Effects of Steric Bulkiness of Substituents on Quantum Yields of Photochromic Reactions of Furylfulgides

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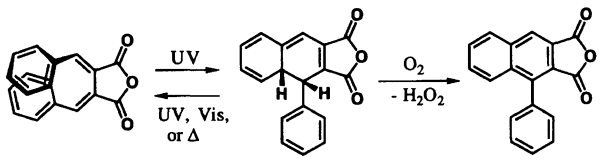
(Received May 9, 1994)

Furylfulgides with different sizes of alkyl substituents were synthesized and their photochromic properties were examined. While the quantum yield of coloring reaction increased and the quantum yield of the *E*-to-*Z* isomerization decreased as the steric bulkiness of the alkyl substitutent on the 2,5-dimethyl-3-furylmethylidene moiety increased, the bleaching quantum yield increased as the isopropylidene group was replaced by an adamantylidene group. Both effects worked independently, and a furylfulgide with an isopropyl group on the furylmethylidene moiety and an adamantylidene group in one molecule showed the coloring quantum yield of 0.51 (366 nm) and the bleaching quantum yield of 0.26 (492 nm) in toluene.

Fulgides have been known as photochromic compounds since the beginning of the twentieth century, when Stobbe synthesized a series of substituted phenyl derivatives.[1] The structures of photocyclized colored products had not been clarified until 1968 when Santiago and Becker identified the dehydrogenated product of a photocyclized isomer of bisbenzylidenesuccinic anhydride to be a naphthalene derivative,[2] thus confirming the mechanism of photochromism of fulgides (Scheme 1).



Scheme 1.

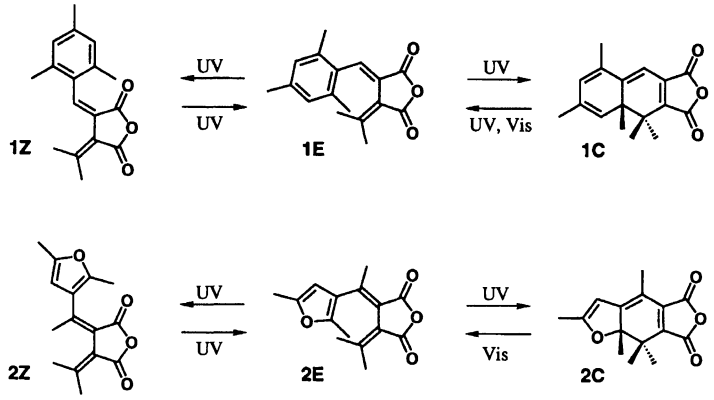
In 1974, Heller and his co-workers synthesized the first *thermally irreversible* photochromic fulgide, (*E*)-2-isopropylidene-3-mesitylmethylenesuccinic anhydride (**1E**)[3], although the ratio of conversion to the colored form was too low to measure. Improvement of **1E** was done in 1981 by the same research group. They presented the synthesis of (*E*)-2-[1-(2,5-dimethyl-3-furyl)-ethylidene]-3-isopropylidenesuccinic anhydride (**2E**).[4] Conversion of this compound to the colored form at the photostationary state of UV light irradiation was practically 100%. The colored species **2C** was entirely bleached to give **2E** again, without any serious side reactions (Scheme 2). Thus, introduction of a methyl group on the aromatic ring carbon atom that participates to form a C–C single bond upon UV irradiation prevented: (1) thermal coloring and bleaching reactions, (2) oxidation to afford aromatic dibasic acid anhydride derivatives, and (3) pericyclic hydrogen shift reactions.

This observation, i.e. only light irradiation, not thermal treatment, can cause isomerization between two chemical species quantitatively, stimulated a number of industrial and academic chemists to pursue the possibility that fulgides would be applicable to photon-mode rewritable optical memory,[5] since organic photochromic compounds so far were thermally reversible and not suitable to store information. To realize such rewritable photomemory, however, many problems had to be solved: (1) fatigue resistivity,[6] (2) thermal stability,[6] (3) high efficiency of photoreactions, (4) diode laser sensitivity,[7] (5) development of a non-destructive readout method,[8] (6) usability in polymer matrix.[6,9] Among them, the third one (high efficiency of photochromic processes) is not indispensable but strongly required because it directly concerns the laser power and irradiation time of write/read/erase procedures and therefore the lifetime of the memory media. We here describe our effort to obtain furylfulgides with high quantum yields of photochromic reactions.[10—12]

Results and Discussion

Effects of Steric Bulkiness of Alkyl Groups on the Furylmethylidene Moiety of Furylfulgides. In 1981, Heller and co-workers synthesized (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (**2E**).[4] This colorless compound turned to its colored isomer **2C**, with some double-bond isomerization to **2Z**, upon irradiation of UV light such as 366-nm light from a mercury lamp. As the bleaching reaction of **2C** to **2E** by the UV irradiation was negligible because of the small molar absorption coefficient of **2C** at 366 nm, the photostationary state of UV-irradiation between **2E**, **2Z**, and **2C** was 100% **2C** in most of common solvents. The red-colored **2C** underwent reverse reaction to its colorless isomer **2E** upon irradiation with visible light such as 500-nm light. The most striking feature of **2** is that the interconversion between **2E** and **2C** did not occur thermally at room temperature.

At the outset of our research on photochromic fulgides, we aimed to remove the *E*–*Z* isomerization from the photochromic process of furylfulgide **2E**, which is an energy-wasting process of light and slows down the



Scheme 2.

apparent rate of the coloring process. The prevention of *E–Z* isomerization would then cause increase in quantum yield of coloring.

The idea for how to prevent *E–Z* isomerization was quite simple. Increases in size of the alkyl group on the furylmethylidene moiety would interfere with *E–Z* isomerization because of steric repulsion between the alkyl group and the *E*-methyl of the isopropylidene group. Thus, the synthesis of three furylfulgides (**3** (R=Et), **4**(R=Pr), and **5** (R=*i*Pr), each of which has an alkyl group with larger steric bulkiness than the methyl group, was done (Chart 1).

While the condensation of 2,5-dimethyl-3-propanoylfuran with diethyl isopropylidenesuccinate to synthesize **3** was successful as described in the literature using sodium ethoxide (generated from sodium hydride and ethanol in toluene),[4] condensation of alkanoylfurans with the succinate using the same method, leading to **4** and **5**, failed. This was overcome by using lithium diisopropylamide (LDA) in tetrahydrofuran (THF) as the base to generate an enolate from diethyl isopropylidenesuccinate, and gave a mixture of the corresponding lactones **6** (a mixture of diastereomers) and the half ester **7** in good yields. The fulgides were obtained as a mixture of *E* and *Z* isomers, which were easily separated by flash column chromatography (Scheme 3). Before photoreaction, fulgides were recrystallized from a hexane/ether mixture.

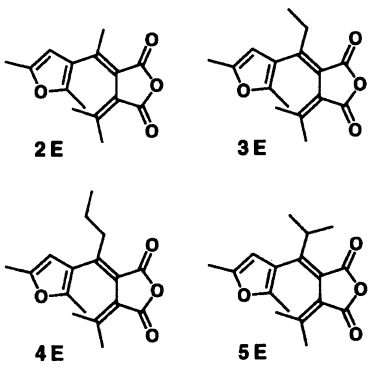


Chart 1.

Table 1 summarizes the absorption maximum (λ_{max}) and the molar absorption coefficient (ε_{max}) of furylfulgides **2**—**5** in chloroform. Although the λ_{max} values of **E**, **Z**, and **C** isomers are not affected by the change of bulkiness of the alkyl group, the ε_{max} values of **E** and **Z** isomers changed dramatically. Namely, the ε_{max} values of both **E** and **Z** isomers decreased as the bulkiness of alkyl group increased, and the ε_{max} values of **5E** and **5Z** are considerably smaller than **2E**—**4E** and **2Z**—**4Z**, respectively. This result might be caused from the change in ground-state conformation from **2E**—**4E** to **5E**. This may strongly relate to the difference in coloring quantum yields.

Quantum yields of the photoreactions of furylfulgides are shown in Table 2. Some notable effects of steric bulkiness are pointed out as follows. (1) While Φ_{ZE} was not affected by the change of steric bulkiness, Φ_{EZ} became smaller as the size of the alkyl group increased. The reduction of Φ_{EZ} was what we had aimed at, and

Table 1. Absorption Spectral Data of Furylfulgides with Bulky Alkyl Substituents in Chloroform

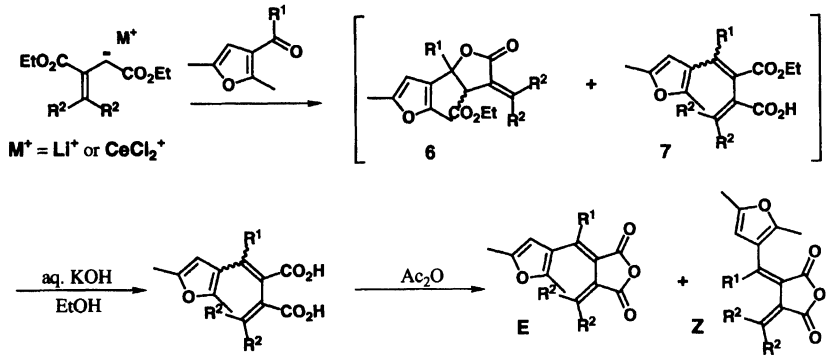
	E	Z	C
	λ_{max}/nm (ε_{max})[a)]	λ_{max}/nm (ε_{max})[a)]	λ_{max}/nm (ε_{max})[a)]
2	347 (6780)	358 (8900)	510 (9690)
3	349 (6690)	358 (8480)	510 (10270)
4	348 (6210)	358 (7460)	510 (9590)
5	347 (4080)	360 (4700)	510 (9320)

a) ε_{max}/mol^{-1} dm^3 cm^{-1}.

Table 2. Quantum Yields of Photoreactions of Furylfulgides with Bulky Alkyl Substituents in Chloroform

	Φ_{EC}[a)]	Φ_{EZ}[a)]	Φ_{ZE}[a)]	Φ_{CE}[b)]
2	0.19	0.13	0.11	0.035
3	0.34	0.06	0.12	0.027
4	0.45	0.04	0.10	0.044
5	0.62	0.00	0.06	0.040

a) 366-nm light irradiation. b) 492-nm light irradiation.



Scheme 3.

what we did. This can be explained by an increase in steric repulsion between the alkyl group and the *E*-methyl group of the isopropylidene group decreasing the portion of formation of *Z* form from the twisted excited state between *E* and *Z* forms. A schematic explanation of the steric repulsion mentioned above in the twisted excited state is given in Fig. 1. After the absorption of a photon, the resulting excited *E* form of a furylfulgide molecule (Franck–Condon state) begins to twist the double bond between the acid anhydride and the furan ring toward the less sterically congesting direction to reduce the antibonding overlap of the p orbitals of the singly occupied energetically higher orbital, and reaches the twisted excited state. Fulgides with a bulky substituent like **5** cannot continue rotation of the bond to reach the *Z* form because of the increasing steric repulsion between R and the *E*-methyl group of the isopropylidene group, resulting in either deactivation to *E* form or generation of *C* form. (2) Φ_{EC} increased as the steric bulkiness of the alkyl group increased. This tendency seems to be rationalized by the fact that Φ_{EZ} is smaller for fulgides with larger alkyl groups. However, the disappearance of the *E*–*Z* isomerization for fulgide **5** cannot increase the Φ_{EC} to the extent of more than threefold (0.19 for **2** and 0.62 for **5**) even if the portion of *E*–*Z* isomerization of **2** ($\Phi_{EZ}=0.13$) was forced to cyclize in the case of **5**. The data in Table 2 also shows that the portion of deactivation decreased as the steric bulkiness of the alkyl group increased. These facts indicate that the steric bulkiness seriously changed the fulgide reactivity. One possible explanation is the change of ground-state conformation of *E* forms as mentioned previously with regard to the difference of molar absorption coefficients. This subject will be discussed elsewhere from the viewpoint of crystal structure, NMR behavior, and molecular orbitals calculations. (3) The quantum yield of photobleaching, Φ_{CE}, was not affected by the bulkiness of the alkyl group. The alkyl group is far from the breaking bond during the *C*-to-*E* conversion. Increase of the bleaching quantum yield was the next subject to be considered.

Effects of Steric Bulkiness of the Alkylidene Moiety of Furylfulgides. In 1983, Heller briefly mentioned that the replacement of an isopropylidene (IPD) group by an admantylidene (ADD) group on the furylfulgide greatly increased the bleaching quantum yield.[13—15] Kiji et al. reported, however, that the introduction of a long alkyl chain to the bottom alkylidene part decreased the bleaching quantum yield.[16]

Encouraged by our success in increasing the quantum yield of coloring, we next tried to synthesize a furylfulgide having both large coloring and bleaching quantum yields. To examine the effects of the steric bulkiness of the bottom part and to find whether the bulkiness of the alkylidene moiety is independent of the coloring quantum yield or not, we chose **8**, **9**, **10**, and **11** as the molecules to be synthesized (Chart 2).

While these fulgides with large alkylidene groups were obtained by the LDA method, use of anhydrous cerium trichloride to exchange the counter cation of the enolate generated from diethyl alkylidenesuccinate and LDA, from lithium to cerium(III) greatly improved the chemical yield of fugides.[17]

Tables 3 and 4 shows the absorption spectroscopic data and quantum yields of photoreactions of fulgides **2**, **5**, and **8**—**11** in toluene, respectively. Absorption spectra of **11E**, **11Z**, and the photostationary state of 366-nm light irradiation to **11E** are shown in Fig. 2.

The absorption maximum wavelength of the colored form increased as the bulkiness of the bottom alkylidene part increased. As the conformation of the colored form changed due to the steric congestion for norbornylidene and adamantylidene fulgides **8**—**11** (vide infra), slight change in the degree of π-conjugation occurred.

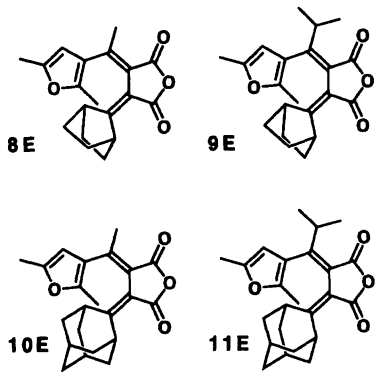


Chart 2.

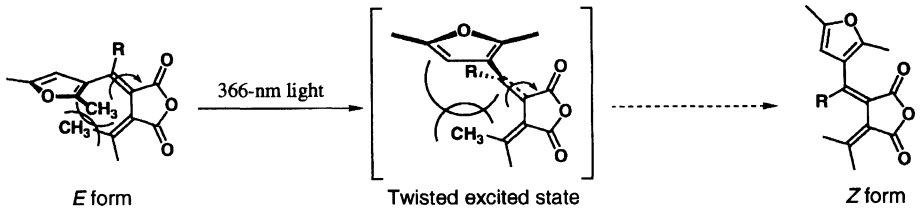


Fig. 1. Possible isomerization route from *E*-form to *Z*-form of furylfulgides.

Table 3. Absorption Spectral Data of Furylfulgides with Bulky Alkylidene Substituents in Toluene

	E	Z	C
	λ_{max}/nm (ε_{max})[a]	λ_{max}/nm (ε_{max})[a]	λ_{max}/nm (ε_{max})[a]
2	343 (6700)	353 (8400)	494 (9230)
5	342 (4250)	354 (4070)	494 (9150)
8	348 (5140)	355 (8750)	514 (7340)
9	343 (3500)	— (—)	515 (7250)
10	344 (5190)	357 (9090)	519 (6880)
11	337 (4200)	355 (5000)	520 (7000)

a) ε_{max}/mol^{-1} dm^3 cm^{-1}.

Table 4. Quantum Yields of Photoreactions of Furylfulgides with Bulky Alkylidene Substituents in Toluene

	Φ_{EC}[a]	Φ_{EZ}[a]	Φ_{ZE}[a]	Φ_{CE}[a]	Φ_{CE}[b]
2	0.18	0.13	0.11	0.00	0.048
5	0.58	0.00	—	0.00	0.043
8	0.20	0.30	0.42	0.01	0.057
9	0.56	0.01	0.01	0.00	0.049
10	0.12	0.10	0.10	0.06	0.21
11	0.51	0.02	0.05	0.28	0.26

a) 366-nm light irradiation. b) 492-nm light irradiation.

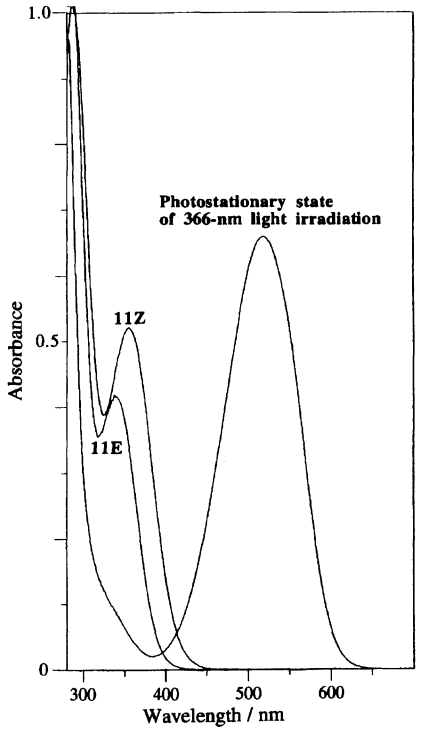


Fig. 2. Absorption spectra of **11E**, **11Z**, and the photostationary state of 366-nm light irradiation to **11E** in toluene. **11E** and photostationary state: 1.00×10^{-4} mol dm^{-3}, **11Z**: 1.04×10^{-4}mol dm^{-3}.

As seen in Table 4, the steric bulkiness of the 7-norbornylidene (NBD) group does not work effectively to increase Φ_{CE}, suggesting that only a huge alkylidene group such as an adamatylidene group is necessary. Furthermore, the steric congestion of the adamantylidene group was independent of the coloring quantum yield. Fulgide **11**, having an isopropyl group and an adamantylidene group together, showed the coloring quantum yield Φ_{EC} to be 0.51 (nearly threefold that of **2**) and the bleaching quantum yield Φ_{CE} to be 0.26 (fivefold that of **2**). It should be noted that for fulgides **10** and **11**, the adamantylidene derivatives, the bleaching quantum yields of UV irradiation are not negligible. Thus, the bulky adamantylidene group also enhanced the bleaching quantum yield during UV irradiation.

Although the reason why the adamantylidene group enlarged the quantum yield of bleaching is not clear, one possibility is as follows: The sterically demanding adamantylidene group introduced more destabilization to the rigid colored form than to the flexible colorless form. This destabilization caused reduction of a portion of deactivation to the colored form from the excited state of the colored form. This was supported by the molecular orbitals calculations. The results of AM1 calculations[18] of furylfulgides **2C**, **8C**, and **10C** are summarized in Fig. 3.

The order of length of the single bond between C_7 and C_{7a} (benzofuran numbering) is **10C**>**2C**≈**8C**, and the order of the angle composed of C_6–C_7–C_{7a} is **2C**>**8C**>**10C**. This means the bulky adamantylidene group induced distortion of the cyclohexadiene part of the molecule, causing destabilization of the colored form.

In conclusion, we have succeeded in synthesizing a furylfulgide having both large coloring and bleaching quantum yields by introducing an isopropyl group and an adamantylidene group. The effects of these large substituents are independent, thus showing that the photochromic quantum yields are controllable by the bulkiness of substituents. For the thienylfulgides, however, it was reported recently that the steric bulkiness did not work independently.[12] In the meantime, Tomoda et al. reported that a benzylidene-type disubstituted mesitylfulgide **12**, closely related to **1**, had a

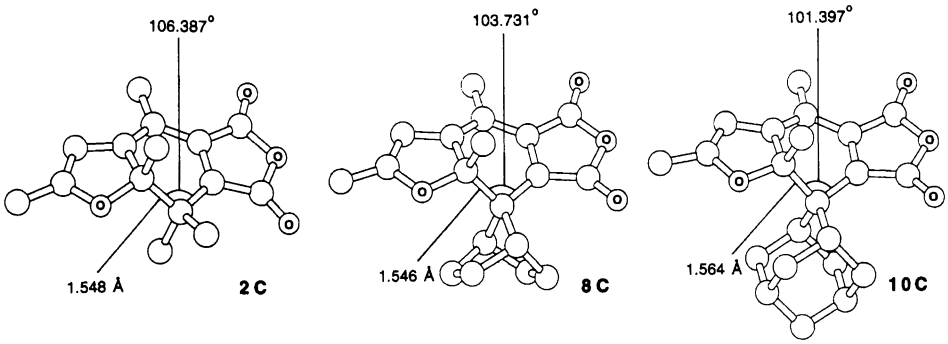
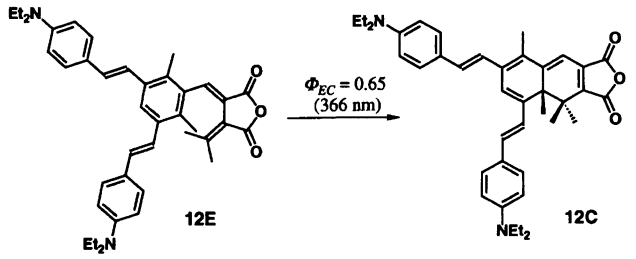


Fig. 3. Most stable conformation of the colored form of furylfulgides **2C**, **8C**, and **10C**. Calculated with AM1 molecular orbitals calculations.

large coloring quantum yield (Scheme 4).[19] Although these results indicate that there are more factors that govern the magnitude of photochromic quantum yields than the size of substituents, the tendencies of quantum yield values are predictable by the size of substituents for similar fulgides.[20]

Experimental

General. IR spectra were measured using a JASCO A-202 IR spectrometer. ^{1}H NMR spectra were recorded with JEOL JNM-EX-270 (270 MHz), JEOL JNM-FX-90Q (90 MHz), or JEOL JNM-PMX-60 (60 MHz) spectrometers in $CDCl_3$ unless otherwise noted. Signals are expressed as ppm downfield from tetramethylsilane used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; sep, sepret; m, multiplet; br, broad. The low- and high-resolution mass spectra were taken with a JEOL JMS D-300 mass spectrometer. UV-vis spectra were recorded on a Hitachi UV-200-20 Spectrometer or on a JASCO Ubest-50 UV-vis Spectrophotometer. UV light source was 500 W high pressure mercury lamp (Ushio Electric), from which 366-nm light was isolated by filters (aqueous solution of $CuSO_4$, Toshiba UV-D35 and UV-35 glass filters). Visible lights used were 502 and 492 nm. The former was taken from an Ar ion laser (Lexel Co., Model 95-4) and was spread by a convex lens, and the latter was isolated from a 500 W xenon lamp (Ushio Electric) through a 10-cm water filter and Toshiba glass filters (IRA-25S, Y-46, and KL-50). The light intensity was measured with a photometer (IL-1350, International Light Inc.) with detectors (SED400 for UV light and SED038 for visible light), calibrated with iron(III) trioxalate chemical actinometer. Measurements of concentration of components during the photoreaction were done by high pressure liquid chromatography (Shimadzu LC-6A) and a detector (Shimadzu SPD-6AV) using a silica gel column (Yamamura Chemical Lab., Co., A-002 SIL, 4.6 mm×150 mm) with a mixture of hexane and benzene as eluent. Flash column chromatography was done with Merck Kieselgel 60 (230—400 mesh) with a mixture of hexane and ethyl acetate as an elution system. Analytical thin-layer chromatography was done on Merck pre-coated silica gel 60 F-254, 0.25 mm thick TLC plates. All synthetic reactions were done under dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl, diethyl ether was distilled from $LiAlH_4$, and dichloromethane was distilled from calcium hydride, immediately before use.



Scheme 4.

Analysis of Photoreactions Photoreaction was done in a quartz cell with the pass length of 1 cm. Fulgides were dissolved in chloroform or toluene to prepare solutions of 1.0×10^{-4} mol dm^{-3}. Photoreaction was monitored by a UV-vis spectrometer and a high pressure liquid chromatograph (HPLC) with a silica gel column and a UV detector. Concentration of fulgide isomers (**E**, **Z**, and **C**) were measured directly from an HPLC chromatogram of the solution and their molar absorption coefficient at the detecting wavelength. It should be noted that fulgide isomers **E**, **Z**, and **C** do not interconvert to each other by contact with the silica gel of the HPLC column, which was confirmed by the fact that the change of flow rate of the solvent (i.e. change of the contact time of fulgide isomers with silica gel) did not affect the ratio of **E**/**Z**/**C** to any extent.

The changes in component concentration with the light-irradiation time were analyzed as follows:

The reaction-rate equations of photoreactions are presented as Eq. 1[21,22].

$$dC_i/dt = (-\sum_i \kappa_{ij} C_i + \sum_j \kappa_{ji} C_j)F \quad (i \neq j), \qquad (1)$$

where C_i is the concentration of the component i, $F=(1-10^{-A})/A$, where A is the absorbance of the solution at the irradiated wavelength and is the function of irradiated time, $\kappa_{ij}=\varepsilon_i \Phi_{ij} I_0$, were ε_i is the molar absorption coefficient of the component i at the irradiated wavelength, Φ_{ij} is the quantum yield of the photoreaction from the component i to j at the irradiated light wavelength, and I_0 is the light intensity, i.e., mol photons irradiated per unit cross section per unit time.

As the general analytical solution of the reaction rate equations (Eq. 1) could not be obtained, they were numerically integrated with a set of provisional κ_{ij}. To reduce the deviation of the calculated concentration of components

from the observed ones obtained from the HPLC analysis, the set of κ_{ij} was calculated by the least squares method. The set of κ_{ij} that gives the minimum deviation was then found. Each quantum yield was obtained from each κ_{ij} thus obtained, by dividing it by the molar absorption coefficient of the corresponding light-absorbing species at the irradiated wavelength and the light intensity.

Synthesis of Furylfulgides (*E*)- and (*Z*)-2-[1-(2,5-Dimethyl-3-furyl)propyldene]-3-isopropylidenesuccinic Anhydride (3E and 3Z). A mixture of sodium hydride (0.5 g, 12.5 mmol, 2.2 equiv, about 60% dispersed in mineral oil), toluene (15 ml), 2.5-dimethyl-3-propanoylfuran (0.98 g, 6.46 mmol, 1.1 equiv), and diethyl isopropylidenesuccinate (1.24g, 5.78 mmol) was heated to 80 °C, then a few drops of methanol was added. After the evolution of hydrogen gas ceased, the reaction mixture was cooled, and was poured into a mixture of ice and 5 mol dm^{-3} aq HCl. The mixture was extracted with ether, and from the ethereal solution, acidic materials were extracted with 10% aq Na_2CO_3. To this aqueous solution 1 mol dm^{-3} aq HCl was added until the solution became strongly acidic, and the liberated oily material (mainly composed of the half acid) was extracted with ether. The organic layer thus obtained was dried with anhydrous Na_2SO_4, the solvent removed in vacuo. The acidic material (1.248 g) was then refluxed with a mixture of potassium hydroxide (1.0 g) in ethanol for 5 h. The reaction mixture was acidified with dil hydrochloric acid and the mixture was extracted with ether. The organic layer was dried with anhydrous Na_2SO_4, and the solvent evaporated. The residue thus obtained (1.123 g) was treated with acetic anhydride (20 ml) at 80 °C for 30 min, and acetic anhydride was removed in vacuo. The residue was extracted with toluene, and the organic layer was washed with dil aq Na_2CO_3 and sat. aq NaCl, and was dried with anhydrous Na_2SO_4. The solvent was removed in vacuo, and the residue (0.921 g) was purified with column chromatography.

Fulgide **3*E*** (124 mg., 7.8%): Mp 104—105 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.06 (3H, t, J=7.4 Hz), 1.35, 1.95, 2.26, 2.34 (each 3H, s), 3.03 (2H, q, J=7.4 Hz), 5.94 (1H, s); IR (Nujol) 1800, 1760, 1220, 940 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 274 (M^+, 62), 259 ($(M-CH_3)^+$, 100). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61%. Found: C, 69.78; H, 6.71%.

Fulgide **3*Z*** (58 mg, 3.7%): Mp 123—124 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.05 (3H, t, J=7.4 Hz), 2.03, 2.20, 2.27, 2.42 (each 3H, s), 2.45 (2H, d, J=7.5 Hz), 5.90 (1H, s); IR (Nujol) 1800, 1755, 1215, 920 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 274 (M^+, 69), 259 ($(M-CH_3)^+$, 100). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61%. Found: C, 69.94; H, 6.68%.

(*E*)- and (*Z*)-2-[1-(2,5-Dimethyl-3-furyl)butylidene]-3-isopropylidenesuccinic Anhydride (4E and 4Z). To a solution of lithium diisopropylamide (generated from 2.84 ml diisopropylamine and 9.33 ml hexane solution of butyllithium (1.56 mol dm^{-3}) and a small amount of bipyridyl (indicator) in 40 ml THF at −78 °C was added a solution of didethyl isopropylidenesuccinate (2.357 g in 5 ml THF) slowly and the mixture was stirred for 30 min at that temperature. A solution of 3-butanoyl-2,5-dimethylfuran (1.69 g in 5 ml THF) was added and the mixture was stirred for 30 min and then warmed to r.t. slowly. The reaction mixture was acidified with dil hydrochloric acid, the aqueous layer was saturated with solid NaCl, and the organic layer separated. The aqueous layer was extracted with ether, and the combined organic layer was washed with 10% aq $NaHCO_3$ and sat. aq NaCl successively. The organic layer was dried with anhydrous Na_2SO_4, and the solvent removed in vacuo. The residue thus obtained was refluxed in 70 ml ethanol with 3.5 g of potassium hydroxide for 16 h, and the mixture was acidified with hydrochloric acid to pH 1. Organic materials were extracted for several times with ether, the combined organic layer dried with anhydrous Na_2SO_4, and the solvent evaporated in vacuo. The product thus obtained was heated with 40 ml acetic anhydride at 80 °C for 30 min. After acetic anhydride was removed in vacuo, ethanol (0.5 ml) and toluene (30 ml) were added to the residue successively, and the solution was washed with sat. aq $NaHCO_3$ and then sat. aq NaCl, and dried with anhydrous Na_2SO_4. Toluene was removed in vacuo, and the residue was purified with silica-gel flash column chromatography.

Fulgide **4E** (663 mg, 23%): Mp 78—79 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=0.93 (3H, t, J=7.1 Hz), 1.35, 1.94, 2.26, 2.34 (each 3H, s), 1.47 (2H, m), 3.02 (2H, t, J=7.8 Hz), 5.93 (1H, s); IR (Nujol) 1805, 1755, 1225, 930 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 288 (M^+, 76), 273 ($(M-CH_3)^+$, 100). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%. Found: C, 70.60, H, 7.02%.

Fulgide **4Z** (269 mg, 9%): Mp 90—91 C°; ^{1}H NMR (90 MHz, $CDCl_3$) δ=0.96 (3H, t, J=7.1 Hz), 1.59 (2H, m), 2.04, 2.20, 2.27, 2.42 (each 3H, s), 2.37 (2H, t, J=7.9 Hz), 5.89 (1H, s); IR (Nujol) 1800, 1765, 1210, 920 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 288 (M^+, 56), 273 ($(M-CH_3)^+$, 100). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%. Found: C; 70.89; H, 7.20%.

With a procedure similar to that described above, fulgides **5E** and **5Z**, **8E** and **8Z**, **9E**, **11E** and **11Z** were obtained (**9Z** was not isolated in sufficient amount for characterization, and the details of synthesis of **10E** and **10Z** have been reported[15]).

(*E*)- and (*Z*)-2-[1-(2,5-Dimethyl-3-furyl)-2-methylpropylidene]-3-isopropylidenesuccinic Anhydride (5E and 5Z). Fulgide **5E** (14%): Mp 127—128 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=0.88 (3H, bd), 1.25 (3H, bd), 1.38, 1.89, 2.28, 2.40 (each 3H, s), 4.29 (1H, m), 5.93 (1H, s); IR (Nujol) 1800, 1755, 1220, 920 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 288 (M^+, 100), 273 ($(M-CH_3)^+$, 69). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%. Found: C, 70.78; H, 6.99%.

Fulgide **5Z** (24%): Mp 122—123 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.00 (3H, d, J=7.1 Hz), 1.19 (3H, d, J=7.1 Hz), 2.06, 2.15 (each 3H, s), 2.28 (6H, s), 2.84 (1H, m), 5.88 (1H, s); IR (Nujol) 1800, 1760, 1220, 910 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 288 (M^+, 56), 273 ($(M-CH_3)^+$, 100). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%. Found: C, 70.56; H, 6.83%.

(*E*)- and (*Z*)-2-[1-(2,5-Dimethyl-3-furyl)ethylidene]-3-(7-norbornylidene)succinic Anhydride (8E and 8Z). Synthesis of 7-norbornanone was done according to the procedure described in the literature.[23]

Fulgide **8E** (15%): Mp 158—159 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.1—1.7 (9H, m), 2.04, 2.25, 2.54 (each 3H, s), 3.73 (1H, bt, J=4.31), 5.98 (1H, s); IR (KBr) 1805, 1767, 1222, 906 cm^{-1}; MS (EI, 70eV) m/z (rel intensity) 312 (M^+,

100), 297 ($(M-CH_3)^+$, 36). Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%. Found: C, 73.00; H, 6.67%.

Fulgide **8Z** (5%): Mp 147—149 °C; ^{1}H NMR (60 MHz, CCl_4) δ=0.9—1.8 (9H, m), 2.17, 2.20, 2.31 (each 3H, s), 3.97 (1H, m), 5.92 (1H, s); MS (EI, 70 eV) m/z (rel intensity) 312 (M^+, 100), 297 ($(M-CH_3)^+$, 39). Found: m/z 312.1270. Calcd for $C_{19}H_{20}O_4$: M, 312.1361.

(*E*)-2-[1-(2,5-Dimethyl-3-furyl)-2-methylpropylidene]-3-(7-norbornylidene)succinic Anhydride (9E). Fulgide **9E** (8%): Mp 136—137 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ=0.8—1.8 (15H, m), 1.96, 2.28 (each 3H, s), 3.71 (1H, m), 4.31 (1H, m), 6.04 (1H, s); IR (Nujol) 1803, 1767, 1217, 921 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 340 (M^+, 100), 325 ($(M-CH_3)^+$, 23). Found: m/z 340.1706. Calcd for $C_{21}H_{24}O_4$: M, 340.1675.

(*E*)- and (*Z*)-2-[1-(2,5-Dimethyl-3-furyl)-2-methylpropylidene]-3-(2-adamantylidene)succinic Anhydride (11E and 11Z). According to the method described in Ref. 17, anhydrous cerium(III) chloride (1.55 g, 6.3 mmol) suspended with 6 ml of THF at 0 °C was prepared. To it was added a solution of 2,5-dimethyl-3-(2-methylpropanoyl)furan (0.73 g, 4.42 mmol) in 6 ml THF, and the resulting mixture was cooled to −50 °C. To this mixture was added a solution of lithium enolate of diethyl adamantylidenesuccinate, generated from a THF solution of LDA (5.71 mmol) and diethyl adamantylidenesuccinate (1.51 g, 4.92 mmol) in 25 ml THF at −50 °C, and the resulting mixture was gradually warmed to r.t., and was stirred for 4 h. To the reaction mixture was added sat. aq ammonium chloride and the insoluble material was filtered off using Celite. The same workup for the synthesis of **4** followed by hydrolysis, dehydrative acid anhydride formation, and purification with flash column chromatography yielded **11E** and **11Z**.

Fulgide **11E** (279 mg, 16%): Mp 175—176 °C ; ^{1}H NMR (270 MHz, $CDCl_3$) δ=0.47 (bd, 1H, J=12.87 Hz), 0.82 (d, 3H, J=6.59 Hz), 1.28 (d, 3H, J=7.25 Hz), 1.47 (1H, dd, J=2.64, 12.54 Hz), 1.6−2.0 (m, 10H), 1.99, 2.27 (each 3H, s), 2.40 (1H, bs), 4.19 (1H, bs), 4.25 (1H, sep, J=6.93 Hz), 5.92 (1H, s); IR (KBr) 1805, 1757, 1609, 1576, 1220, 927 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 380 (M^+, 100), 365 ($(M-CH_3)^+$, 11), 337 (30). Found: m/z 380.1960. Calcd for $C_{24}H_{28}O_4$: M, 380.1988.

Fulgide **11Z** (132 mg, 8%): Mp 143—146 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ=0.93 (3H, d, J=6.60 Hz), 1.19 (3H, d, J=6.93 Hz), 1.7—2.2 (12H, m), 2.12, 2.27 (each 3H, s), 2.72 (1H, bs), 2.87 (1H, sep, J=6.93 Hz), 4.25 (1H, bs), 5.87 (1H, s); IR (KBr) 1805, 1761, 1609, 1573, 1218, 919 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 380 (M^+, 100), 365 ($(M-CH_3)^+$, 12), 337 (29). Found: m/z 380.1984. Calcd for $C_{24}H_{28}O_4$: M, 380.1988.

Part of this study was supported by the Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials - Design, Preparation, and Control (Nos. 62604548, 63604537, and 01604542), from the Ministry of Education, Science and Culture.

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