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Microenvironmental Control of Enantiodifferentiating Photocyclization of 5-Hydroxy-1,1-diphenylpentene through Selective Solvation

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ABSTRACT For mechanistic elucidation of the photosensitized cyclization of 5-hydroxy-1, 1-diphenylpentene (**1**), its methyl ether (**4**) was synthesized as an unreactive "dummy" substrate and used as a quencher of the sensitizer fluorescence to reveal the intervention of an exciplex intermediate that was unable to detect when reactive substrate **1** was used as a quencher/reactant In the enantiodifferentiating photocyclization of **1** to 2-(diphenylmethyl)tetrahydrofuran (**2**) sensitized by a chiral saccharide ester of 1,4-naphthalenedicarboxylate (**3**), the enantiomeric excess (ee) of chiral product **2** obtained in methylcyclohexane (MCH) at 25 °C was significantly enhanced from 20% to 35% upon 10-fold dilution of the sample solution by MCH, for which the reduced solvent polarity, discouraging dissociation of the intervening radical ionic exciplex, is likely to be responsible. Further attempts to microenvironmentally control the photochirogenic reaction and enhance the product's ee through selective solvation of polar cosolvent to the diastereomeric exciplex pair in nonpolar solvent were not successful probably due to the inherently high local polarity around the exciplex of saccharide-appended **3** with alcoholic substrate **1**. *Chirality 24:400–405, 2012.*

KEY WORDS: photochirogenesis; enantioselectivity; photosensitization; solvent polarity

INTRODUCTION

Chiral photochemistry, or photochirogenesis, becomes more popular, and a variety of molecular and supramolecular photochirogenic reactions have been investigated particularly in recent years.[1–5] Nevertheless, precisely controlling photochirogenic process is still a significant challenge, and indeed the optical yields reported so far are generally modest in particular for the most chiral source-efficient enantiodifferentiating photosensitizations,[1–5] indicating that both general strategies and practical tactics are definitely needed for understanding the factors and mechanisms operating in photochirogenic processes and improving the optical yields derived therefrom.

In a series of studies, we have demonstrated that various entropy-related factors, such as temperature,[6–8] pressure,[9–12] and solvation,[13–15] play vital roles in the essential enantiodifferentiating steps of various chiral photosensitizations to critically manipulate the relative stability and/or reactivity of the diastereomeric exciplex pair of chiral sensitizer with prochiral substrate.[2] In particular, the selective solvation to exciplex becomes a dominant factor determining product's enantiomeric excess (ee), when the exciplex is polarized or radical ionic in nature.[13–15] Thus, the chiral sense of product obtained in the photoisomerization of (*Z*)-cyclooctene sensitized by chiral pyromellitates is dramatically switched from *R* to *S* upon addition of diethyl ether to the pentane solution.[13]

The enantiodifferentiating polar addition of alcohol to 1, 1-diphenylalkene in methylcyclohexane (MCH) sensitized by chiral naphthalene(di)carboxylates is also sensitive to the solvent polarity, affording higher ee at lower concentration of alcohol added as a reagent.[14,15] However, the detailed examination of selective solvation was not feasible in this system because of the presence of the alcohol reagent inevitably added to the solution. We therefore employed 5-hydroxy-1, 1-diphenylpentene (**1**), which is known to cyclize to 2-(diphenylmethyl)tetrahydrofuran (**2**) upon photosensitization with electron-accepting sensitizers,[17,18] as a "self-containing" substrate for the enantiodifferentiating photocyclization sensitized by bis(1,2;4,5-di-*O*-isopropylidene-α-fructopyranosyl) 1,4-naphthalenedicarboxylate (**3**) (Scheme 1) in supercritical carbon dioxide ($scCO_2$).[16] Possessing a built-in hydroxyl, this substrate allowed us to closely investigate the effects of diethyl ether added as an entrainer (cosolvent) to $scCO_2$ on the enantiodifferentiating photocyclization of **1**, revealing that the addition of ether significantly enhances the ee of cyclization product **2** as a result of the clustering of ether molecules around the exciplex intermediate in less polar $scCO_2$. This intriguing result prompted us to expand the concept of the microenvironmental control in $scCO_2$ to the chiral photoreaction in conventional media exploiting the selective solvation of polar cosolvent in nonpolar solvent; the results of which will be reported in the following text.

MATERIALS AND METHODS

General

Mass spectra were recorded on a JEOL (Akishima, Japan) JMS-700 instrument with electron impact ionization and ^1H NMR spectra at 500 MHz on a JEOL JNM-ECP500 instrument. Fluorescence spectra were measured on a

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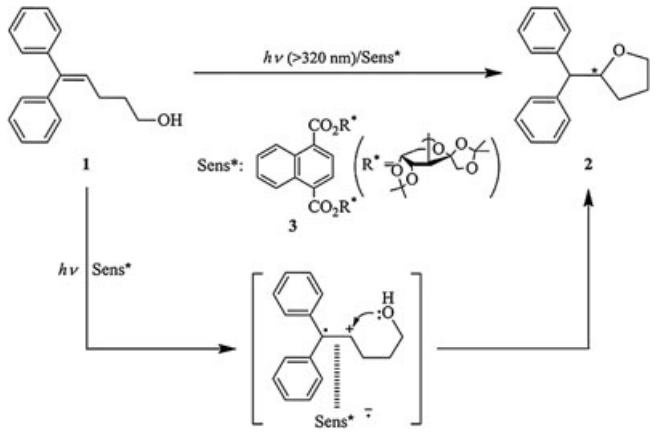


Scheme 1. Enantiodifferentiating photocyclization of 5-hydroxy-1, 1-diphenylpentene (**1**) to chiral cyclization, product (**2**) sensitized by bis(1,2;4, 5-di-O-isopropylidene-α-fructopyranosyl) 1,4-naphthalenedicarboxylate (**3**).

JASCO (Hachioji, Japan) FP-6500 spectrofluorimeter or on an Edinburgh FL920S instrument. Fluorescence lifetimes were determined by the time-correlated single-photon-counting technique, using an Edinburgh FL920S instrument equipped with a pulsed H_2 light source or a Hamamatsu C4334 instrument equipped with an N_2 laser (Usho KEC-160, Osaka, Japan).

All chemicals were purchased from Wako (Osaka, Japan) and used without further purifications. Spectrograde solvents were used throughout the work.

5-Hydroxy-1,1-diphenylpentene (**1**) was prepared as reported previously.[16] 5-Methoxy-1,1-diphenylpentene (**4**) employed as a "dummy" substrate was prepared from **1** by the Williamson ether synthesis by using iodomethane and sodium hydride (Scheme 2);[18] ^{1}H NMR ($CDCl_3$): δ 1.72 (tt, J = 7.1 Hz, 2H), 2.18 (dt, J = 7.6 Hz, 2H), 3.29 (s, 3H), 3.36 (t, J = 6.6 Hz, 2H), 6.09 (t, J = 7.5 Hz, 1H), 7.17–7.38 (m, 10H); mass spectrometry (electron impact ionization) m/z (relative intensity) 252 (M^+, 4), 236 (30), 207 (41), 166 (100),77 (28); high-resolution mass spectrometry Calcd for $C_{18}H_{20}O$ (M^+): 252.1514. Found: 252.1514.

Photolysis and Product Analysis

Solutions of substrate **1** (2 or 20 mM) and sensitizer **3** (0.3 or 3 mM) in quartz cells were purged with nitrogen gas at 0 °C, placed in a Unisoku (Hirakata, Japan) CoolspeK cryostat maintained at a given temperature and then irradiated at wavelengths >320 nm (effective wavelength: 313 nm) with a 500-W high-pressure mercury lamp through a 5-cm water layer and a Toshiba (Tokyo, Japan) UV-31 or UV-D36B filter.

Irradiated samples were subjected to gas chromatographic (GC) analysis on a Zebron (Torrance, CA, USA) ZB-WAXplus (0.25 mm ϕ × 30 m) or GL Science TC-1 column (0.25 mm ϕ × 30 m) to determine the conversion (consumption of **1**) and chemical yield of **2** on the basis of consumed **1**.[15] The GC analyses were performed at a head pressure of 100 kPa with a temperature program, where the column temperature was kept at 180 °C for first 8 min, raised to 220 °C at a rate of 20 °C/min, and then hold at that temperature for 40 min. Under the condition employed, the retention times of substrate **1** and product **2** were 36 min and 13 min, respectively, on the ZB-WAXplus column and 15 min and 13 min, respectively, on the TC-1 column.

The ee of product **2** was determined by chiral high-performance liquid chromatography on a JASCOplus instrument equipped with a UV detector (detection wavelength: 220 nm).[16] The chiral high-performance liquid chromatography analysis was run at 5 °C on a Daicel (Osaka, Japan) Chiralpak IB column (5 μm particles, 4.6 mm ϕ × 250 mm) eluted with a 98:1:1 mixture of *n*-hexane/isopropanol/1,2-dichloroethane at a flow rate of 0.3 ml/min under the isocratic condition. The enantiomer peaks were well separated at retention times 22 and 25 min, from the integrated areas of which the product's ee was calculated with an error of ±2% ee.

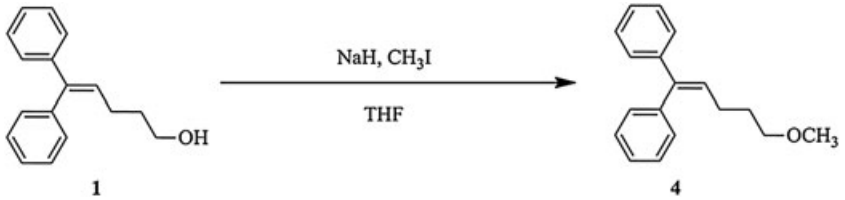
RESULTS AND DISCUSSION

Fluorescence Quenching

In our previous study,[16] we found that the fluorescence of sensitizer **3** was efficiently quenched upon addition of substrate **1** to give cyclization product **2** in good yield but failed to unambiguously prove the intervention of an exciplex intermediate in the photocyclization process by detecting the exciplex fluorescence. The lack of fluorescence is presumably due to the fast intramolecular nucleophilic attack of the terminal hydroxyl to the radical-cationic olefin moiety of **1**, leading to cyclization product **2** (Scheme 1). If this is indeed the case, the exciplex lifetime is expected to be appreciably elongated by blocking the cyclization path to **2** through methylation of the terminal OH of **1**. In the present study, we therefore employed 5-methoxy-1,1-diphenylpentene (**4**)[18] (Scheme 2) as an unreactive "dummy" substrate that possesses the same donor moiety as **1** but never yields the cyclization product and compared its fluorescence quenching behavior with that of intact substrate **1**.

We first examined the fluorescence quenching behavior of sensitizer **3** with substrate **1** in diethyl ether at room temperature. As shown in Figure 1(a), gradual addition of **1** of up to 10 mM to an ether solution of **3** (10 μM) led to an efficient fluorescence quenching. According to the Stern–Volmer (S–V) equation, $I_F^0/I_F = 1 + k_Q\tau^0[Q]$, where k_Q denotes the apparent quenching rate constant and τ^0 the natural lifetime of **3**; the relative fluorescence intensity (I_F^0/I_F) was plotted against the quencher concentration [Q] (Q = **1**) to give a straight line (Fig. 1(b)). The S–V constant, defined as the slope of the S–V plot, is a product of the apparent quenching rate constant (k_Q) and the inherent lifetime (τ^0) of fluorophore **3**. The τ^0 value was independently determined as 8.7 ns by using the single-photon counting technique in the absence of a quencher under a comparable condition. From the S–V constant ($k_Q\tau^0$) and the lifetime (τ^0), we obtain the quenching rate constant: $k_Q = 7.9 \times 10^9\ M^{-1}\ s^{-1}$ (Table 1).

Similar fluorescence quenching experiments were performed with "dummy" substrate **4** in MCH, toluene, diethyl ether, and acetonitrile and also in MCH-containing acetonitrile (0.6 M) or propionitrile (0.1-0.6 M) as a cosolvent to give the quenching parameters summarized in Table 1.



Scheme 2. Synthesis of 5-methoxy-1,1-diphenypentene (**4**).

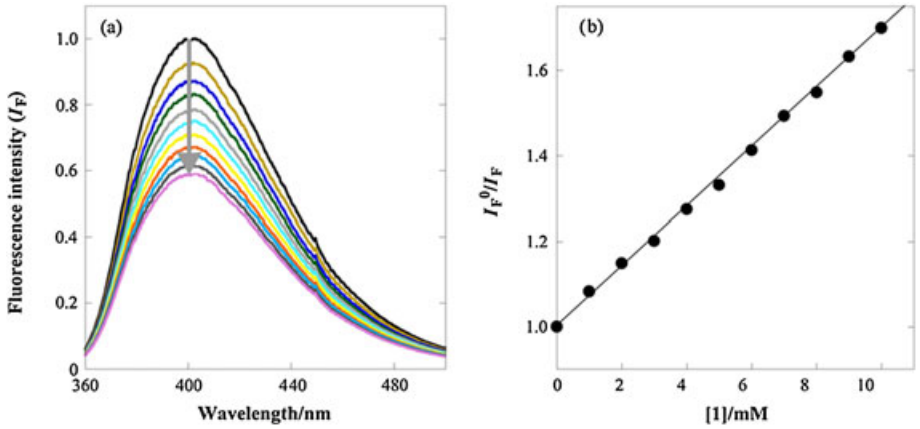


Fig. 1. (**a**) Fluorescence quenching of sensitizer **3** (0.01 mM) by substrate **1** (0–10 mM, from top to bottom) in diethyl ether at room temperature, excitation wavelength: 340 nm, and (**b**) the Stern–Volmer plot obtained therefrom.

TABLE 1. Fluorescence maxima (λ_{max}), Stern–Volmer constants ($k_Q\tau$), fluorescence lifetimes (τ^0), and quenching rate constants (k_Q) obtained upon fluorescence quenching of chiral sensitizer 3 (10 μM) with substrate 1 (0–10 mM) and "dummy" substrate 4 (0–7.2 mM) in various solvents at room temperature in the presence and absence of cosolvent

Quencher	Solvent	Cosolvent	λ_{max}/nm	$k_Q\tau^0/M^{-1}$	τ^0/ns	$k_Q/10^9\ M^{-1}\ s^{-1}$
1	Et_2O	none	405	69	8.7	7.9
4	MCH[a]	none	396	30	5.8	5.2
		AN[a] (0.6 M)	402	36	7.1	5.1
		PN[a] (0.1 M)	397	34	6.4	5.3
		(0.3 M)	400	38	6.6	5.8
		(0.6 M)	404	40	6.8	5.9
	toluene	none	423	17	11.6	1.5
	Et_2O	none	405	51	8.7	5.9
	AN[a]	none	419	66	10.5	6.3

[a]MCH, methylcyclohexane; AN, acetonitrile; PN, propionitrile; cosolvent concentration in the parentheses.

In contrast to the monotonous decrease of fluorescence intensity over the entire wavelength range (360–500 nm) upon addition of reactive substrate **1** (0–10 mM) (Fig. 1(a)), the addition of "dummy" substrate **4** (0–7.2 mM) quenched the fluorescence at the main band but induced a new weak emission at >490 nm with accompanying isoemissive point at ca. 490 nm (Fig. 2(a), inset), which is assignable to an exciplex of sensitizer **3** with "dummy" substrate **4**. The elongated lifetime and/or enhanced fluorescence efficiency, as a consequence of the blockage of the subsequent cyclization path, are likely to be responsible for the successful detection of the exciplex fluorescence. Unfortunately, the intensity of the exciplex fluorescence was too weak to determine its lifetime.

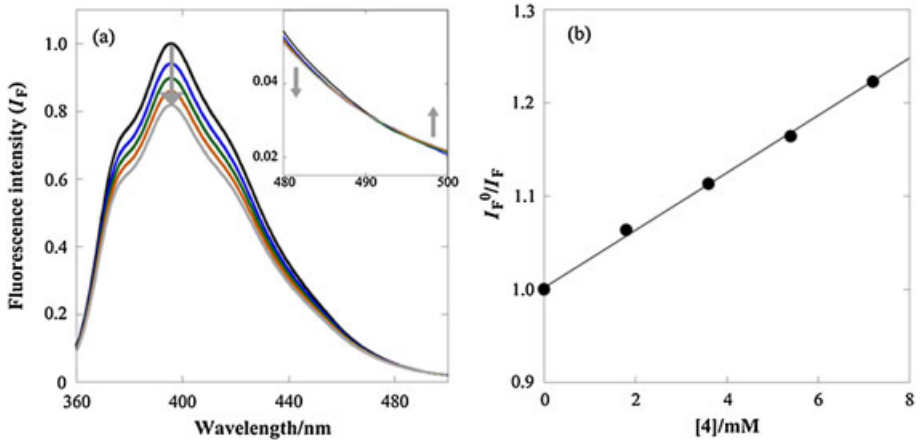


Fig. 2. (**a**) Fluorescence quenching of sensitizer **3** (0.01 mM) by "dummy" substrate **4** (0–7.2 mM, from top to bottom) in methylcyclohexane at room temperature, excitation wavelength: 340 nm, and (**b**) the Stern–Volmer plot obtained therefrom.

It is to note however that the k_Q value obtained for "dummy" substrate **4** in ether reaches 5.9×10^9 M^{-1} s^{-1}, which is only 25% smaller than that for reactive substrate **1** (7.9×10^9 M^{-1} s^{-1}); see Table 1. Furthermore, the fluorescence quenching turned out to be less sensitive to the solvent polarity, affording comparable k_Q values of 5.2-6.3 $\times$ 10^9 M^{-1} s^{-1} for MCH, ether, and acetonitrile. Another crucial finding coherent to this is the effect of polar cosolvents added to MCH. As shown in Table 1, the addition of 0.6 M acetonitrile to MCH did not appreciably alter the original k_Q value, and the addition of 0.1–0.6 M propionitrile only slightly elongated the k_Q value from 5.2 to 5.3–5.9 M^{-1} s^{-1}. These observations are rationalized by assuming that the cyclization path is not a dominant decay route of the exciplex, and the apparent quenching rate constant k_Q is governed not only by the chemical and physical decay processes but also by the reverse reaction regenerating excited sensitizer and ground-state substrate, as clearly demonstrated for the polar photoaddition of methanol to 1,1-diphenylpropene.[14]

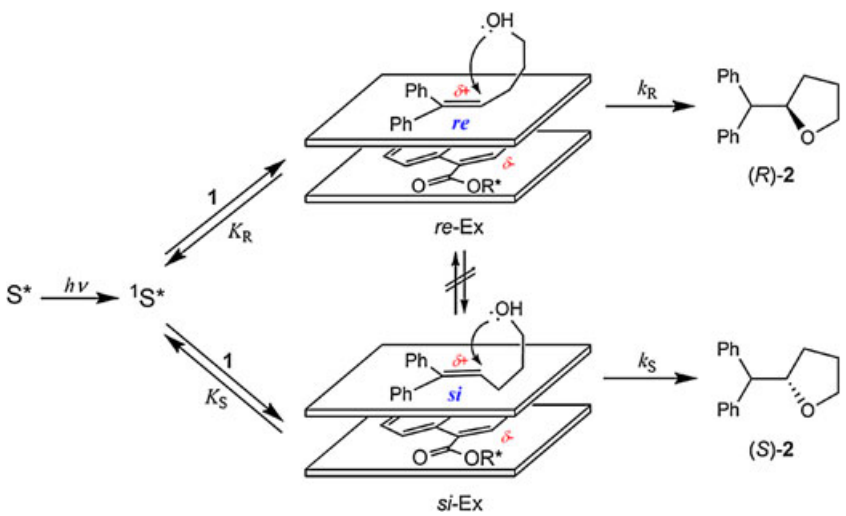
The only exception was toluene, which substantially reduced the k_Q value down to 1.5×10^9 M^{-1} s^{-1}. This may be attributed to the π–π stacking solvation to excited **3**, which energetically stabilizes the excited state and also hinders the attack of substrate. This rationale is experimentally supported by the bathochromic shift of the fluorescence to 423 nm and the elongated lifetime of 11.6 ns in toluene, both of which are greater than the corresponding values in polar acetonitrile (Table 1).

Photoreaction

The photosensitized polar addition of alcohols to 1,1-diarylalkenes proceeds through a radical ionic exciplex and is facilitated in polar solvents.[12,14,15] When chiral sensitizer and prochiral substrate are employed, the exciplex-derived therefrom becomes a pair of diastereomers (*re*-Ex and *si*-Ex), as illustrated in Scheme 3, in which either *re*-face or *si*-face of the olefin moiety of **1** is open and therefore attacked intramolecularly by the terminal hydroxyl group. The relative stability of two diastereomeric exciplexes (K_R/K_S) and the relative rate constant of the subsequent cyclization (k_R/k_S) are the two dominant factors determining the ee of the alcohol adduct produced. An analogous general diastereodifferentiating mechanism may operate in the present case, excepting that the hydroxyl group introduced to the substrate is expected to stabilize the exciplex intermediate, facilitate its charge separation, and eventually accelerate the subsequent cyclization process, as demonstrated by the fluorescence quenching experiments described earlier.

The enantiodifferentiating photocyclization of **1** was first examined in MCH at a relatively high substrate concentration of 20 mM to afford cyclic ether **2** in modest 20%–26% ee at temperatures ranging from 25 to −20 °C (Table 2, runs 1–3). The photocyclization in toluene at 25 °C (run 9) and in ether from 25 to −20 °C (runs 10–12) afforded **2** in higher ee's of 28% and 22%–35%, respectively. However, the use of more polar acetonitrile as a solvent led to the formation of almost racemic product (0%–5% ee) from 25 to −20 °C (runs 13–15). This somewhat irregular trend of the product's ee seems reasonable because the radical cationic nature of **1** in the exciplex intermediate is promoted by increasing the solvent polarity to accelerate the cyclization to **2**, whereas the diastereodifferentiating interaction of substrate with chiral sensitizer in the exciplex is maintained in less polar solvents such as toluene and ether but damaged in a polar solvent like acetonitrile by the dissociation or solvent separation of the radical ionic exciplex.

When ether (0.6 M) was added to the MCH solution as a cosolvent, the product's ee obtained was appreciably improved from 20% to 27% at 25 °C and from 26% to 30% at 0 °C; compare runs 4 and 5 with runs 1 and 2. This ee enhancement is presumably due to the selective solvation of added ether to the radical cationic exciplex, which enhances the local polarity around the exciplex to promote its charge separation and facilitate the intramolecular attack of the terminal hydroxyl, whereas its dissociation to a solvent-separated or free radical ion pair is discouraged by the low bulk polarity of MCH. Because the radical cationic exciplex is indeed a pair of *re*-face and *si*-face stacked diastereomeric isomers, the relative stability and/or cyclization rate should be critically affected by the microenvironmental change caused by the selective solvation. More polar acetonitrile added to MCH as a cosolvent was apparently not effective in enhancing the enantioselectivity, affording comparable 19%–23% ee upon addition of 0.3–0.6 M



Scheme 3. Mechanism of the enantiodifferentiating photocyclization of **1** to enantiomeric **2** via a diastereomeric exciplex pair (*re*-Ex and *si*-Ex), which either dissociates to singlet-excited sensitizer (^{1}S*) and **1** or suffers intramolecular attack of the terminal OH from the open *re*-face or *si*-face of radical cationic $\mathbf{1}^{\delta+}$ to afford (*R*)-**2** or (*S*)-**2**.

TABLE 2. Enantiodifferentiating polar photocyclization of 1 to 2 sensitized by 3 in various solvents with and without added cosolvent[a]

Run	**1**/mM	**3**/mM	Solvent	Cosolvent	Temperature/°C	Conversion/%	Yield/%	ee/%
1[b]	20	3	MCH[c]	none	25	*d*	*d*	20
2					0	*d*	*d*	26
3					−20	*d*	*d*	21
4[b]				Et_2O (0.6 M)	20	*d*	*d*	27
5					0	*d*	*d*	30
6				AN[c] (0.3 M)	25	*d*	*d*	19
7					0	*d*	*d*	23
8				(0.6 M)	25	*d*	*d*	19
9[b]			toluene	none	25	24	25	28
10[b]			Et_2O	none	25	68	12	22
11					0	30	13	33
12					−20	63	6	35
13[b]			AN[c]	none	25	18	14	5
14					0	30	13	1
15					−20	33	12	0
16				Et_2O (0.6 M)	0	23	13	0
17	2	0.3	MCH[c]	none	25	51	18	35
18					0	37	24	33
19					−20	9	67	33
20				PN[c] (0.1 M)	25	33	18	33
21				(0.3 M)	25	39	31	33
22					0	24	42	33
23				(0.6 M)	25	18	44	28
24					0	14	43	24
25					−20	4	*d*	9
26			Et_2O	none	25	36	31	28
27					0	12	25	35

[a]Irradiated at 313 nm for 2 h.
[b]Data cited from Reference 16.
[c]MCH, methylcyclohexane; AN, acetonitrile; PN, propionitrile.
[d]Not determined.

acetonitrile (runs 6–8). However, these modest ee's are rather extraordinary in view of the extremely low 0–5% ee obtained in pure acetonitrile (runs 13–15) and in an acetonitrile–ether mixture (run 16) and indicate that acetonitrile added to MCH solvates selectively to the radical cationic exciplex, whereas the low bulk polarity of MCH confines the radical cationic exciplex in a polar solvation shell of acetonitrile surrounded by bulk MCH to eventually afford the ee's comparable with those obtained in pure MCH.

Unexpectedly, the product's ee obtained upon photolysis in MCH from 25 to −20 °C was significantly enhanced from 20%–26% (Table 2, runs 1–3) to 33%–35% (runs 17–19) by simply diluting the sample solution by 10 times to 2 mM substrate and 0.3 mM sensitizer concentrations. Intriguingly, this apparently strange concentration dependence of ee seems specific to the photocyclization in MCH. When the photocyclization was performed in ether at 0–25 °C, the ee was only slightly improved from 22%–33% (runs 10 and 11) to 28%–35% (runs 26 and 27) by reducing the substrate concentration from 20 mM to 2 mM. On the other hand, the product becomes almost racemic upon irradiation in polar acetonitrile (runs 13–15), as stated earlier. Thus, the lower ee's obtained in MCH at a higher substrate concentration (20 mM) may be attributed at least, in part, to the increased polarity of solvent MCH mixed with inherently polar alcoholic substrate **1**. Other possible explanations for the concentration effect, including the hydrogen-bonding self-aggregation of substrates and the hydrogen-bonding interaction between the substrate's OH and the sensitizer's carbonyl in the ground state, may be ruled out because the addition of good hydrogen-bond acceptor, such as ether (0.6 M) or acetonitrile (0.3–0.6 M), to MCH did not influence the product's ee (Table 2, runs 4–8).

We therefore re-examined the effects of selective solvation on the enantioselectivity of photocyclization under the dilute condition by using less polar propionitrile as a cosolvent. As shown in Table 2, the product's ee was not appreciably affected by the addition of 0.1–0.3 M propionitrile (runs 20–22), holding the original 33%–35% obtained in pure MCH (runs 17–19). Furthermore, the addition of 0.6 M propionitrile noticeably reduced the ee to 28% at 25 °C, to 24% at 0 °C, and even to 9% at −20 °C (runs 23–25), which may be attributed to a greater contribution of the solvent-separated radical ion pair facilitated by the high local polarity caused by excessive solvation around the exciplex upon addition of 0.6 M propionitrile, in particular, at lower temperatures. It is concluded therefore that the concept of microenvironmental polarity control is of great importance for the enantiodifferentiating polar photoaddition/cyclization of diphenylalkene derivatives lacking polar substituent but does not contribute as a convenient effective tool for enhancing the product's ee for such substrates with polar substituent(s).

CONCLUSION

In this study to microenvironmentally control the photochirogenic reaction, we first obtained the evidence that supports the intervention of an exciplex intermediate in the photocyclization of 5-hydroxy-1,1-diphenylpentene **1** by

using a "dummy" substrate **4**. The enantiodifferentiating photocyclization of **1** sensitized by chiral naphthalene derivative **3** turned out to be significantly dependent on the substrate concentration, affording enantiomeric ester **2** in 20% ee at 20 mM but much higher 35% ee at 2 mM, which is probably attributable to the reduced solvent polarity upon 10-fold dilution of the polar substrate. However, the attempts to enhance the product's ee by selective solvation to the intervening diastereomeric exciplex pair were not successful, which is presumably due to the inherently augmented local polarity around the exciplex as a result of intramolecular solvation of the built-in hydroxyl group to the radical cationic olefin part of substrate **1**. This is a bitter but valuable lesson, which should be taken into account in designing such chiral photoreaction systems that involve polarized or radical ionic exciplex intermediates.

LITERATURE CITED

1. Griesbeck AG, Meierhenrich UJ. Asymmetric photochemistry and photochirogenesis. Angew Chem Int Ed 2002;41:3147–3154.
2. Inoue Y, Ramamurthy V, editors. Chiral photochemistry. New York: Marcel Dekker; 2004.
3. Müller C, Bach T. Chirality control in photochemical reactions: enantioselective formation of complex photoproducts in solution. Aust J Chem 2008;61:557–564.
4. Hoffmann N. Photochemical reactions as key steps in organic synthesis. Chem Rev 2008;108:1052–1103.
5. Ramamurthy V, Inoue Y, editors. Supramolecular Photochemistry. Hoboken, NJ: Wiley; 2011.
6. Inoue Y, Yokoyama T, Yamasaki N, Tai A. Temperature switching of product chirality upon photosensitized enantiodifferentiating cis-trans isomerization of cyclooctene. J Am Chem Soc 1989;111:6480–6482.
7. Inoue Y, Yamasaki N, Yokoyama T, Tai A. Enantiodifferentiating *Z-E* photoisomerization of cyclooctene sensitized by chiral polyalkyl benzenepolycarboxylates. J Org Chem 1992;57:1332–1345.
8. Inoue Y, Yamasaki N, Yokoyama T, Tai A. Highly enantiodifferentiating photoisomerization of cyclooctene by congested and/or triplex-forming chiral sensitizers. J Org Chem 1993;58:1011–1018.
9. Inoue Y, Matsushima E, Wada T. Pressure and temperature control of product chirality in asymmetric photochemistry. Enantiodifferentiating photoisomerization of cyclooctene sensitized by chiral benzenepolycarboxylates. J Am Chem Soc 1998;120:10687–10696.
10. Kaneda M, Asaoka S, Ikeda H, Mori T, Wada T, Inoue Y. Discontinuous pressure effect upon enantiodifferentiating photosensitized isomerization of cyclooctene. Chem Comm 2002;1272–1273.
11. Kaneda M, Nakamura A, Asaoka S, Ikeda H, Mori T, Wada T, Inoue Y. Pressure control of enantiodifferentiating photoisomerization of cyclooctenes sensitized by chiral benzenepolycarboxylates. The origin of discontinuous pressure dependence of the optical yield. Org Biomol Chem 2003;1:4435–4440.
12. Kaneda M, Nishiyama Y, Asaoka S, Mori T, Wada T, Inoue Y. Pressure control of enantiodifferentiating polar addition of 1,1-diphenylpropene sensitized by chiral naphthalenecarboxylates. Org Biomol Chem 2004;2:1295–1303.
13. Inoue Y, Ikeda H, Kaneda M, Sumimura T, Everitt, SRL, Wada T. Entropy-controlled asymmetric photochemistry: switching of product chirality by solvent. J Am Chem Soc 2000;122:406–407.
14. Asaoka S, Kitazawa T, Wada T, Inoue Y. Enantiodifferentiating anti-Markovnikov photoaddition of alcohols to 1,1-diphenylalkenes sensitized by chiral naphthalenecarboxylates. J Am Chem Soc 1999;121:8486–8498.
15. Asaoka S, Wada T, Inoue Y. Microenvironmental polarity control of electron-transfer photochirogenesis. Enantiodifferentiating polar addition of 1, 1-diphenyl-1-alkenes photosensitized by saccharide naphthalenecarboxylates. J Am Chem Soc 2003;125:3008–3027.
16. Nishiyama Y, Wada T, Asaoka S, Mori T, McCarty TA, Kraut ND, Bright FV, Inoue Y. Entrainer effect on photochirogenesis in near- and supercritical carbon dioxide: Dramatic enhancement of enantioselectivity. J Am Chem Soc 2008;130:7526–7527.
17. Mizuno K, Tamai T, Nishiyama T, Tani K, Sawasaki M, Otsuji Y. Intramolecular photocyclization of ω,ω-diphenyl-(ω-1)-alken-1-ols by an exciplex quenching mechanism. Angew Chem Int Ed 1994;33:2113–2115.
18. Ishii H, Imai Y, Hirano T, Maki S, Niwa H, Ohashi M. Isoquinoline formation by a novel photochemical intermolecular cycloaddition of 1, 1-diphenylethene derivatives to 1,4-dicyanobenzene. Tetrahedron Lett 2000;41:6467–6471.