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Diastereoselective [2 + 2] Photocycloaddition of Stilbene to Chiral Fumarate. Direct versus Charge-Transfer Excitation

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Abstract: The selective excitation of the charge-transfer (CT) complex and the direct excitation of the substrate gave distinctly different product ratios and diastereomeric excesses (de's), as well as their temperature dependencies, in [2 + 2] photocycloaddition of (*E*)-stilbene to bis((*R*)-1-methylpropyl) fumarate, clearly demonstrating that the excited CT complex and the conventional exciplex differ in structure and reactivity. This conclusion is supported by the contrasting fluorescence behavior exhibited by the relevant excited species, particularly at low temperatures.

Introduction

Chirality control in asymmetric photochemical reactions, or photochirogenesis, is one of the most intriguing and challenging subjects in current chemistry as a unique alternative to conventional thermal asymmetric synthesis.[1−4] Recent studies on photochirogenesis have revealed that a variety of ground- and excited-state intermolecular interactions, such as exciplex formation,[5] hydrogen bonding,[6−8] hydrophobic interactions,[9] and electrostatic interactions,[10] function as crucial factors that control the stereochemical outcome of asymmetric photoreactions.

The charge-transfer (CT) interaction between a donor (D) and an acceptor (A) is one of the weak ground-state interactions.[11−15] An attractive feature of the CT complex is the development of a new absorption band at wavelengths longer than the absorption edges of both D and A. Thus, the CT-complex approach in photochirogenesis provides us with not only a new tool for controlling the chirogenic process but also several advantages over the thermal counterpart, enabling us to switch the mode of activation from direct to CT excitation and to change the reaction temperature over a wide range. Indeed, the possibility of CT excitation has been studied in considerable detail.[16−20] Nevertheless, chirality control, utilizing this unique feature of CT complexes, does not appear to have been explored comprehensively. This is due in part to the rather discouraging results obtained in the foregoing comparative studies of direct and CT excitations, which showed practically indistinguishable, or only slightly different, photophysical and photochemical behavior in both excitation modes.[21−24]

In general, an excitation of CT complexes leads to the formation of an ion radical pair, which either reverts to the initial CT pair or dissociates to free radical ions.[25] The resulting radical ions are highly reactive, and therefore the original chiral information of the substrate, if existing at all, is not efficiently transferred or preserved in the final product. For example, Green, Lewis, and co-workers closely examined the [2 + 2] photocycloaddition of (*E*)-stilbene with dimethyl fumarate, and found that, although the direct and CT excitations afford the same cycloadducts in appreciably different quantum yields ($\Phi_{direct} \neq \Phi_{CT}$), the limiting quantum yield (Φ_{direct}^{∞}), obtained by the

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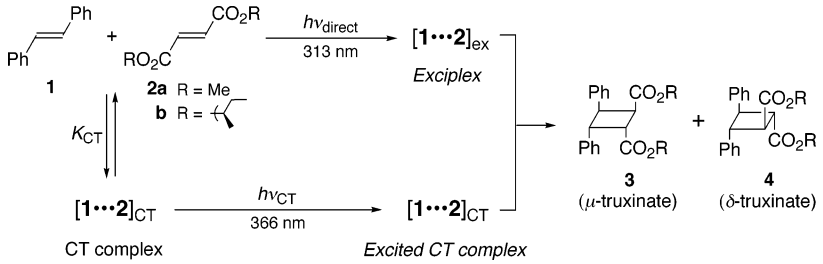
Scheme 1. Charge-Transfer (CT) versus Direct Excitation in [2 + 2] Photocycloaddition of (*E*)-Stilbene (**1**) to Fumarate (**2**)



extrapolation to the infinite fumarate concentration, is practically the same as Φ_{CT}; i.e., $\Phi_{direct}^{\infty} = \Phi_{CT}$.[24] These results indicate that the reactivity of the exciplex obtained by direct excitation is very close to that of the excited CT complex, and further suggests that the overall efficiency of the photocycloaddition is not appreciably affected by the mode of excitation or the intermediates involved. This means that both excitation modes lead to a common ultimate excited species that is the immediate precursor to the final photoproduct. However, Haga, Takayanagi, and Tokumaru recently reported that the quantum yield of photoelectron transfer from acenaphthylene to benzoquinones differs significantly upon direct and CT excitation, although the product distribution does not appreciably change.[26] There are many other examples of the identical photochemical behavior reported for direct and CT excitations of donor−acceptor pairs.[27−32] Similarly, the photophysical behavior of the excited species generated by direct and CT excitation is essentially indistinguishable. For example, a donor−acceptor dyad, in which both moieties are linked through a ligating oligo(ethylene glycol) tether for a Ca^{2+}-induced CT interaction, showed practically the same fluorescence maxima, attributable to the excited intramolecular CT complex, and only slightly different fluorescence quantum yields and decay constants upon direct and CT exciation.[33] Hence, the unequivocal discrimination of photobehavior of an exciplex derived from the direct excitation from an excited CT complex is thought to be quite difficult and controversial in most cases. In this context, the asymmetric photochemical approach, using a chiral auxiliary introduced to the substrate, is a sensible choice for detecting such a seemingly small difference in photobehavior between the exciplex and excited CT species generated via the two excitation modes.

It is well documented that the photoirradiation of (*E*)-stilbene (**1**) with dimethyl fumarate (**2a**) affords two stereoisomeric [2 + 2] cycloadducts, i.e., μ- and δ- truxinates (**3** and **4**), in good combined yield (Scheme 1).[24,34,35] Tolbert and Ali performed the diastereodifferentiating [2 + 2] photocycloaddition initiated by direct irradiation of **1** in the presence of optically active alkyl fumarates, such as di-*l*-bornyl and methyl *l*-bornyl esters, to find that the diastereomeric excess (de) of **3** is a critical function of the chiral auxiliary introduced, reaching 90%.[36] However, they did not further examine the selective excitation of the CT band. More recently, it has been shown that the photoinduced electron transfer from (*E*)-stilbene to fumaronitrile proceeds with unexpectedly large quantum yields upon selective excitation of the CT complex, for which a rapid relaxation of the excited Franck−Condon CT complex to a loose ion pair is thought to be responsible, at least in part.[37]

In this study, to conclude this longstanding elusive discussion, we employed (*E*)-stilbene (**1**) as the donor and bis((*R*)-1-methylpropyl) fumarate (**2b**) as the acceptor. The choice of the simplest chiral alkyl auxiliary for the substrate may lead to photocycloaddition, giving **3** and **4**, in relatively low diastereoselectivities, which are however favorable for more sensitive detection of the structural variations in the intervening species, and hence suitable for a close stereochemical inspection of the similarity and dissimilarity of the photobehavior upon direct and CT excitation. We have also examined the photophysical (fluorescence) behavior of the excited species involved in both excitation modes.

Results and Discussion

Charge-Transfer Complexation. The CT complex formation was quantitatively investigated at 25 °C in various solvents. Upon gradual addition of donor **1** to a solution of acceptor **2b** at a fixed concentration, a new absorption, assignable to a CT complex, emerged at wavelengths 340−400 nm (Figure 1). The association constant (K_{CT}) was determined from the absorbance changes at 350−360 nm in each solvent by a nonlinear least-squares fit (Figure 2); the results are shown in Table 1. It is interesting to note that the solvent polarity does not greatly affect the K_{CT} value, which exhibits a nonsystematic variation in a narrow range of 0.5−1.6 M^{-1} in nonpolar and highly polar solvents. Similarly, the absorption edge of the CT band (λ_{edge}), defined as the wavelength that gives absorption of 0.005, is not significantly affected by the solvent polarity. The K_{CT} values at lower temperatures could not be measured due to factors including the instrumental limitation and the decreased solubility.

Fluorescence Behavior. To elucidate the photophysical consequences of direct and CT excitation, fluorescence spectral measurements at varying excitation wavelengths were performed with a solution of donor **1** in the presence/absence of acceptor **2b**. Under direct excitation conditions (i.e., the exclusive

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Table 1. Association Constant (K_{CT}) and Related Spectral Parameters of the CT Complex of **1** with **2b** in Various Solvents[a]

solvent	μ[b]	ϵ[c]	K_{CT}/M^{-1}	λ_{edge}[d]	[CT][e]/M	A_{CT}/A_1[f]	ϵ_{366}[g]
hexane	0	1.9	0.58	397	0.0060	4	8
methylcyclohexane	0	2.62	1.2	398	0.012	3	3
benzene	0	2.27	1.2	404	0.012	3	4
toluene	0.37	2.38	1.3	401	0.012	5	4
m-xylene	0.02	2.27	0.56	407	0.0053	3	8
mesitylene	0	2.28	1.1	401	0.011	3	4
dioxane	0.4	2.21	1.3	399	0.012	4	4
ether	1.17	4.22	0.51	398	0.0049	3	6
dichloromethane	1.62	8.9	0.59	408	0.0059	3	6
methanol	1.69	32.6	1.6	411	0.013	4	4

[a] Values determined for solutions of [**1**] = [**2b**] = 0.1 M. [b] Dipole moment. [c] Dielectric constant. [d] Absorption edge of CT complex (defined as the wavelength at which the absorbance becomes 0.005). [e] Concentration of CT complex under the conditions employed. [f] Absorbance of CT complex (A_{CT}) and **1** (A_1) at 366 nm. [g] Molar extinction coefficient of CT complex at 366 nm.

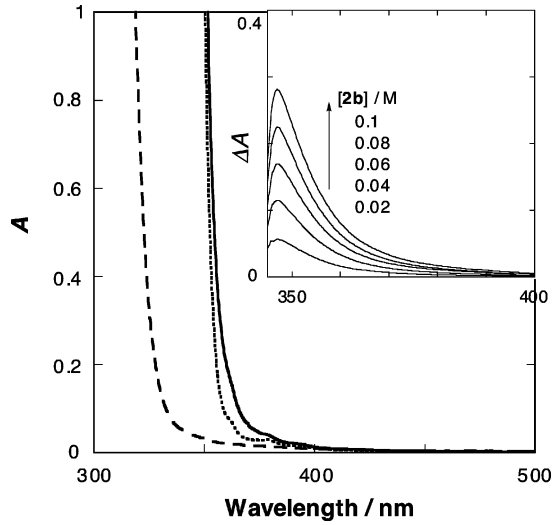

Figure 1. UV−vis spectra of **1** (0.1 M, dotted line), **2b** (0.1 M, broken line), and **1** + **2b** (solid line) in toluene at 25 °C. The difference spectra, developing with increasing **2b** concentration (inset), indicates the formation of the CT complex of **1** with **2b**.

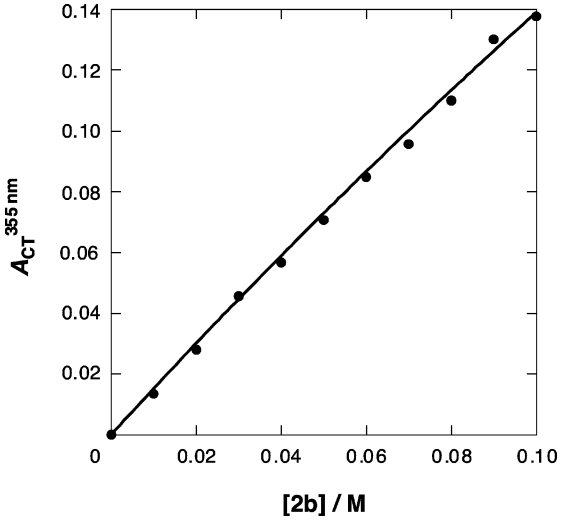

Figure 2. Plot of UV absorbance of CT complex at 355 nm (obtained from the data shown in Figure 1) versus [**2b**] in toluene at 25 °C. The solid line indicates the best fit curve for $K = 1.3\ M^{-1}$, obtained by the nonlinear least-squares fitting procedure.

excitation of **1** at 313 nm), stepwise additions of **2b** to a toluene solution of **1** ($3.4 \times 10^{-5}\ M^{-1}$) caused gradual decreases in the fluorescence intensity (Figure 3), which is accompanied by the corresponding growth of a very weak exciplex fluorescence at

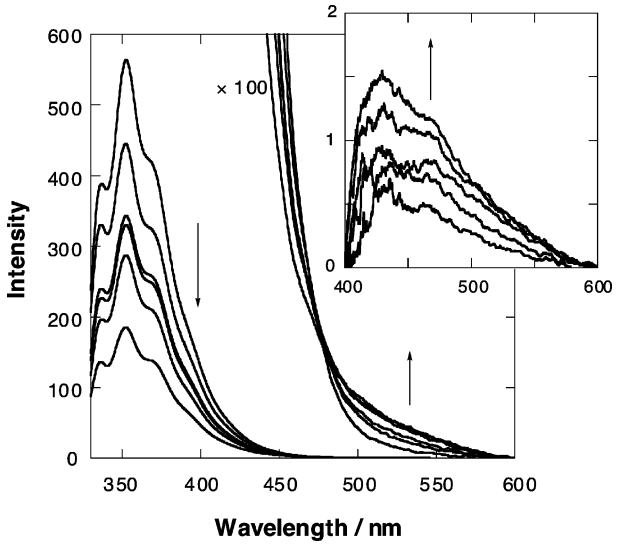

Figure 3. Fluorescence quenching of (*E*)-stilbene (**1**) by bis((*R*)-1-methylpropyl) fumarate (**2b**) excited at 313 nm in toluene at 25 °C. A toluene solution of [**1**] (4.8×10^{-6} M) was quenched by 1.4×10^{-2} M portions of **2b**. The inset shows the exciplex fluorescence spectra obtained by the spectral subtraction.

ca. 430 nm with an isoemissive point (Figure 3, enlargement). Unfortunately, the exciplex fluorescence in toluene (Figure 3, inset) was too weak to be confidently compared in detail with that obtained by CT excitation. However, the quenching experiment in nonpolar methylcyclohexane gave much stronger exciplex fluorescence by a factor of 30 than in toluene, as shown in Figure 4. In these two solvents, the original fluorescence intensity of **1** in the absence of a quencher is comparable, whereas the exciplex fluorescence significantly differs in intensity. Judging from the comparable K_{CT} values (1.2−1.3 M^{-1}) in both solvents, the fluorescence efficiency should be greatly reduced in toluene, probably through the donating interaction of toluene to the exciplex, which may accelerate the nonradiative decay paths, such as internal conversion, intersystem crossing, and product formation. In contrast, methylcyclohexane does not actively interact with the exciplex or accelerate the radiationless decay processes, and therefore the exciplex shows intense fluorescence.

As can be seen from Figure 4, not only the monomer fluorescence of **1** but also the exciplex fluorescence displays vibrational fine structures with the most intense peak occurring at the 0−1 and 0−3 band, respectively. Interestingly, although the spectral shape, or the relative intensity of the progressive peaks, is significantly different for the monomer and exciplex

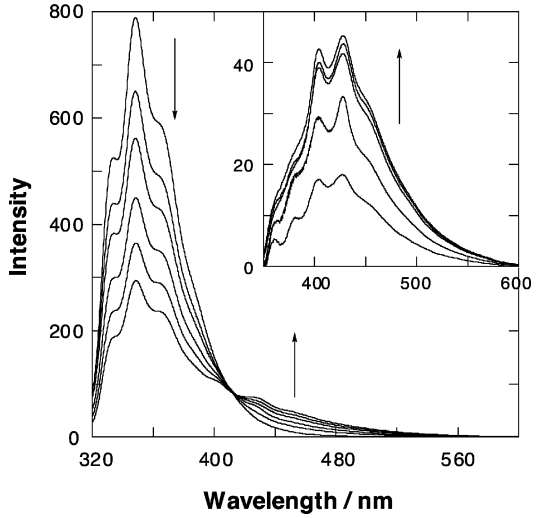

Figure 4. Fluorescence quenching of (*E*)-stilbene (**1**) by bis((*R*)-1-methylpropyl) fumarate (**2b**) excited at 313 nm in methylcyclonexane at 25 °C. A toluene solution of [**1**] (4.8×10^{-6} M) was quenched by 1.4×10^{-2} M portions of **2b**. The inset shows the exciplex fluorescence spectra obtained by spectral subtraction.

fluorescence, the interval of each vibrational band is almost the same for the monomer and excimer, giving vibrational gaps of 1340−1390 cm^{-1} in both cases. These values are very close to that of the vibrational 0−1 transition of **1** determined by IR spectroscopy, which may be assigned to the aromatic, or olefinic, C−H deformation band that appears at 1337 or 1322 cm^{-1}.[38] This agreement may indicate that the photophysical process of the exciplex occurs on a potential surface very similar to that of donor **1**.

From the conventional Stern−Volmer analyses of the data obtained in the above fluorescence quenching experiments (see Supporting Information for the plots), we obtain the Stern−Volmer constants ($k_q\tau$) of 19 and 14 M^{-1} s^{-1} for the fluorescence quenching of **1** by **2b** in toluene and methylcyclohexane, respectively. These values are in good agreement with those reported for the fluorescence quenching of **1** by **2a** (7.6 and 8.3 M^{-1} s^{-1})[24,36] and other methyl/*l*-bornyl/(*R*)-2-methyl-1-butyl fumarates (11.3−12.8 M^{-1} s^{-1}).[36]

Selective CT excitation was made possible by irradiating a toluene solution of **1** (0.1 M) and **2b** (1.0 M) at 380 nm, with the fluorescence from the excited CT complex observed at 400−600 nm (Figure 5). In contrast, a toluene solution containing only **1** (0.1 M) excited at the same wavelength (380 nm) merely displayed a weak dispersion tail at 400−500 nm under comparable conditions (Figure 5a, dashed line). By subtracting the fluorescence spectra obtained in the presence/absence of **2b**, we obtain the fluorescence spectrum of the CT complex, shown in Figure 5a (inset). This CT fluorescence appears slightly different in shape from the exciplex fluorescence observed upon direct excitation at 313 nm of **1** in toluene or methylcyclohexane (Figures 3 and 4). Temperature effects on the CT fluorescence were also examined in a temperature range of 25 to −50 °C. A moderate enhancement of the fluorescence intensity was observed by lowering the temperature, for which the increased formation of CT complex is mostly responsible, while no significant change in shape or vibrational structure was observed over the temperature range employed. Again, the vibrational

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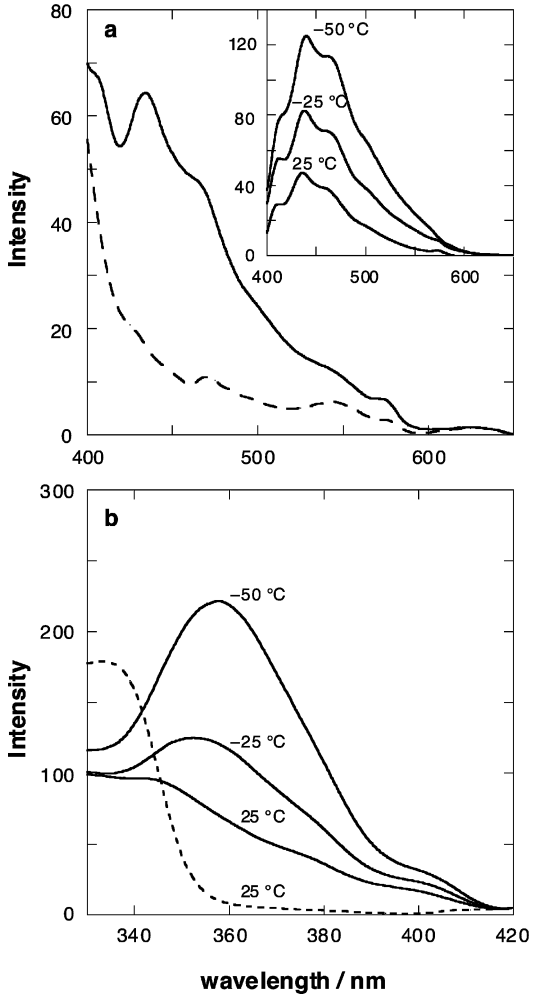

Figure 5. (a) Fluorescence spectra of **1** (0.1 M) (broken line) and **1** + **2b** (0.1 and 1.0 M, respectively) (solid line), both excited at 380 nm in toluene at 25 °C. The inset shows the fluorescence spectra of the CT complex at 25, −25, and −50 °C, obtained by spectral subtraction. (b) The corresponding excitation spectra of **1** at 25 °C (broken line) and of **1** + **2b** at 25, −25, and −50 °C (solid lines); fluorescence observed at 467 nm.

spacing (1340 cm^{-1}) between the 412 and 436 nm peaks is close to that (1390 cm^{-1}) of the corresponding peaks of exciplex fluorescence in methylcyclohexane,as mentioned above, and also to the IR band (1337 or 1322 cm^{-1}) of **1** in the ground state.

To further characterize the emitting species, we measured the excitation spectrum of the CT fluorescence at 467 nm by using the same toluene solution of **1** and **2b** at temperatures varying from +25 to −50 °C. As can be seen from Figure 5b, the excitation spectra obtained at −25 and −50 °C, which display a peak around 350−360 nm, are very different from the absorption spectra of **1**, but are in good agreement with the CT absorption shown in Figure 1. It is interesting that, although the fluorescence spectra differ only slightly between both excited species, the excitation spectra are quite different. We may propose therefore that we can discriminate the excited CT complex from the exciplex by examining the excitation spectral behavior at low temperatures, where the CT complexation is enhanced.

Photocycloaddition of (*E*)-Stilbene with Bis((*R*)-1-methylpropyl) Fumarate. It is known that the photoreaction of **1** with dimethyl fumarate **2a** affords regioisomeric cyclobutanes **3a** and **4a** as the major photoadducts and smaller amounts of

Scheme 2. Photoreaction of (*E*)-Stilbene with Dimethyl Fumarate

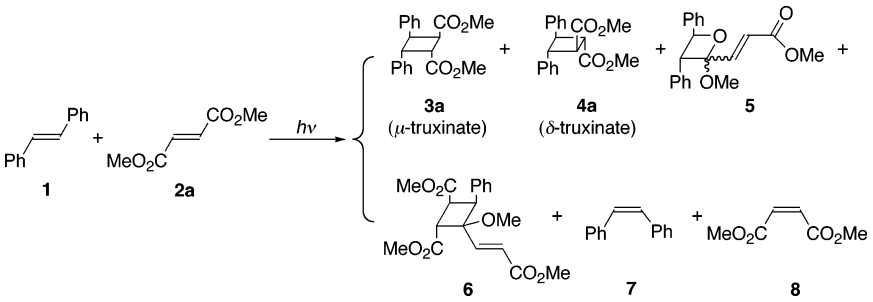

Table 2. Diastereodifferentiating [2 + 2] Photocycloaddition of (*E*)-Stilbene **1** to Bis((*R*)-1-methylpropyl) Fumarate **2b** upon Direct and Charge-Transfer Band Excitation[a]

					% yield[d] (% de[e])	
solvent	excitation mode[b]	temperature/°C	% conversion[c]	**4**/**3**	**3**	**4**
toluene	direct	75	6	0.8	24 (87)	19 (5)
		50	6	1.0	19 (79)	19 (11)
		25	5	1.2	17 (58)	21 (10)
		0	5	1.3	11 (24)	14 (5)
		−25	4	1.2	7 (−7)	9 (2)
		−50	5	0.9	6 (−53)	5 (1)
	CT	75	4	0.9	11 (95)	10 (−2)
		50	6	1.1	6 (90)	7 (8)
		25	3	1.4	11 (85)	15 (2)
		0	5	1.8	5 (77)	9 (7)
		−25	4	2.2	5 (66)	10 (−2)
		−50	5	2.8	4 (52)	10 (−9)
ether	direct	25	4	1.3	11 (77)	14 (6)
		0	3	1.9	9 (43)	16 (6)
		−25	5	1.7	4 (3)	7 (0)
		−50	5	1.3	5 (−27)	6 (3)
	CT	25	4	1.4	5 (83)	7 (9)
		0	17	2.1	2 (72)	3 (9)
		−25	4	2.8	4 (65)	10 (−3)
		−50	3	3.1	5 (28)	16 (−9)

[a] [**1**] = 0.02 M, [**2b**] = 0.2 M. [b] Irradiation was performed either at 313 nm for 10 min (direct excitation) or at 366 nm for 3 h (CT excitation) under an argon atmosphere. [c] Consumption of **1**; the photoisomerization to (*Z*)-stilbene was not taken into account. [d] GC yield based on the conversion of **1**. [e] The negative or positive de is not related to the sign of the product's optical rotation but means the predominant formation of the first- or second-eluted diastereomer on GC, respectively (Varian CP-Sil 8CB column).

oxetane (**5a**) and secondary 2:1 adduct (**6a**), along with the (*Z*)-isomers of the substrate, i.e., **7** and **8** (Scheme 2).[24] In the present study using chiral substrate **2b**, we also observed the formation of **5**−**8** as minor side products, but we will concentrate our discussion on the effects of excitation mode upon the product ratio and diastereoselectivity of cycloadducts **3** and **4**.

Direct versus CT Excitation. A toluene or ether solution (1 mL) of **1** (0.02 M) and **2b** (0.2 M) was irradiated under argon either at 313 nm (the effective radiation for direct excitation) or at 366 nm (the effective radiation for CT excitation), by using a 300-W medium-pressure mercury lamp fitted with a Pyrex or Toshiba UV-37 glass filter, respectively. Under this irradiation condition, the extremely large absorbance of **1** at 313 nm ($A_{313}^{\text{direct}} = 1300$), overwhelming the inherently weak absorption of the CT complex, allows the exclusive excitation of **1**. On the other hand, the selective CT excitation can be done at 366 nm, as the relative absorbance of CT complex and **1** ($A_{366}^{\text{CT}}/A_{366}^{\text{direct}}$) is 5 at 366 nm. Although this $A_{366}^{\text{CT}}/A_{366}^{\text{direct}}$ value only guarantees 83% CT-selective excitation, the following factors enhance the contribution of photoproducts arising from the CT excitation. First, a twice as large quantum efficiency was reported for the CT excitation as for the direct excitation in the photocycloaddition of **1** (0.11 M) to **2a** (0.42 M); i.e., the quantum yields of **3a** obtained upon CT and direct excitation in toluene are 0.035 and 0.018, respectively.[24] Second, the K_{CT} value is considered to increase as the temperature decreases, enabling highly CT-selective excitation particularly at low temperatures.

Product Ratio. Photoirradiations of toluene or ether solutions (1 mL) of **1** (0.02 M) and **2b** (0.2 M) were performed at temperatures ranging from −50 to +75 °C. The photolysates obtained were analyzed by GC to give the conversions, yields, product ratios, and de's shown in Table 2. The major photoreaction observed is the geometric isomerization to the (*Z*)-isomer. Hence, to avoid any complication which could be caused by possible contamination with secondary photoreactions of the (*Z*)-isomer[24,35] or any other products, only the product yields and de's obtained at low conversions (≤5%) will be used in the following discussion. In representative runs, this condition was fulfilled by irradiating the sample for 10 min at 313 nm (for direct excitation) and for 3 h at 366 nm (for CT excitation).

In toluene at 25 °C, the direct and CT excitation gave only slightly different **4**/**3** ratios of 1.2 and 1.4, respectively. However, the two excitation modes displayed completely different temperature-dependence profiles. Over the temperature range examined (+75 to −50 °C), the direct irradiation gave only slightly varying **4**/**3** ratios of 0.8−1.3, while the ratio obtained upon CT excitation steadily increased from 0.9 to 2.8 by decreasing the temperature from 75 to −50 °C. Exactly the same trends were observed upon irradiation in ether. Thus, the

temperature dependence is much more evident for CT, rather than direct, excitation. As shown in Table 2, direct and CT excitation gave almost identical **4**/**3** ratios of 1.3 and 1.4 at 25 °C, but substantially different ratios of 1.3 and 3.1 at −50 °C. In summary, the **4**/**3** ratio shows different temperature-dependence profiles for the direct and CT excitation, leading to an unambiguous distinction at low temperatures. Since the **4**/**3** ratio upon CT excitation should reflect the relative stability of the diastereomeric precursor CT complexes in the ground state, it is sensible to consider that the enhanced population of the less hindered precursor complex at low temperatures, leading to the formation of **4**, is responsible at least in part for the increased **4**/**3** ratio. On the other hand, the exciplex formation and the subsequent cycloaddition are less sensitive to steric hindrance as well as temperature changes, as judged from the comparable formation of **3** and **4** at varying temperatures and in different solvents. It is apparent from the **4**/**3** ratios obtained by direct or CT excitation that the excited CT complex possesses a more compact structure than the exciplex, which may lead to the different reactivities observed upon the two excitation modes. From the synthetic point of view, the low-temperature CT excitation is the right protocol for obtaining a high stereoselectivity for **4**.

Diastereoselectivity. The stereochemical examinations using chiral substrate **2b** revealed more clear and intriguing differences between direct and CT excitation. It turned out that the product de and its temperature-dependence profile critically depend on the mode of excitation. As shown in Table 2 (note that the negative or positive de sign does not mean the formation of levo- or dextrorotatory product, but simply indicates a predominant formation of the first or second eluted diastereomer on GC), direct and CT excitation in toluene at 25 °C gave cycloadduct **3** in 58% and 85% de and **4** in 10% and 2% de, respectively. The much smaller de's obtained for **4** seem reasonable and are attributed to the least hindered all-trans configuration, in which control of the newly generated stereogenic centers through the inter-/intramolecular interactions with the chiral auxiliary may be difficult.

It should be noted that the product de increases with increasing temperature upon direct and CT excitation, and also that the temperature switching of the product chirality occurs upon CT excitation. The de of **3** strongly depends on the temperature, but the dependence profile is totally different between the direct and CT excitation. Upon CT excitation in toluene, the de of **3** showed a moderate decrease from 95% to 52% by decreasing the temperature from 75 to −50 °C. In contrast, the direct irradiation at varying temperatures led to an inversion of the product chirality, affording the antipodal **3** in 87% and −53% de at 75 and −50 °C, respectively. This enables us to switch the diastereoselectivity by changing the irradiation temperature. On the other hand, the de of **4** stayed low (≤10%) over the temperature range employed; probably, the chiral auxiliary employed in this study is too small to effectively control the stereochemistry of the least hindered **4**. The temperature-dependence profiles in ether are very similar to those observed in toluene, exhibiting a moderate temperature dependence of de upon CT excitation but a switching of product chirality by temperature upon direct excitation.

A more quantitative analysis was performed for the temperature dependence of the de of **3**, by using the whole de data

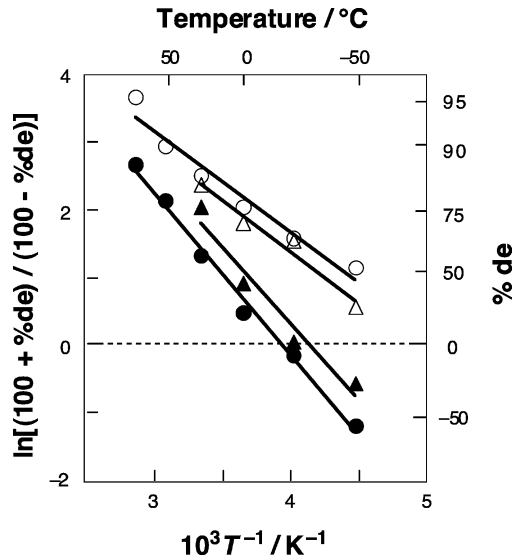

Figure 6. Temperature dependence of the de of **3b** obtained upon direct excitation in toluene (●) and in ether (▲), and upon CT excitation in toluene (○) and in ether (△).

Table 3. Activation Parameters Determined from the Temperature Dependence of the de of **3** Obtained in the Diastereodifferentiating Photocycloaddition of **1** with **2b**

excitation mode	solvent	$\Delta\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
direct	toluene	19.9	78.5
	ether	18.8	78.1
CT	toluene	12.4	63.7
	ether	12.6	62.2

obtained in toluene at temperatures ranging from −50 to +75 °C and in ether at −50 to +25 °C. According to the differential Eyring equation derived for stereodifferentiating reactions,[2,5] the logarithm of the relative formation rate of diastereomeric **3**, i.e., $\ln(k_+/k_-)$ or ln[(100 + % de)/(100 − % de)], was plotted against the reciprocal temperature. Although the de of **3** decreases with decreasing temperature to give a good straight line in each case, the changing profile depends critically on the excitation mode and slightly on the solvent employed. The linear correlations obtained for the direct and CT excitations in both solvents afford the differential activation parameters listed in Table 3. The good fit to a single straight line over the entire temperature range indicates that a single diastereodifferentiating mechanism operates in each excitation mode, while the distinctly different activation parameters obtained for each mode indicate that the photocycloaddition proceeds through separate mechanisms and transition states upon direct and CT excitation. It is interesting that the alteration of solvent affects only slightly the $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values, indicating a less important role of solvation in the diastereodifferentiating process.

Conclusions

In the present study of the direct and CT-excited photocycloaddition of (*E*)-stilbene **1** to bis((*R*)-1-methylethyl) fumarate **2b**, we have unequivocally demonstrated that the excited CT complex is different both in fluorescence behavior and in structure and reactivity from the conventional exciplex obtained by direct excitation. Thus, the excitation spectra of the CT fluorescence at low temperatures show a structureless broad peak, which is red-shifted from the stilbene absorption but nicely

corresponds in shape and position to the CT absorption. The photoreactivity, i.e., the product ratio and de, also differs significantly. Particularly interesting are the different temperature-dependence profiles of the de obtained in the two excitation modes, which unequivocally reveal that the exciplex formed upon direct irradiation and the excited CT complex do not interconvert to each other in the temperature range examined. This means that we have acquired a new versatile tool for controlling the stereoselectivity in photochirogenesis at least at low conversions.

It is also noted that *the product de increases with increasing temperature* and *the product chirality is switched by changing the temperature*. Similar phenomena have been reported for the enantiodifferentiating photosensitized geometric isomerization of cyclooctene and the polar addition of methanol to 1,1-diphenylpropene,[5] demonstrating the pronounced contribution of the entropic, over enthalpic, factor in this diastereodifferentiating photocycloaddition governed by noncovalent weak interactions in the ground and/or excited states. Further attempts to reveal the mechanism and factors controlling the diastereoselectivity in both excitation modes and also to expand the scope of the CT-mediated photochirogenesis are currently in progress.

Experimental Section

General. Melting points were measured with a Yanaco MP-21 apparatus and are uncorrected. IR spectra were obtained on a JASCO FT/IR-230 spectrometer. UV−vis absorption spectra were recorded on a JASCO V-550 spectrophotometer (response medium; bandwidth 2.0 nm; scanning rate 200 nm/min). Fluorescence spectra were obtained on a JASCO FP-6500 spectrophotometer (excitation bandwidth 5 nm; observation bandwidth 5 and 10 nm for direct and CT excitation, respectively; response 1 s; sensitivity medium; scanning rate 200 nm/min; excitation at either 313 or 380 nm for direct and CT excitation, respectively). Gas chromatographic analyses were performed on a Shimadzu GC-14B instrument fitted with a Varian CP-Sil 8CB capillary column (30 m × 0.25 mm; 0.25 μm stationary phase; initial column temperature 130 °C; injector and detector temperature 280 °C). Immediately after the injection of sample, the column temperature was raised to 180 °C at a rate of 5 °C/min and then to 280 °C at 2.5 °C/min, and kept at that temperature for 10 min. All GC peaks were integrated on a Shimadzu CR-6A integrator. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX-400 spectrometer in chloroform-*d* with Me_4Si as an internal standard. GC−MS (CI and EI) analyses were performed on a Hewlett-Packard HP 5890 Series II and HP 5971A mass selective detector with an applied voltage of 70 eV. Elemental analysis was performed at the Center for Chemical Analyses, Osaka University.

Materials. Anhydrous toluene (99.8% purity), obtained from Riedel de Haën, was refluxed over CaH_2 for 3 h and then distilled under argon atmosphere, prior to use. Anhydrous diethyl ether (99.5% purity) from Riedel de Haën was refluxed over P_2O_5 for 5 h, and the result was decanted and fractionally distilled from Na and benzophenone under argon atmosphere, prior to use. (*E*)-Stilbene (**1**) (Wako) was purified by recrystallization from ethanol.

Bis((*R*)-1-methylpropyl) fumarate (**2b**) was prepared as follows. Fumaroyl chloride (Wako, 5.2 g, 34 mmol) and triethylamine (6.8 g, 67 mmol) were added dropwise to a THF solution of (*R*)-(−)-2-butanol (5.0 g, 67 mmol) (Aldrich, 99% pure) over 30 min, and the mixture was refluxed for 10 h under an argon atmosphere. The resulting mixture was cooled to room temperature and the solvent evaporated under a reduced pressure. The residue obtained was purified by flash chromatography on silica gel with a hexanes−ethyl acetate eluent (98:2) to give colorless oil (5.5 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 6H), 1.26 (d, J = 6.4 Hz, 6H), 1.61 (dq, J = 6.4 Hz, 7.3, 4H), 4.95 (tq, J = 6.4 Hz, 2H), 6.83 (s, 2H); IR (neat) ν_{max}/cm^{-1} 2974, 2939, 2881, 1718, 1647, 1458, 1381, 1356, 1259, 1223, 1159, and 1093; CI-MS *m*/*z* (relative intensity) 229 ($M^+ + 1$, 10), 173 (100), 157 (5), 117 (14), 99 (2), Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 62.86; H, 8.90.

Photoreaction. All irradiations were performed under an argon atmosphere in a temperature-controlled water (from 25 to 75 °C) or methanol/2-propanol (from −50 to 0 °C) bath. For a direct excitation of stilbene, the solution was irradiated with a 300-W high-pressure mercury lamp (Eikosha, PIH type) fitted with a Pyrex filter (cutoff wavelength, 280 nm). A Toshiba UV-37 filter was used for a selective CT excitation at 366 nm.

Bis((*R*)-1-methylpropyl) μ-truxinate (3). Colorless crystal; mp 70−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.537 (t, J = 7.62, 6H), 0.974 (d, J = 6.16, 6H), 1.04−1.16 (m, 4H), 3.85 (d, J = 9.42, 2H), 4.54 (tq, J = 6.16, 2H), 4.60 (d, J = 9.42, 2H), 7.15−7.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.10, 18.9, 28.1, 44.2, 44.8, 72.7, 126.9, 127.4, 128.9, 139.1, 171.6; EI-MS *m*/*z* (relative intensity) 408 (M^+, 1.3), 306 (42.5), 250 (62.5), 205 (53.2), 180 (98.5), 148 (100); IR (KBr) ν_{max}/cm^{-1} 3062, 3030, 2976, 2937, 2879, 1711, 1637, 1560, and 1543. Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.36; H, 8.10.

Bis((*R*)-1-methylpropyl) δ-truxinate (4). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.33, 6H), 1.21 (d, J = 6.22, 6H), 1.49−1.66 (m, 4H), 3.37 (d, J = 9.53, 2H), 3.80 (d, J = 9.52, 2H), 4.92 (tq, J = 6.23, 2H), 7.21−7.34 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.65, 19.5, 28.8, 45.5, 46.4, 72.9, 126.8, 126.9, 128.6, 141.4, 172.3; EI-MS *m*/*z* (relative intensity) 408 (0.95), 306 (20.6), 250 (21.3), 204 (30.2), 148 (100), 131 (42.9); IR (neat) ν_{max}/cm^{-1} 3062, 3030, 2974, 2935, 2879, 1728, 1603, 1496, 1454, 1414, 1379, 1360, and 1319. Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.01; H, 7.77.

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Supporting Information Available: Stern−Volmer plots for fluorescence quenching of **1** with **2b** in toluene and in methylcyclohexane. This material is available free of charge via the Internet at http://pubs.acs.org.

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