range. This clearly indicates that the product ee is determined in a single enantiodifferentiating step. Thus, either the relative stability of the diastereomeric exciplex pair or the relative rate of methanol addition is responsible for the product ee obtained; both factors, however, are rarely involved simultaneously at least at low temperatures.

As shown in Table 3, the differential enthalpies and entropies of activation ($\Delta\Delta H_{R-S}^{\ddagger}$ and $\Delta\Delta S_{R-S}^{\ddagger}$) obtained for hemichiral 1,4- and 2,6-naphthalenedicarboxylates **8** and **13** are reduced to almost one-half of the original activation parameters obtained with the corresponding fully chiral esters **7** and **12**. Interestingly, the hemichiral 2,3-naphthalenedicarboxylates **11** behave quite differently, affording ee's (Table 1, entries 286−301) and activation parameters (Table 3) almost comparable to those for the fully chiral diesters **10**. A similar cooperation between two adjacent alkoxycarbonyl groups has been reported for the enantiodifferentiating photoisomerization of cyclooctene sensitized by chiral *ortho*-benzenedicarboxylates.[5g] Thus, hemichiral (−)-menthyl methyl phthalate affords ee and activation parameters ($\Delta\Delta H_{S-R}^{\ddagger}$ and $\Delta\Delta S_{S-R}^{\ddagger}$) almost comparable to those obtained with (−)-dimenthyl phthalate. It was concluded that the two alkoxycarbonyl groups at the ortho position do not act as two independent chiral auxiliaries, but function as a single cooperative chiral moiety. A similar situation should be encountered in the chiral 2,3-naphthalenedicarboxylate cases, and the ortho effect may be rationalized by the interaction between neighboring chiral groups.

Structure of Chiral Auxiliary. To further investigate the effect of the chiral auxiliary upon product ee, a broader spectrum of saccharide auxiliaries (**d′** and **f**−**m**) was introduced to the 1,4- and 2,6-naphthalenedicarboxylate sensitizers **7** and **12**. The enantiodifferentiating photoaddition sensitized by these chiral esters was performed in diethyl ether at various temperatures ranging from +25 to −68 °C. The results are summarized in Table 1. Reasonably, both of the antipodal sensitizer pairs **7d**/**7d′** and **12d**/**12d′** gave the respective enantiomer pair, (+)-(*R*)- and (−)-(*S*)-**3a**, in the same ee at each temperature (entries 121−126 and 153−156, 329−334 and 347−350). Significantly, it turned out that the (*S*)-tetrahydrofuran-3-yl skeleton (**f**) shared by all furanose saccharides (**b**, **c**, **g**−**i**) is not particularly advantageous as a polar chiral auxiliary, giving only moderate yields and low ee's (<6%) upon sensitization with **7f** and **12f** (entries 166−169 and 359−361). By introducing isopropylidene-protected erythrose (**g**), which is more bulky and polar than **f**, 1,4-naphthalenecarboxylate **7g** resulted in an appreciable improvement in ee at each irradiation temperature (entries 170−173). This result demonstrates that the bulkiness and polarity of the isopropylidene protecting group, as well as the increased number of stereogenic centers in **g**, are indispensable in the increasing of the product ee up to 12%. Possessing an additional isopropylidene-protected substituent at the C-4 of furanose, the mannose esters **7i** and **12i** gave much higher ee's of 17−20% (entries 178−181 and 362−364), which are comparable to those obtained with the corresponding glucose esters **7b** and **12b**.

Protected allose (**h**) and psicose (**j**), which are epimeric to glucose (**b**) at C-3 and to fructose (**d**) at C-2, respectively, were also examined as chiral auxiliaries. Despite the inverted stereochemistry at C-3, to which the sensitizer is bonded, allose esters **7h** and **12h** gave the same (*S*)-(−)-enantiomer as glucose esters **7b** and **12b** in decreased or comparable ee's (entries 174−177 and 362−365). In contrast, the antipodal (*R*)-(+)-**3a** was obtained upon sensitization with psicosyl 1,4-naphthalenedicarboxylate **7j** (entries 182−185), although the 2,6-diester **12j** gave the same (*S*)-(−)-enantiomer as the fructose ester **12d** (entries 369−372). It is interesting to note that the present results are quite different from those reported for the enantiodifferentiating photoisomerization of (*Z*)-cyclooctene sensitized by benzenetetracarboxylates with the same saccharide auxiliaries, where the epimeric saccharide auxiliaries give the antipodal (*E*)-cyclooctene in similar ee's.[5m−o] These results and comparison indicate that the product chirality is not simply controlled by the stereochemistry of the stereogenic center nearest to the chromophore, but rather by the "global" stereochemical interactions with the saccharide moiety/substituent within the reach

of interacting substrate, particularly in the case of substrate **1** which is larger in size than cyclooctene.

Protected fucose (**k**), which possesses the same stereochemistry at C-2 and a less-substituted C-1 as compared to that of fructose (**d**), is suitable for examining the effects of neighborhood bulkiness at the carbon next to C-2 which is directly connected to the chromophore. The two fucosyl naphthalenedicarboxylates **7k** and **12k** exhibited contrasting results, giving significantly reduced and almost comparable ee's, respectively (entries 186−189 and 373−376). This is in line with the above conclusion that not the "point" but the "global" chirality influences the enantioselectivity in this photosensitized polar addition. However, it should be emphasized again that the cyclohexylidene-protected glucose (**c**), fructose (**e**) esters **5**−**7**, **9**, **10** (with a few exceptions), and **12** give ee's that strikingly resemble those obtained with the isopropylidene-protected analogues (**b** and **d**), indicating that the peripheral modification does not work. Furthermore, when the protected saccharide is a primary alcohol and therefore connected to the chromophore through a methylene group, the product ee suffered disastrous effects. Photosensitization by 1,4- and 2,6-naphthalenedicarboxylates with protected fructose **l** (which is isomeric to **d**) and galactose **m** moieties consistently gave extremely low ee's below 3% at all temperatures examined (entries 190−197 and 377−383). These observations not only reinforce the previous conclusion that only modification close to the chromophore can affect the stereochemical outcome of the asymmetric photosensitization,[1] but are useful also in selecting a chiral auxiliary and promoting our understanding of the detailed mechanism of enantiomer differentiation in the excited state.

Sensitizer Fluorescence Quenching. To elucidate the excited state involved and evaluate the rate constants for the relevant processes in the photosensitized polar addition of methanol to **1**, fluorescence quenching experiments were performed with chiral naphthalene(di)carboxylate sensitizers in polar and nonpolar solvents. Fluorescence spectra were recorded in the presence and absence of 0.5 M methanol in nondegassed methylcyclohexane, diethyl ether, and acetonitrile at room temperature. As can be seen from Table 4, the fluorescence maxima of saccharide esters **5b**, **5d**, **6b**, **6d**, **7b**, **7d**, **10b**, **10d**, and **12b**, **12d** exhibit consistent bathochromic shifts of 3−8 nm in comparison to the corresponding menthyl (**a**) esters (except for **9**), with the addition of methanol also causing similar or even larger shifts. Such bathochromic shifts are attributable to the stabilization of the emitting species caused by increased "microenvironmental" and bulk solvent polarity.[16b]

The sensitizer fluorescence was efficiently quenched by substrate **1** in all cases examined. Representative fluorescence quenching behavior is illustrated in Figures 3−5 for **7b**, **9b**, and **12b** in methylcyclohexane (top) and in 0.5 M methanol-containing methylcyclohexane (bottom). The intensity of sensitizer fluorescence was gradually decreased by adding the quencher **1** up to 80 mM, and a new weak emission attributable to an exciplex intermediate emerged at longer wavelength with an accompanying isoemissive point; however, no appreciable exciplex emission was observed for **5**, **6**, or **10** under comparable conditions. The exciplex fluorescence maxima, determined from the differential spectra obtained by spectrum subtraction (Figures 3−5, inset), observed for **7b**, **9b**, and **12b** in methylcyclohexane are 459, 408, and 412 nm, respectively; relevant results are

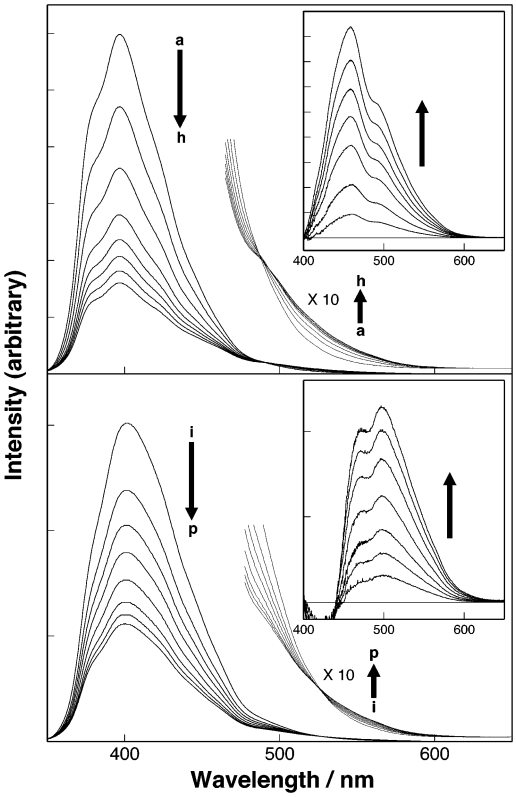


Figure 3. Fluorescence spectra of **7b** excited at 340 nm in methylcyclohexane in the presence (lower traces) and absence (upper traces) of methanol (0.5 M) with varying concentrations of **1**: (a) 0, (b) 9, (c) 20, (d) 33, (e) 43, (f) 51, (g) 61, (h) 72 mM; (i) 0, (j) 13, (k) 22, (l) 31, (m) 44, (n) 57, (o) 67, (p) 75 mM. Exciplex fluorescence obtained by spectral subtraction is shown in the inset.

summarized in Table 4. The exciplex fluorescence of saccharide esters **7b**, **9b**, and **12b** appears at longer wavelengths (by 9−22 nm) as compared to those of the corresponding menthyl esters (**a**), indicating extra stabilization of the exciplex by a higher microenvironmental polarity around the sensitizer with polar saccharide moieties. Completely parallel fluorescence behavior was observed for **7d** and **12d**. Interestingly, the exciplex fluorescence peaks observed for saccharide esters **7b**, **7d** and **12b**, **12d** in methylcyclohexane coincide with those of the menthyl esters **7a** and **12a** in the same solvent containing 0.5 M methanol, indicating that the microenvironmental polarity around the exciplex of saccharide esters is comparable to the bulk polarity of methylcyclohexane containing 0.5 M methanol. In this context, it seems curious that exciplexes derived from menthyl and fructosyl 1,8-naphthalenedicarboxylates **9a** and **9d** fluoresce at the same wavelengths (391 nm in methylcyclohexane and 402 nm in methanol-containing methylcyclohexane), while those from glucose ester **9b** fluoresce at longer wavelengths (408 nm in methylcyclohexane and 422 nm in methanol-containing methylcyclohexane). Probably, the more bulky fructose moieties in **9d** prevent the intimate electron-transfer interaction in the exciplex, thus giving polarity-insensitive exciplex fluorescence along with low chemical and optical yields of **9b**, as described above.

The presence of 0.5 M methanol added to methylcyclohexane and other polar solvents did not significantly affect the fluorescence behavior of the sensitizer, except for the small shifts of 2−5 nm in methylcyclohexane and 0−1 nm in ether or acetonitrile. However, much greater bathochromic shifts were

Table 4. Fluorescence Quenching of Chiral Sensitizers by 1,1-Diphenyl-1-alkenes **1** and **2** in the Presence and Absence of Alcohols[a]

alkene	alcohol	sensitizer	solvent	[alcohol]/M	$k_Q\tau^0$/M^{-1}	τ^{0b}/ns	k_Q/10^9 M^{-1} s^{-1}	λ_{max}/nm sensitizer	λ_{max}/nm exciplex[c]
1	MeOH	**5a**	methylcyclohexane	0	4.5	0.89	5.1	345	*d*
				0.5	6.5	0.93	7.0	350	*d*
		5b	methylcyclohexane	0	6.4	0.76	8.4	350	*d*
				0.5	10.1	1.1	8.9	355	*d*
		5d	methylcyclohexane	0	7.0	1.1	6.6	349	*d*
				0.5	9.4	1.3	7.4	353	*d*
		6a	methylcyclohexane	0	3.6	8.3	0.43	353	*d*
				0.5	4.4	8.5	0.52	355	*d*
		6b	methylcyclohexane	0	8.3	7.5	1.1	356	*d*
				0.5	10.6	7.7	1.4	358	*d*
		6d	methylcyclohexane	0	5.9	8.4	0.71	356	*d*
				0.5	6.7	8.2	0.82	358	*d*
		7a	methylcyclohexane	0	16.3	4.6	3.6	389	438
				0.5	13.6	2.9	4.7	393	459
			diethyl ether	0	40.1	6.5	6.1	396	453
				0.5	36.5	5.2	7.1	397	456
		7b	methylcyclohexane	0	38.7	6.0	6.4	397	459
				0.5	22.8	3.5	6.5	402	471
		7d	methylcyclohexane	0	30.5	5.8	5.2	396	459
				0.5	22.1	4.0	5.5	400	467
			diethyl ether	0	75.2	8.6	8.8	405	463
				0.5	64.8	7.4	8.8	405	462
			acetonitrile	0	88.7	10.5	8.5	418	*d*
				0.5	83.7	9.9	8.5	418	*d*
		9a	methylcyclohexane	0	3.1	0.55	5.6	355	391
				0.5	3.0	0.49	6.1	357	402
		9b	methylcyclohexane	0	5.1	0.58	8.8	356	408
				0.5	4.6	0.47	9.8	359	422
		9d	methylcyclohexane	0	3.5	0.55	6.4	355	391
				0.5	3.5	0.50	7.0	357	402
		10a	methylcyclohexane	0	2.6	6.7	0.39	358	*d*
				0.5	3.5	6.8	0.51	359	*d*
		10b	methylcyclohexane	0	9.9	6.7	1.5	362	*d*
				0.5	12.2	6.5	1.9	364	*d*
		10d	methylcyclohexane	0	5.6	6.7	0.84	360	*d*
				0.5	7.1	6.4	1.1	362	*d*
		12a	methylcyclohexane	0	2.3	9.7	0.24	354	*d*
				0.5	6.1	10.4	0.58	357	411
			diethyl ether	0	2.1	10.3	0.21	356	*d*
				0.5	3.1	10.6	0.30	357	*d*
		12b	methylcyclohexane	0	20.7	9.8	2.1	357	412
				0.5	35.4	10.4	3.4	362	427
		12d	methylcyclohexane	0	14.6	10.2	1.4	357	411
				0.5	30.7	10.7	2.9	361	428
			diethyl ether	0	21.3	11.9	1.8	360	420
				0.5	28.7	12.4	2.3	361	421
			acetonitrile	0	73.0	10.8	6.8	366	*d*
				0.5	73.7	10.9	6.8	366	*d*
	EtOH	**7d**	diethyl ether	0.5	54.6	7.1	7.7	406	464
		12d	diethyl ether	0.5	20.5	11.0	1.9	361	424
	2-PrOH	**7d**	diethyl ether	0.5	58.0	7.5	7.7	406	464
		12d	diethyl ether	0.5	26.2	11.0	2.4	361	425
2	MeOH	**7d**	diethyl ether	0	58.1	8.4	7.0	405	463
				0.5	50.3	7.0	7.2	406	464
		12d	diethyl ether	0	16.8	11.1	1.5	360	413
				0.5	21.3	11.4	1.9	361	418
	EtOH	**7d**	diethyl ether	0.5	50.5	7.1	7.1	406	463
		12d	diethyl ether	0.5	21.7	11.6	1.9	361	417

[a] Measured with a 0.01 mM aerated solution of sensitizer at 25 °C. [b] Fluorescence lifetime of sensitizers in aerated solution at 25 °C. [c] Exciplex fluorescence obtained by spectrum subtraction. [d] Exciplex emission not observed.

observed for the exciplex fluorescence (Figures 3−5, lower traces) with the quenching rate constants appreciably increased, as described below (Table 4).

According to the Stern−Volmer equation (eq 2), the relative fluorescence intensity (I_F^0/I_F) obtained in the quenching experiment was plotted against the concentration of added **1** to give an excellent straight line for each sensitizer examined, as exemplified in Figure 6.

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

The Stern−Volmer constant ($k_Q\tau^0$) was obtained from the slope of the plot, with the fluorescence lifetime (τ^0) determined independently by using the single photon-counting technique. From these values, we calculated the apparent quenching rate constants (k_Q) for each sensitizer, which are summarized in Table 4. It should be pointed out that the k_Q value does not rigorously correlate with the product yield. Thus, the very fast quenching at $k_Q > 5 \times 10^9$ M^{-1} s^{-1} (of, e.g., **5** and **9**) does not necessarily guarantee the formation of photoadduct in high yield, although slow quenching at $k_Q \leq 1 \times 10^9$ M^{-1} s^{-1} (of, e.g., **6**)

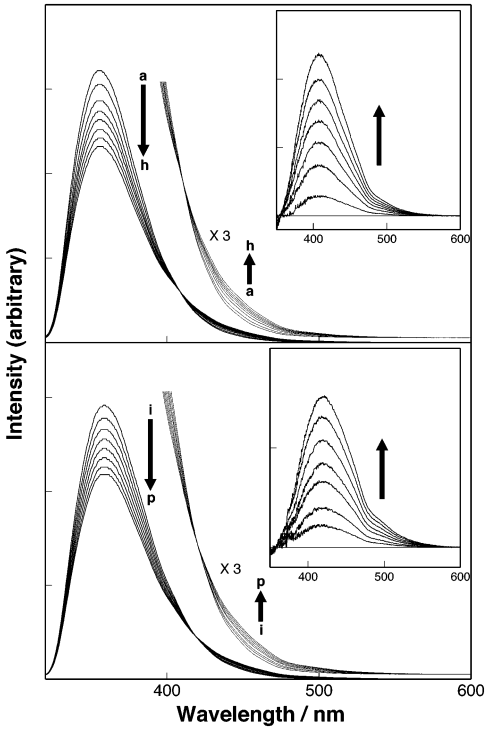


Figure 4. Fluorescence spectra of **9b** excited at 310 nm in methylcyclohexane in the presence (lower traces) and absence (upper traces) of methanol (0.5 M) with varying concentrations of **1**: (a) 0, (b) 10, (c) 24, (d) 36, (e) 45, (f) 54, (g) 64, (h) 76 mM; (i) 0, (j) 11, (k) 20, (l) 32, (m) 41, (n) 52, (o) 62, (p) 72 mM. Exciplex fluorescence obtained by spectral subtraction is shown in the inset.

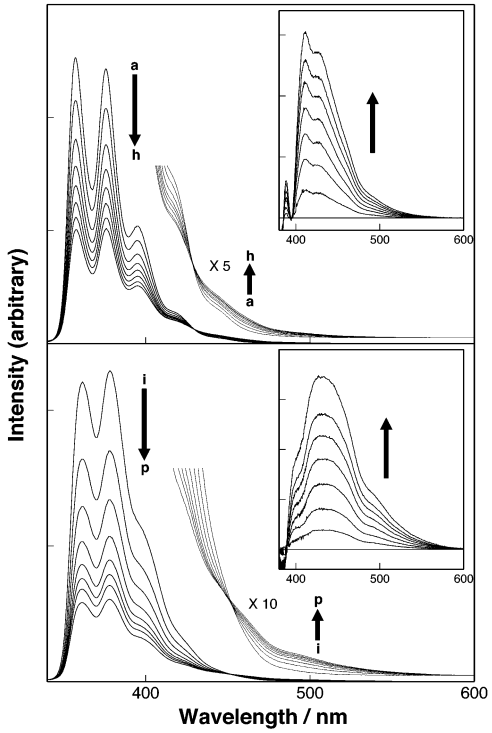


Figure 5. Fluorescence spectra of **12b** excited at 330 nm in methylcyclohexane in the presence (lower traces) and absence (upper traces) of methanol (0.5 M) with varying concentrations of **1**: (a) 0, (b) 10, (c) 21, (d) 31, (e) 41, (f) 51, (g) 62, (h) 73 mM; (i) 0, (j) 10, (k) 21, (l) 33, (m) 44, (n) 54, (o) 63, (p) 79 mM. Exciplex fluorescence obtained by spectral subtraction is shown in the inset.

never leads to a high yield. The introduction of saccharide auxiliaries (**b** and **d**) to naphthalene(di)carboxylate, the use of more polar solvents (ether or acetonitrile), and the addition of methanol to methylcyclohexane solvent significantly accelerate the fluorescence quenching process, indicating a polar nature of the exciplex intermediate involved. Simultaneously, the product yield is also enhanced by the increased microenvironmental and/or solvent polarity in many cases, while the steric hindrance of the bulky substituents in sensitizer may disturb it. Particularly, in the case of 1,8-naphthalenedicarboxylates **9a**, **9b**, and **9d**, the sensitizer fluorescence is rapidly quenched at $6-10 \times 10^9$ M^{-1} s^{-1} by **1** to give the exciplex fluorescence at longer wavelengths. However, the rate with subsequent methanol addition is thought to be decelerated as a result of insufficient electron transfer within the exciplex due to the severe steric hindrance of the dual peri-substitution in **9**.

Exciplex Fluorescence Quenching. For a further elucidation of the kinetic details of the nucleophilic attack of methanol, the quenching of exciplex fluorescence by methanol was investigated with 1,4- and 2,6-naphthalenedicarboxylates **7** and **12** in both methylcyclohexane and diethyl ether. Because the exciplex fluorescence is fairly weak and partly obscured by the sensitizer fluorescence, the fluorescence lifetime, instead of intensity, was measured in the presence of methanol at various concentrations of up to 1.0 M, by using the time-correlated single-photon-counting method. The fluorescence decay profile obtained was nicely analyzed in each case by a sum of two single-exponential decays of fast and slow components that correspond to the sensitizer and exciplex fluorescence, respectively. While the sensitizer lifetime (τ) was slightly affected by the addition of methanol up to 1.0 M, the exciplex lifetime (τ_{ex})

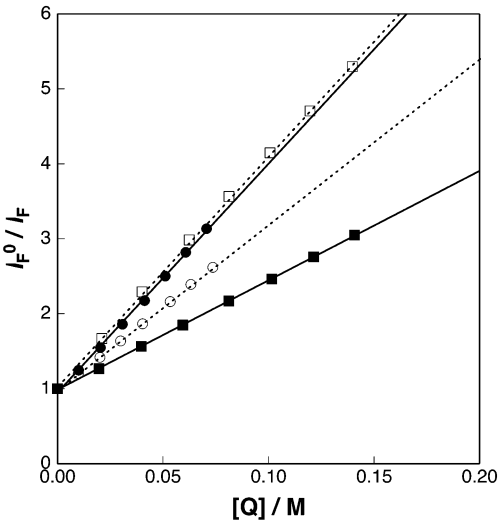


Figure 6. Stern−Volmer plots for fluorescence quenching of **7d** by **1** in the presence (○) and absence (●) of 0.5 M methanol and of **12d** by **1** in the presence (□) and absence (■) of 0.5 M methanol in methylcyclohexane.

was significantly shortened; see the Supporting Information for detailed lifetime data. According to the modified Stern−Volmer equation (eq 3), the relative fluorescence lifetime ($\tau_{ex}^{\circ}/\tau_{ex}$) was plotted as a function of the methanol concentration to give a straight line for each sensitizer, as exemplified in Figure 7.

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

The Stern−Volmer constant (k_A) is obtained for each sensitizer from the slope of the plot, and the results for **7a**, **7b**, **7d** and **12a**, **12b**, and **12d** are listed in Table 5.

Table 5. Rate Constants for the Photoaddition of Alcohol to 1,1-Diphenyl-1-alkenes **1** and **2** Sensitized by Chiral Sensitizers **7** and **12**[a]

alkene	alcohol	sensitizer	solvent	k_A/M^{-1}	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}
1	MeOH	**7a**	methylcyclohexane	0.61	8.2	11.5	12.1	8.8	72	−2.3
			diethyl ether	0.40	11.6	10.6	9.0	11.8	110	−2.6
		7b	methylcyclohexane	3.9	6.5	0.27	58.2	14.5	2450	−4.2
		7d	methylcyclohexane	1.3	5.8	0.82	14.1	8.0	706	−3.6
			diethyl ether	0.75	8.6	<0.1	6.1	8.4	*d*	*d*
		12a	methylcyclohexane	0.29	2.9	10.2	3.2	0.91	29	−1.8
			diethyl ether	0.11	2.0	10.1	1.2	1.2	20	−1.6
		12b	methylcyclohexane	1.0	6.0	10.2	15.8	5.6	59	−2.2
		12d	methylcyclohexane	0.35	11.2	11.2	4.4	1.6	100	−2.5
			diethyl ether	0.20	7.5	9.0	2.4	2.9	83	−2.4
	EtOH	**7d**	diethyl ether	0.50	8.8	<0.1	4.3	8.6	*d*	*d*
		12d	diethyl ether	0.16	2.8	4.4	2.0	8.1	63	−2.2
	2-PrOH	**7d**	diethyl ether	0.16	8.8	<0.1	1.3	7.9	*d*	*d*
2	MeOH	**7d**	diethyl ether	0.30	9.2	2.0	2.5	6.3	459	−3.3
	EtOH	**7d**	diethyl ether	0.18	9.2	2.0	1.5	6.2	467	−3.3

[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}. [d] Not determined.

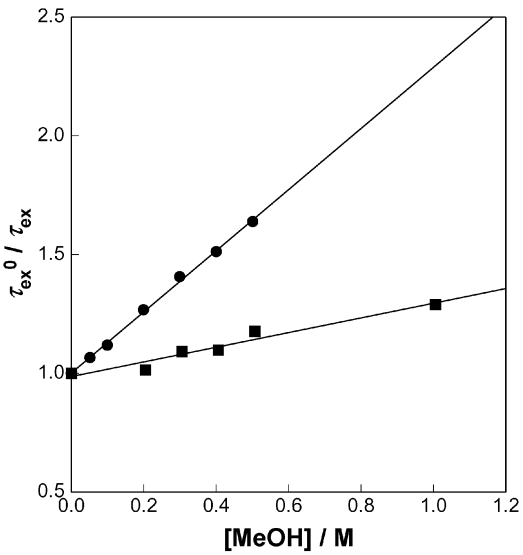


Figure 7. Stern−Volmer plots for fluorescence lifetime of the exciplex between **1** and **7d** (●) or **12d** (■) in the presence of varying amounts of methanol in methylcyclohexane.

Mechanism and Kinetics. Previously,[16b] we have proposed a mechanism for this photosensitized enantiodifferentiating polar addition, which involves the formation of a diastereomeric exciplex pair equilibrating with the singlet excited sensitizer and the subsequent enantioface-selective nucleophilic attack of alcohol to afford the enantiomeric photoadduct.

The mechanism of the enantiodifferentiating photoaddition of alcohol sensitized by chiral sensitizer (**S**) is illustrated in Scheme 2, where k_q and k_{-q} represent the rate constants for the association and dissociation of exciplex, k_d represents the nonradiative decay from exciplex, and k_a represents the addition of alcohol to exciplex (the subscripts R and S refer to the absolute configuration of product **3a**).

The specific rate constants can be determined from the apparent quenching rate constants k_Q and k_A obtained by the above Stern−Volmer analyses. The calculated rate constants are summarized in Table 5.

$$k_Q = k_q(1 - k_{-q}/(k_{-q} + k_d + k_a[\mathrm{MeOH}])) \quad (4)$$

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

1,4-Naphthalenedicarboxylates **7b**,**d** bearing saccharide auxiliaries give significantly larger exciplex formation constants (K_{ex}) than does the menthyl analogue **7a**, as a consequence of the highly negative ΔG_{et} (Table 2). It is noted that the enhancement of K_{ex} is caused not by the acceleration of quenching (k_q) but by the deceleration of the back reaction (k_{-q}) by a factor of >10, although the more moderate enhancement of K_{ex} observed for 2,6-naphthalenedicarboxylates **12b**,**d** is ascribed to the acceleration of quenching by a factor of 2−3 (Table 5). In particular, the large K_{ex} (700−2500 M^{-1}) for **7b**,**d** means that the exciplex formation of these saccharide esters with substrate **1** is practically irreversible.

By using the fluorescence maxima of the sensitizer and exciplex (Table 4) and the free-energy change upon exciplex formation (ΔG_{ex}) as calculated from the equilibrium constant (K_{ex}) in Table 5, we can draw detailed energy diagrams for sensitizers **7a** versus **7d** and **12a** versus **12d** in methylcyclohexane (Figure 8). Although the excited singlets of **7a** and **7d** and of **12a** and **12d** are very close in energy, a greater stabilization upon exciplex formation occurs for the saccharide esters (**7d**, **12d**) than for the corresponding menthyl esters (**7a**, **12a**). Similar, but less extensive, extra stabilization for the saccharide ester exciplex is also observed in diethyl ether. The greater bathochromic shifts, longer lifetimes, and larger equilibrium constants observed indicate that the exciplex of saccharide sensitizers with **1** is more polarized, stabilized, and tightly bound than that of menthyl ester.

Although the formation of exciplex proceeds at a rate comparable to diffusion in both methylcyclohexane ($k_{diff} = 1.4 \times 10^{10}$ M^{-1} s^{-1})[19] and diethyl ether ($k_{diff} = 4.5 \times 10^{10}$ M^{-1} s^{-1}),[19] the subsequent nucleophilic addition of methanol to the electron-deficient substrate $\mathbf{1}^{\delta+}$ in the exciplex is much slower (k_a[MeOH] = 0.6−29.1 × 10^7 s^{-1}), which is comparable to the exciplex decay (k_d = 0.9−14.5 × 10^7 s^{-1}). Thus, the methanol attack is concluded to be the rate-determining step in the overall adduct **3a** yielding reaction. The faster addition rate (k_a) for saccharide sensitizers is reasonably accounted for in

(18) (a) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51. (b) Salikhov, K. M.; Molin, Y. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: Amsterdam, 1984. (c) Turro, N. J. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 609. (d) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369.
(19) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 207.

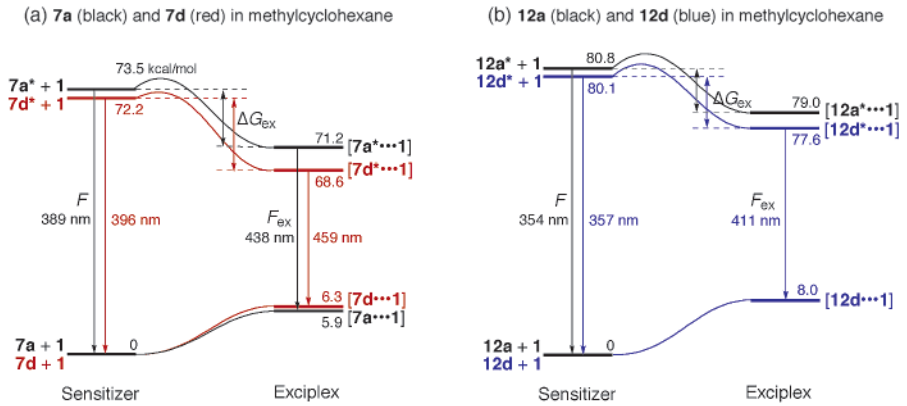
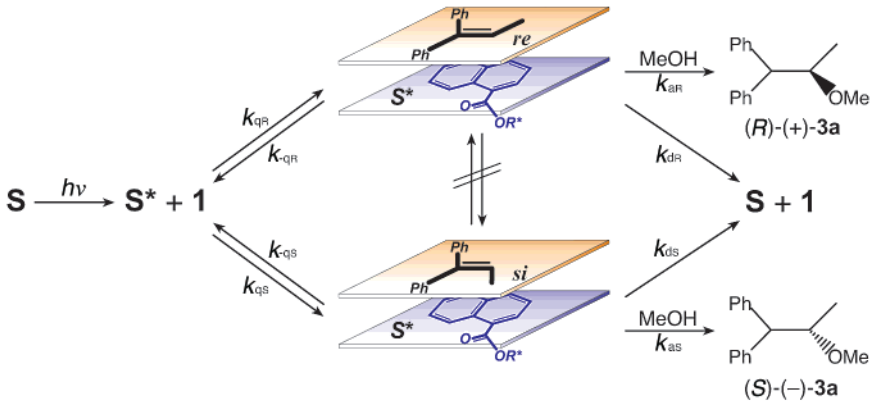


Figure 8. Energy diagrams for sensitizers **7a**,**d** and **12a**,**d** and their exciplexes with substrate **1** in methylcyclohexane at 25 °C.

Scheme 2



terms of the more polarized exciplex intermediate with the highly electron-deficient substrate **1**, which facilitates the subsequent methanol attack. The rate of methanol addition is also affected by the bulkiness of chiral auxiliaries, as the fructose esters (**7d**, **12d**) constantly give appreciably smaller k_a than do the glucose esters (**7b**, **12b**).

As shown in Scheme 2, the product ee is not a simple function of a single pair of rate constants for an enantiodifferentiating process giving (*R*)- and (*S*)-adducts, but is determined thermodynamically through the stability difference between the diastereomeric exciplex pair and also kinetically through the difference in the rate of subsequent methanol addition. According to the mechanism in Scheme 2, the apparent enantioselectivity (k_R/k_S) is expressed by the combination of the relevant rate/equilibrium constants (eq 6).

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

Thus, both the relative stability between the diastereomeric exciplex pair (K_{exR}/K_{exS}) and the relative rate of methanol addition (k_{aR}/k_{aS}) are eligible as factors controlling the product ee. The saccharide auxiliaries enhance the microenvironmental polarity around the chromophore to give a more polarized, stabilized, and tightly bound exciplex, which in turn leads to the large K_{ex} and k_a values (Table 5). The greater stabilization upon exciplex formation means more intimate interactions, which can lead to a larger stability difference between the diastereomeric exciplex pair formed. As mentioned above, the greater K_{ex} is realized not by accelerating the quenching (k_q) but by decelerating the decomplexation (k_{-q}). However, k_q is close to the diffusion rate and should not be enantiodifferentiating, while k_{-q} can be decelerated to different extents depending on the diastereomeric exciplex structure and therefore is most probably responsible for the increased ee's upon introduction of the saccharide auxiliaries. Similarly, the faster methanol attack can lead to a lower enantioface-selectivity, if the rate is close to that of the diffusion. However, the methanol attack is at least 1 order of magnitude slower than the diffusion ($k_a < 6 \times 10^8$ M^{-1} s^{-1} $\ll k_{diff} \approx 10^{10}$ M^{-1} s^{-1}) and is thus in competition with the decay and/or decomplexation of the exciplex (k_a[MeOH] $\approx k_d$ and k_{-q}). Because the methanol attack on the open face of the substrate in exciplex does not appear to experience any severe steric hindrance from the sensitizer substituents, the rate is affected by the degree of positive-charge development on the attacked carbon. In this context, it is important to note that the fructose esters **7d** and **12d** give better ee's than do the glucose esters **7b** and **12b** despite the 2−4 times smaller k_a's, which are very close to those obtained with menthyl esters **7a** and **12a**. We may conclude therefore that the attacking rate k_a plays a minor role in determining the product ee.

Magnetic Field Effect. In search of a new tool for controlling the product chirality and ee in asymmetric photochemistry, the effect of magnetic field on the present enantiodifferentiating photoaddition was investigated. The magnetic field is also interesting from the mechanistic point of view, because only the triplet state suffers appreciable magnetic field effect through the hyperfine coupling mechanism, which decelerates the triplet−singlet intersystem crossing through a Zeemann splitting

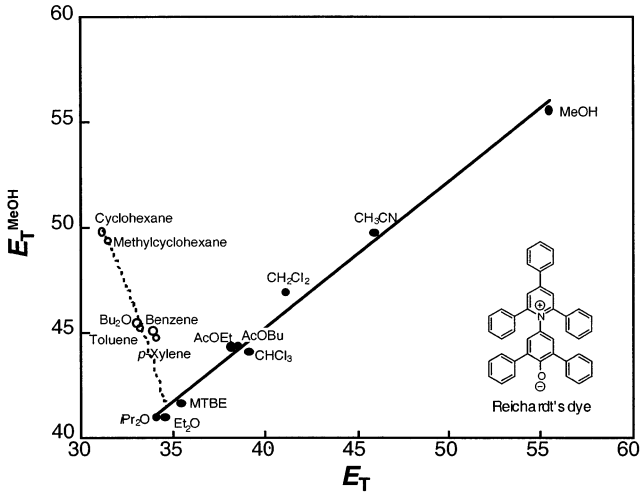


Figure 9. The E_T values of various solvents containing 0.5 M methanol (E_T^{MeOH}) as a function of the E_T value of the solvent.

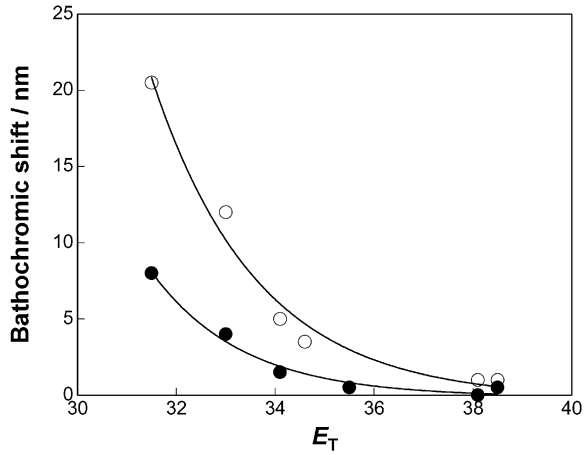


Figure 10. Bathochromic shift of the fluorescence maximum of the exciplex of **1** with **7a** (○) or **7d** (●), caused by adding 0.5 M methanol to a solvent of varying original E_T value.

of the triplet level.[18] The enantiodifferentiating photosensitization of **7d** and **12d** under a magnetic field was investigated in diethyl ether. As shown in Table 1 (entries 122−123 and 330−331), no appreciable change in chemical or optical yield of adduct **3a** was observed under magnetic fields of up to 8 T. It may be concluded therefore that the contribution of the triplet sensitization mechanism is negligible and the magnetic field is not effective at least in controlling the enantiodifferentiating process of this photosensitized methanol addition to **1**.

Solvent Effect. The effect of bulk solvent polarity upon the role of microenvironmental polarity around the sensitizer was investigated in the enantiodifferentiating photosensitizations of **7a** and **7d** (and to some extent with **12d**) in various solvents. The results are shown in Table 1. As anticipated from the electron-transfer nature of the methanol addition, the product yield upon sensitization with **7a** and **7d** was gradually reduced with decreasing solvent polarity from methanol (E_T 55.5)[20] or acetonitrile (E_T 46.0)[20] to diethyl ether (E_T 34.6)[20] (entries 79−104 and 121−152), but was unexpectedly increased again by further reducing the polarity to methylcyclohexane (E_T 31.5)[20] (entries 77−78 and 119−120).

To get a handle on this puzzling behavior of the product yield, the effective polarities (E_T^{MeOH}) of the methanol-containing solvents used in this study were independently determined from the spectral shift of Reichardt's dye (illustrated in Figure 9) in each solvent containing 0.5 M methanol and are plotted against the conventional E_T values of the pure solvents in Figure 9. Interestingly, the effective solvent polarity E_T^{MeOH} is not a simple linear function of the original polarity of pure solvent. Thus, the E_T^{MeOH} value linearly decreases from 49.7 to 41.0 kcal/mol when the original solvent polarity is lowered from acetonitrile to diethyl or diisopropyl ether, but it suddenly starts to deviate from the line at $E_T = 34$ kcal/mol and increases by further lowering the solvent polarity down to dibutyl ether and aromatics and then to saturated hydrocarbons. This unusual behavior nicely coincides with the trend of the product yield obtained via a polarized exciplex intermediate in the enantiodifferentiating photosensitization, both of which are reasonably accounted for in terms of the selective solvation to the highly polarized Reichardt's dye or exciplex intermediate particularly in the low-polarity solvents.

The bathochromic shift induced by adding methanol (0.5 M) to a methylcyclohexane solution of **7**−**12** is much greater for the exciplex fluorescence (8−21 nm) than for the sensitizer fluorescence (1−5 nm), which is in support of the exciplex's polarized structure. By using **7a** and **7d**, the bathochromic shift of exciplex fluorescence upon addition of 0.5 M methanol was more quantitatively evaluated in solvents of different polarity; the results are plotted against the solvent E_T in Figure 10. Particularly in solvent less polar than diethyl ether, $E_T \leq 34.6$ kcal/mol, the fructose ester **7d** gives bathochromic shifts obviously smaller than those observed with menthyl ester **7a**, for which the increased microenvironmental polarity around **7d** is responsible. It is noted also that the degree of shift is not a linear function of E_T, but rapidly increases with decreasing solvent polarity, ultimately amounting to 21 nm (3.0 kcal/mol stabilization) for **7a** and 8 nm (1.1 kcal/mol stabilization) for **7d** in methylcyclohexane. This behavior is fully compatible with the selective solvation by methanol of the exciplex intermediate in solvents less polar than diethyl ether, which is in good agreement with the unusual enhancement of E_T^{MeOH} in low-polarity solvents (Figure 9). Thus, the increased yield of **3a** in methylcyclohexane is reasonably attributed to the selective solvation by methanol of the exciplex, which accelerates the electron transfer and therefore the subsequent methanol addition. On the other hand, the strong solvation of methanol and the high microenvironmental polarity induced inevitably render the exciplex more loosely bound and less-structured, thus lowering the product ee. Indeed, most sensitizers give the highest ee not in methylcyclohexane but in diethyl ether which exhibits the lowest E_T^{MeOH}. The more loosely bound exciplex intervening in the enantiodifferentiating step may rationalize the consistently larger contribution of entropy ($\Delta\Delta S^{\ddagger}$) and the unusual switching of product chirality by temperature in methylcyclohexane rather than in diethyl ether. It is thus revealed that the product ee of the enantiodifferentiating polar photoaddition can be optimized (without seriously lowering the yield) by minimizing the bulk polarity of the actual reaction media, which is evaluated by Reichardt's dye. This strategy is likely to be applicable in

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

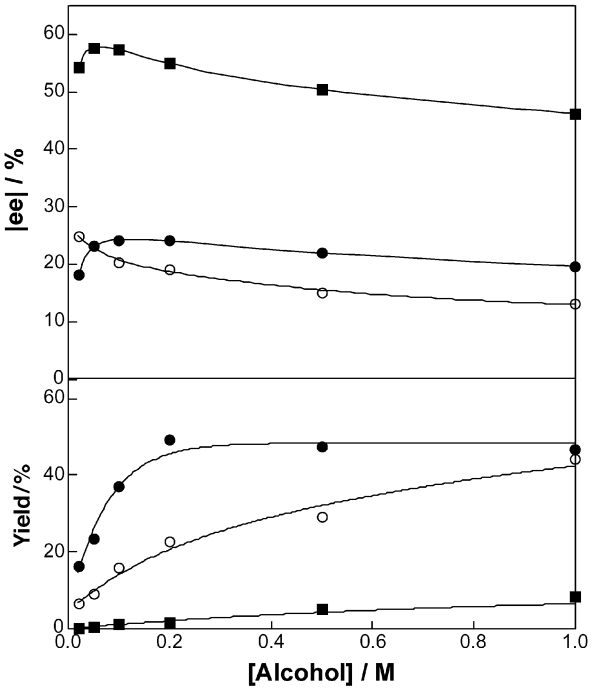


Figure 11. Enantiomeric excess (upper trace) and chemical yield (lower trace) as functions of alcohol concentration upon enantiodifferentiating photosensitized addition of methanol to **1** sensitized by **7d** in toluene (○) and diethyl ether (●), and of 2-propanol to **1** sensitized by **12d** in diethyl ether (■).

general to other asymmetric photochemical reactions involving polar exciplex/intermediates.

To our surprise, the photosensitization of **1** with **7d** in pure methanol afforded nonracemic **3a** (5−7% ee) in 74−86% yield (Table 1, entries 149−152). This is not expected to occur in such a high-polarity solvent as methanol (E_T 55.5).[20] Indeed, the same photoreaction performed in acetonitrile (E_T 46.0) gave a merely racemic **3a** in 73% yield (entries 147−148), as the radical ionic sensitizer−substrate pair is readily dissociated in highly polar solvents. Hence, the appreciable ee obtained in methanol may indicate that the diastereomeric exciplex or radical ionic intermediate is rapidly trapped by pure methanol (24.7 M), probably at a rate competitive with the spontaneous dissociation to the solvent-separated or free ionic species upon electron transfer.

Effects of Methanol Concentration. Although the methanol concentration was fixed at 0.5 M in the above experiments, the bulk solvent polarity and the selective solvation of methanol were demonstrated to significantly affect the product ee. For further elucidation of the effect of methanol concentration on the product ee, the photosensitization of **1** by **7d** was performed in toluene and diethyl ether containing 0.02−1.0 M methanol under comparable conditions to give the chemical yields and ee's shown in Figure 11.

As reported previously,[16b] the conversion and chemical yield in toluene rapidly increase with increasing methanol concentration of up to 0.2 M and then level off, giving a plateau of 80% conversion and a 50% yield. In contrast, the growths of conversion and yield in diethyl ether were more slow and steady and did not show any saturation up to 1.0 M. Hence, the rapidly saturating conversion and yield in toluene indicate the operation of some extra stabilization mechanism for the partially charge-transferred exciplex intermediate in addition to the polarity enhancement by the added methanol, probably through the stacking interaction of the aromatic solvent accelerating the methanol attack of the stabilized intermediate.

The absolute ee of product **3a** continuously increased up to 25% with decreasing methanol concentration from 1.0 to 0.02 M in toluene (Figure 11, ○), which is reasonable because the sensitizer−substrate interactions in the exciplex are expected to be more intimate and enantiodifferentiating as the solvent polarity decreases.[16b] However, in diethyl ether, the product ee exhibited significantly different behavior particularly at low methanol concentrations. As can be seen from Figure 11 (●), the ee in ether increased up to 24% with decreasing methanol concentration from 1.0 to 0.2 M, leveled off at 0.1−0.2 M, and then started to decrease below 0.1 M, affording 18% ee at 0.02 M. Although the details will be reported below, similar behavior was also observed upon photosensitized addition of 2-propanol (Figure 11, ■). At present, we have no plausible explanation for this puzzling dependence of product ee on alcohol concentration, which is however rationalized by assuming that the selective solvation of alcohol to the exciplex, leading to a lower product ee, starts to happen even in diethyl ether if the alcohol concentration is sufficiently lowered (<0.1 M). This seems reasonable, because we have judged diethyl ether as one of the "polar" solvents in which 0.5 M methanol does not selectively solvate to Reichardt's dye, but this experiment was done not in pure diethyl ether but in a 0.5 M methanol−ether mixture. In fact, the E_T^{MeOH} value for diethyl ether is critically located right on the bending point in Figure 9, which is however able to move to higher E_T by lowering the "bulk" polarity (i.e., methanol concentration) of the mixed solvent. In such a diethyl ether solution of lower polarity, the added methanol could selectively solvate to the polarized exciplex intermediate, resulting in the decreased product ee.

Effects of Steric Bulk of Substrate and Alcohol. To examine the structural effects of substrate and attacking alcohol on the chemical and optical yields, the photosensitized enantiodifferentiating additions of ethanol and 2-propanol to **1** and of methanol to 1,1-diphenyl-1-butene (**2**) were performed in the presence of **7d** and **12d** as sensitizers in methylcyclohexane and diethyl ether. The results are summarized in Table 6.

The use of ethanol, instead of methanol, as an attacking agent added to solvent did not significantly affect either the chemical or the optical yield of the ethanol adduct **3b** upon sensitization with **7b** and **12b**; compare entries 119−126 (**7d**) and 324−334 (**12d**) in Table 1 with entries 1−8 (**7d**) and 9−16 (**12d**) in Table 6. In contrast, the homologous substrate **2**, possessing an ethyl group at the attacking site, afforded the methanol adduct **4a** in higher ee's of up to 44% in somewhat lower yields, particularly for the diethyl ether upon sensitization with **7d** and **12d**; see entries 43−50 (**7d**) and 51−58 (**12d**) in Table 2. Hence, we further endeavored to optimize the reaction conditions for higher ee's by using **2** as substrate and ethanol as attacking agent (entries 59−74). However, the chemical and optical yields of product **4b** were almost comparable or slightly lower than those of **4a** obtained in the photosensitized methanol addition to **2**.

For further elucidation of the influence of the bulkiness of both substrate and alcohol on the excited-state sensitizer−substrate interaction, fluorescence quenching experiments were carried out with chiral sensitizers **7d** and **12d** in diethyl ether with or without added alcohol. The fluorescence maxima of the

Table 6. Enantiodifferentiating Photoaddition of Methanol, Ethanol, and 2-Propanol to 1,1-Diphenyl-1-alkenes **1** and **2** Sensitized by Chiral Naphthalene(di)carboxylates **7d** and **12d**[a]

entry	alkene	alcohol	solvent	temp/°C	*t*/h[b]	conv[c]/%	yield[d]/%	ee[e]/%	entry	alkene	alcohol	solvent	temp/°C	*t*/h[b]	conv[c]/%	yield[d]/%	ee[e]/%
								7d									
1	**1**	EtOH	methylcyclohexane	60	24	88	56	−15.0	5	**1**	EtOH	diethyl ether	25	24	80	23	−27.4
2	**1**	EtOH	methylcyclohexane	25	24	84	52	−9.5	6	**1**	EtOH	diethyl ether	0	24	87	28	−25.3
3	**1**	EtOH	methylcyclohexane	0	24	53	29	−1.5	7	**1**	EtOH	diethyl ether	−40	24	65	21	−14.0
4	**1**	EtOH	methylcyclohexane	−40[f]	24	11	1	+9.0	8	**1**	EtOH	diethyl ether	−68	24	69	15	−6.8
								12d									
9	**1**	EtOH	methylcyclohexane	60	24	53	15	−23.1	13	**1**	EtOH	diethyl ether	25	24	51	7	−32.9
10	**1**	EtOH	methylcyclohexane	25	24	61	19	−18.9	14	**1**	EtOH	diethyl ether	0	24	50	7	−33.8
11	**1**	EtOH	methylcyclohexane	0	24	43	14	−16.1	15	**1**	EtOH	diethyl ether	−40	24	49	12	−26.4
12	**1**	EtOH	methylcyclohexane	−40	24	47	16	−5.9	16	**1**	EtOH	diethyl ether	−68	24	56	17	−21.9
								7d									
17	**1**	2-PrOH	methylcyclohexane	60	24	57	21	+30.0	23	**1**	2-PrOH	toluene	−40	24	43	18	+26.2
18	**1**	2-PrOH	methylcyclohexane	25	24	64	30	+24.9	24	**1**	2-PrOH	toluene	−68	24	19	5	+26.4
19	**1**	2-PrOH	methylcyclohexane	0	24	51	23	+17.7	25	**1**	2-PrOH	diethyl ether	25	24	63	14	+41.3
20	**1**	2-PrOH	methylcyclohexane	−40[f]	24	17	1	+1.1	26	**1**	2-PrOH	diethyl ether	0	24	71	18	+41.8
21	**1**	2-PrOH	toluene	60	24	48	18	+33.4	27	**1**	2-PrOH	diethyl ether	−40	24	59	16	+33.0
22	**1**	2-PrOH	toluene	25	24	57	27	+31.6	28	**1**	2-PrOH	diethyl ether	−68	24	52	17	+27.3
								12d									
29	**1**	2-PrOH	methylcyclohexane	60	24	40	4	+39.3	36	**1**	2-PrOH	toluene	−68	24	26	4	+31.6
30	**1**	2-PrOH	methylcyclohexane	25	24	39	6	+39.8	37	**1**	2-PrOH	diethyl ether	25	24	39	4	+49.3
31	**1**	2-PrOH	methylcyclohexane	0	24	36	7	+45.4	38	**1**	2-PrOH	diethyl ether	0[g]	24	31	1	+57.7
32	**1**	2-PrOH	methylcyclohexane	−40	24	36	4	+22.6	39	**1**	2-PrOH	diethyl ether	0	24	41	5	+50.4
33	**1**	2-PrOH	toluene	60	24	32	3	+36.1	40	**1**	2-PrOH	diethyl ether	0[h]	24	55	13	+39.3
34	**1**	2-PrOH	toluene	25	24	35	6	+42.6	41	**1**	2-PrOH	diethyl ether	−40	24	46	10	+46.4
35	**1**	2-PrOH	toluene	−40	24	34	10	+36.2	42	**1**	2-PrOH	diethyl ether	−68	24	47	14	+38.3
								7d									
43	**2**	MeOH	methylcyclohexane	60	24	71	36	−17.8	47	**2**	MeOH	diethyl ether	25	24	75	14	−33.8
44	**2**	MeOH	methylcyclohexane	25	24	70	33	−16.4	48	**2**	MeOH	diethyl ether	0	24	72	19	−35.5
45	**2**	MeOH	methylcyclohexane	0	24	42	20	−11.8	49	**2**	MeOH	diethyl ether	−40	24	64	18	−32.7
46	**2**	MeOH	methylcyclohexane	−40[f]	24	14	1	−16.6	50	**2**	MeOH	diethyl ether	−68	24	54	16	−23.0
								12d									
51	**2**	MeOH	methylcyclohexane	60	24	61	14	−25.0	55	**2**	MeOH	diethyl ether	25	24	64	7	−41.7
52	**2**	MeOH	methylcyclohexane	25	24	59	16	−26.1	56	**2**	MeOH	diethyl ether	0	24	52	7	−43.6
53	**2**	MeOH	methylcyclohexane	0	24	40	12	−27.1	57	**2**	MeOH	diethyl ether	−40	24	52	9	−38.5
54	**2**	MeOH	methylcyclohexane	−40	24	39	11	−22.6	58	**2**	MeOH	diethyl ether	−68	24	49	11	−30.3
								7d									
59	**2**	EtOH	methylcyclohexane	60	24	59	26	+26.7	63	**2**	EtOH	diethyl ether	25	24	73	13	+37.7
60	**2**	EtOH	methylcyclohexane	25	24	60	25	+25.6	64	**2**	EtOH	diethyl ether	0	24	75	14	+41.2
61	**2**	EtOH	methylcyclohexane	0	24	38	16	+15.5	65	**2**	EtOH	diethyl ether	−40	24	63	15	+35.5
62	**2**	EtOH	methylcyclohexane	−40[f]	24	22	<1	+2.5	66	**2**	EtOH	diethyl ether	−68	24	57	12	+23.9
								12d									
67	**2**	EtOH	methylcyclohexane	60	24	51	10	+29.6	71	**2**	EtOH	diethyl ether	25	24	60	4	+34.1
68	**2**	EtOH	methylcyclohexane	25	24	54	12	+28.2	72	**2**	EtOH	diethyl ether	0	24	50	5	+40.4
69	**2**	EtOH	methylcyclohexane	0	24	36	11	+23.1	73	**2**	EtOH	diethyl ether	−40	24	44	7	+26.9
70	**2**	EtOH	methylcyclohexane	−40	24	37	8	+10.0	74	**2**	EtOH	diethyl ether	−68	24	43	7	+12.8

[a] [Alkene] = 20 mM; [sens*] = 3 mM; [alcohol] = 0.5 M, unless noted otherwise. [b] Irradiation time. [c] Loss of starting material determined by GC. [d] Chemical yield determined by GC on the basis of the initial concentration of the substrate. [e] Enantiomeric excess determined by chiral GC. [f] [sens*] < 3 mM due to low solubility. [g] [alcohol] = 0.05 M. [h] [alcohol] = 2 M.

sensitizer and exciplex are summarized in the last 10 rows of Table 4. Sensitizer fluorescence of **7d** was efficiently quenched by substrate **1** in ethanol and 2-propanol-containing ether to give the exciplex fluorescence at wavelengths practically indistinguishable from that obtained in methanol-containing ether, indicating that the nature and structure of the added alcohol do not significantly affect the exciplex structure of **7d**. In contrast, the exciplex of **12d** and **1** showed appreciable bathochromic shifts of 3−4 nm in the presence of ethanol or 2-propanol. This suggests the formation of a more stabilized tighter exciplex in the presence of a less-polar alcohol than methanol, which does not however appear to be reflected in the product ee.

Fluorescence quenching by substrate **2** was also performed in methanol- or ethanol-containing diethyl ether. 1,4-Naphthalenedicarboxylate **7d** gave practically the same exciplex fluorescence maxima for both **1** and **2**, while the exciplex of the 2,6-diester **12d** with **2** exhibited noticeable hypsochromic shifts of 3−7 nm in the presence and absence of added methanol or ethanol (Table 4, bottom lines). Because no corresponding change was seen for **7d**, this shift is attributable not to the possible enhancement in microenvironmental polarity caused by the ethyl substituent in **2**, but rather to a destabilization of the exciplex formed, probably arising from the steric hindrance of the ethyl group. This observation further indicates that the exciplex structure is critically affected by the steric bulk of the substituent in the substrate olefin and also by the substitution pattern of the naphthalene sensitizer.

To reveal the steric effects of the substrate and attacking alcohol on the kinetics of the photosensitized polar addition, exciplex fluorescence quenching by ethanol or 2-propanol was performed in diethyl ether, using **1** and **2** as substrates and **7d** and **12d** as sensitizers. The specific rate constants were determined from the apparent quenching rate constants k_Q and k_A as described above. As shown in Table 5, the rates of exciplex formation (k_q) and dissociation (k_{-q}) obtained with **7d** in diethyl

ether are practically the same ($8.6-9.2 \times 10^9$ M^{-1} s^{-1} and $<0.1 \times 10^7$ s^{-1}, respectively) for all substrates (**1** and **2**) and alcohols (methanol, ethanol, and 2-propanol) employed. However, in the case of the exciplex of **12d** with **1**, the use of ethanol simultaneously decelerates the k_q and k_{-q} by a factor of 2−3 to give comparable K_{ex} values of 83 and 63 M^{-1} for methanol and ethanol, respectively. In contrast, the rate of alcohol addition (k_a) is more critically affected by the structures of alcohol and substrate. Upon sensitization with **7d**, the k_a for substrate **1** decreases from 6.1×10^7 to 4.3×10^7 and then to 1.3×10^7 M^{-1} s^{-1} for methanol, ethanol, and 2-propanol, respectively, whereas substrate **2** affords 2.5−2.9 times smaller k_a values: 2.5×10^7 M^{-1} s^{-1} for methanol and 1.5×10^7 M^{-1} s^{-1} for ethanol. Both the accelerated dissociation (k_{-q}) and the decelerated alcohol attack (k_a) observed for the exciplex derived for **7d** and **2** are accounted for in terms of the steric hindrance of the ethyl group of **2**, which contributes substantially to the general enhancement of **2**'s photoproducts ee's up to 44% (Table 6, entry 56).

From the above investigations, we now know that the steric bulk of the attacking site and alcohol greatly contributes to the product ee. Eventually, for the best optimized ee, we performed the enantiodifferentiating photoaddition of 2-propanol to **1** sensitized by **7d** and **12d** in methylcyclohexane, toluene, and diethyl ether. The results are summarized in Table 6. Although the chemical yields of the 2-propanol adduct **3c** (entries 17−42) were more-or-less lower than those of the ethanol adduct **3b** (entries 1−16) obtained under comparable conditions, the product ee's were greatly improved for each sensitizer in all solvents, giving a product ee of 50% in diethyl ether at 0 °C upon sensitization with **12d** in the presence of 0.56 M 2-propanol (Table 6, entry 39). We further endeavored to raise the product ee by changing the concentration of 2-propanol. The results are shown in Table 6 (entries 38−40) and Figure 11. Although the chemical yield of **3c** was decreased by lowering the 2-propanol concentration from 2.0 to 0.05 M, the ee of **3c** was enhanced up to 58%, which is the highest value ever reported for a photosensitized bimolecular enantiodifferentiating reaction.[14−16] Unfortunately, the product ee decreased again by further lowering the concentration (Figure 11).

Because the bulkiness of substrate more critically affects the product ee, a logical extension of the above study is the simultaneous use of more a bulky substrate such as **2** with 2-propanol. In this light, we performed the photoaddition of 2-propanol (0.5 M) to **2** sensitized by **12d** in diethyl ether to give the corresponding adduct **4c**. This resulted in a slightly lower yield than that of **3c** obtained upon photosensitization with **1**, but unfortunately the product ee could not be determined due to incomplete separation by chiral GC despite extensive efforts to find a suitable chiral stationary phase.

Conclusions

In this study using a variety of substrates, alcohols, solvents, and photosensitizers with protected saccharides as chiral auxiliaries, we have elucidated in detail the factors and mechanisms that govern the enantiodifferentiating photoaddition of alcohols to 1,1-diphenyl-1-alkenes sensitized by chiral naphthalene(di)carboxylates and further developed new strategies for enhancing the optical yield which are thought to be applicable in general to diverse bimolecular asymmetric photoreactions involving polarized exciplexes or radical ionic intermediates, as outlined below.

(1) Factors controlling the product ee: Not only the steric and electronic structures of the sensitizer, substrate, and alcohol, but also the solvent polarity and the alcohol concentration play crucial roles in determining the chemical and optical yields of the photoadduct.

(2) Entropy control: The "unusual" temperature dependencies, giving higher ee's at elevated temperatures, and switching of the product chirality by temperature are not just specific to unimolecular photoisomerizations, but are generally observed in both uni- and bimolecular enantiodifferentiating photoreactions, as natural consequences of the entropic contribution. This enables us to use entropy-related factors such as temperature and solvation as convenient and versatile tools for controlling a wide variety of asymmetric photochemical reactions which are governed by weak interactions in exciplex intermediates.

(3) Tradeoff between chemical and optical yields: Introducing polar chiral auxiliaries to the sensitizer, which enhances the microenvironmental polarity around the chromophore and reduces the selective solvation of methanol, is highly effective for overcoming the normally accepted tradeoff between the chemical and optical yields in polar photoadditions.

(4) Mechanisms and intermediates: The detailed reaction and enantiodifferentiation mechanisms and the intermediates involved in the sensitized enantiodifferentiating polar photoaddition have been elucidated by extensive fluorescence quenching experiments and MO calculations. The exciplex model based on the MO calculation, in which the prochiral C-2 carbon of the substrate is located right over the naphthalene's β-carbon, predicted that the chiral auxiliary introduced at the β-position is more effective than that at the α-position in inducing chirality in the product. The saccharide auxiliaries enhance the microenvironmental polarity around the chromophore to afford a more polarized and tightly bound exciplex, which enhances the stability of the exciplex (K_{ex}) and the rate of alcohol addition (k_a). The exciplex stability (K_{ex}) and attacking rate (k_a) were also affected by the bulkiness of both substrate and alcohol. From the detailed study on the kinetics and energetics, we may conclude that the relative stability between the diastereomeric exciplex pair (K_{exR}/K_{exS}) plays a major role in the enantiodifferentiating mechanism.

We believe that these findings and concepts significantly promote our understanding of asymmetric photochemistry, expand its scope, push back its limitations, and enable greater synthetic application to a wide spectrum of uni- and biomolecular asymmetric reactions via photoinduced electron transfer.

Experimental Section

General. Melting points were measured with a YANACO MP-300 apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a JEOL GX-400 or GSX-270 spectrometer in chloroform-*d*. Infrared spectra were obtained on a JASCO FT/IR-230 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 methylcyclohexane or diethyl ether 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 the sample solution was detected through appropriate glass filters: Toshiba UV-33, UV-35, UV-37, L-39, or L-42.

Enantiomeric excesses of **3a**−**c** and **4a**,**b** were determined by gas chromatography over a 30-m chiral capillary column (Astec Chiraldex B-DA or B-PH) using a Shimadzu GC-14B instrument. All GC peaks were integrated with a Shimadzu C-R6A integrator connected to the GC instrument.

Materials. The methylcyclohexane used as solvent was stirred over concentrated sulfuric acid until the acid layer no longer turned yellow, washed with water, neutralized with aqueous sodium hydrogen carbonate, dried over sodium sulfate, and then distilled fractionally. Toluene and alcohols were fractionally distilled in the presence of molten sodium and magnesium turnings, respectively. Ethers were refluxed with potassium hydroxide and then fractionally distilled in the presence of molten sodium. Ethyl acetate and butyl acetate were fractionally distilled in the presence of calcium oxide. Spectrograde acetonitrile (Dojin) was used without further purification.

1,1-Diphenyl-1-alkenes **1** and **2** were synthesized by dehydration of the corresponding 1,1-diphenyl-1-alkanols, which were prepared by the Grignard reaction from the corresponding ketones with the appropriate alkyl bromides, as described previously.[16b]

(−)-Menthol and some of the sugar derivatives employed were commercially available: (−)-menthol from TCI; 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose from Wako; (*S*)-(+)-3-hydroxytetrahydrofuran, 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose, 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose, and 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose from Aldrich; and 1,2:4,5-di-*O*-isopropylidene-*β*-D-psicopyranose from Sigma.

1,2:5,6-Di-*O*-cyclohexylidene-α-D-glucofuranose, 1,2:4,5-di-*O*-isopropylidene-*β*-D-fructopyranose, and 1,2:4,5-di-*O*-cyclohexylidene-*β*-D-fructopyranose were prepared as reported.[14c,16b] The antipodal 1,2:4,5-di-*O*-isopropylidene-*β*-L-fructopyranose was prepared from L-fructose, which was derived from L-sorbose according to the procedure reported by Chen et al.[21a] and Wang et al.:[21b] $[\alpha]^{28}_{D}$ +156.1° (*c* 1.01, acetone) (lit.[21c] $[\alpha]^{28}_{D}$ −156.6° (*c* 1.00, acetone) for D-isomer). ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 3H), 1.45 (s, 3H), 1.52 (s, 3H), 1.54 (s, 3H), 1.97 (d, J = 8.3 Hz, 1H), 3.67 (t, J = 7.3 Hz, 2H), 3.97−4.03 (m, 1H), 4.10−4.23 (m, 4H).

2,3-*O*-Isopropylidene-L-erythrofuranose was prepared from L-rhamnose hydrate according to the procedure reported by Baxter et al.:[22a] $[\alpha]^{28}_{D}$ +76.0° (*c* 2.42, MeOH) (lit.[22b] $[\alpha]_{D}$ −78° (*c* 7.8, MeOH) for D-isomer). ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 3H), 1.47 (s, 3H), 3.29 (d, J = 2.4 Hz, 1H), 4.00−4.10 (m, 2H), 4.58 (d, J = 5.9 Hz, 1H), 4.84 (dd, J = 3.4, 5.9 Hz, 1H), 5.42 (d, J = 2.0 Hz, 1H).

The other cyclic acetal derivatives of saccharide were prepared from the corresponding sugar or sugar derivatives according to the reported procedures.[23,24] 3,4-*O*-Isopropylidene-1-methyl-α-L-fucopyranoside was prepared from methyl-α-L-fucopyranoside (TCI): $[\alpha]^{26}_{D}$ −159.4° (*c* 1.05, acetone). ^{1}H NMR ($CDCl_3$): δ 1.33 (d, J = 6.8 Hz, 3H), 1.36 (s, 3H), 1.52 (s, 3H), 2.27 (br, 1H), 3.44 (s, 3H), 3.79 (dd, J = 3.9, 6.4 Hz, 1H), 4.04−4.22 (m, 3H), 4.72 (d, J = 3.9 Hz, 1H). 2,3:4,5-Di-*O*-isopropylidene-*β*-D-fructopyranose was prepared from D-fructose: $[\alpha]^{25}_{D}$ −41.0° (*c* 2.1, acetone) (lit.[24a] $[\alpha]^{25}_{D}$ −38.1° (*c* 1.7, acetone)). ^{1}H NMR ($CDCl_3$): δ 1.36 (s, 3H), 1.41 (s, 3H), 1.49 (s, 3H), 1.56 (s, 3H), 2.11 (dd, J = 5.1, 8.1 Hz, 1H), 3.68 (m, 2H), 3.78 (dd, J = 1.0, 12.7 Hz, 1H), 3.93 (dd, J = 2.0, 12.7 Hz, 1H), 4.25 (dd, J = 1.2, 7.8 Hz, 1H), 4.35 (d, J = 2.4 Hz, 1H), 4.62 (dd, J = 2.4, 7.8 Hz, 1H).

Chiral naphthalene(di)carboxylates were prepared from the corresponding alcohols and acid chlorides.[14c,16b] The physical properties and spectral data of sensitizers **5c**−**e**, **6c**−**e**, **7d′**−**m**, **9c**−**e**, **10c**−**e**, and **12c**−**f**,**h**−**m** can be found in the Supporting Information.

The mixed 1,4- and 2,6-naphthalenedicarboxylates **8b**,**d** and **13b**,**d** were prepared from the corresponding methyl hydrogen naphthalenecarboxylates,[25] while the mixed 2,3-diester **11b**,**d** was prepared by the O-methylation of the corresponding saccharide half esters;[26] see the Supporting Information for the physical and spectral details.

Photolysis. All irradiations were carried out in a temperature-controlled paraffin (60 °C), water (25 °C), methanol/2-propanol (0 and −40 °C), or methanol/ethanol (−68 °C) bath. The light sources employed were a conventional 300 W high-pressure mercury lamp for irradiations at 60 and 25 °C and an equivalent lamp fitted with a transparent Pyrex vacuum sleeve designed for low-temperature irradiation (Eikosha). A solution (4 mL) containing 1,1-diphenyl-1-alkene **1** or **2** (20 mM), alcohol (0.5 M), optically active sensitizer **5**−**13** (3 mM), and cyclododecane (3 mM) added as an internal standard was irradiated at >280 nm under an argon atmosphere in a Pyrex tube (1 cm i.d.) placed near the lamp surface, and the whole system was immersed in the temperature-controlled bath.

Photolysis under Magnetic Field. All irradiations were conducted in a quartz cylindrical vessel (3 cm i.d. × 1 cm d) placed under the pulsed magnetic field. The details of the apparatus were described by Tanimoto et al.[27] A diethyl ether solution (2 mL) containing **1** (20 mM), methanol (0.5 M), chiral sensitizer **7d**, **12d** (3 mM), and cyclododecane (3 mM) added as an internal standard was placed in the vessel and was degassed by freeze−pump−thaw cycles. The solution placed under a magnetic field of up to 8 T was then irradiated for 2 h with a 250 W high-pressure mercury arc (Ushio UI-501C). The collimated incident beam from lamp housing was focused with a quartz lens placed in front of the vessel, allowing an efficient irradiation.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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