Bull. Chem. Soc. Jpn., ***68***, *1677—1682(1995)*

Steric Effects of Substituents on the Photochromism of Indolylfulgides

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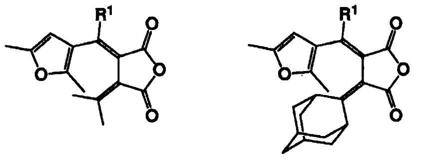
(Received December 14, 1994)

Photochromic fulgides with a bulky 1-alkyl-1-indolylmethylidene and/or a bulky alkylidene substituent were synthesized and their photochromic as well as absorption spectroscopic properties were compared with those of the known prototype indolylfulgide, 3-[1-(1,2-dimethyl-3-indolyl)ethylidene]-4-isopropylidenedihydro-2,5-furandione. An increase in steric bulkiness of the alkyl group (R^1) on the indolylmethylidene group increased the coloring quantum yield ($\Phi_{\mathrm{EC}}=0.046$ (R^1=methyl) to 0.31 (R^1=isopropyl)), whereas an increase in the steric bulkiness of the other alkylidene group (R^2) increased the bleaching quantum yield ($\Phi_{\mathrm{CE}}=0.051$ (R^2=isopropylidene) to 0.42 (R^2=2-adamantylidene)). When both R^1 and R^2 were bulky, however, the coloring quantum yield was not large, although the bleaching quantum yield was still large. When the methyl group on the 2-position of the indole ring was substituted with an ethyl group, the absorption maximum of the colored form showed a 32-nm bathochromic shift.

Because thermally irreversible organic photochromic compounds, such as fulgides[1)] and diarylethenes,[2)] are potential candidates applicable to erasable optical memory media, many chemists have been engaged in research to improve their photochromic properties. A fulgide exhibits a photochromic interconversion between colorless, or slightly colored, *E*-form and deeply colored *C*-form. This photochromic reaction, however, is accompanied by an *E–Z* isomerization, as shown in Scheme 1. The furylfulgide **1**, whose synthesis and photochromic properties had been reported by Heller et al., was practically the first thermally irreversible fulgide with large quantum yields of photoreactions.[3)] We have already reported[4—6)] that (i) the sterically-demanding alkyl-substituted furylmethylidene group increased the coloring quantum yield (Φ_{EC}(UV)) and decreased the quantum yield of *E–Z* isomerization (Φ_{EZ}(UV)), and (ii) an extremely large substituent on the other alkylidene group, such as the 2-adamantylidene group, increased the bleaching quantum yield (Φ_{CE}(Vis)) (Chart 1). Thus, Φ_{EC}(UV) of **2**, having an isopropyl group, is 0.58 in $CHCl_3$, and Φ_{EC}(UV) and Φ_{CE}(Vis) of **3**, having both an isopropyl group and an adamantylidene group, are 0.51 and 0.26, respectively, in toluene. Recently, Kiji et al. have reported on the synthesis and photochromic reactions of furyl- and thienylfulgides having a *t*-butyl group in collaboration with us.[7)] The former (**4**) showed 0.79 as Φ_{EC}(UV) in toluene, which is the largest Φ_{EC}(UV) as a fulgide. It should be noted that the steric bulkiness of the alkyl group on the furylmethylidene group and the other alkylidene group always worked independently.



1 : R^1 = Me
2 : R^1 = *i*-Pr
4 : R^1 = *t*-Bu
3 : R^1 = *i*-Pr

Chart 1.

Since the indolylfulgide **5** had been reported to be more durable to both thermal and photochemical fatigue than furylfulgide **1**,[8)] we were interested in improving the photochromic properties of indolylfulgides. We have already reported on the modification of the electronic character of **5** by adding an electron-donating group to the indole ring in order to lengthen the absorption maximum wavelength of the colored form to reach the emission wavelength of a diode laser apparatus.[9)] This paper deals with how the steric effects worked on the photochromism of indolylfulgides (Chart 2).

Results and Discussion

Synthesis and Characterization. All of the indolylfulgides (**5**—**12**) used in this research were synthesized by Stobbe condensation, as depicted in Scheme 2, using lithium diisopropylamide (LDA) as a base.[6,10)] The reaction mixture, containing the half es-

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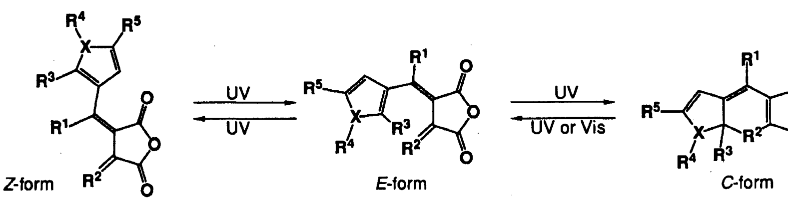
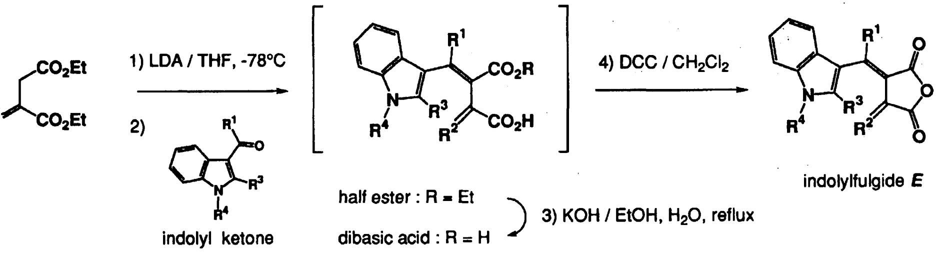
#JSPS Predoctoral Research Fellow.



Scheme 1. Photochromic reactions of fulgides.



Scheme 2. Synthetic route of indolylfulgides.

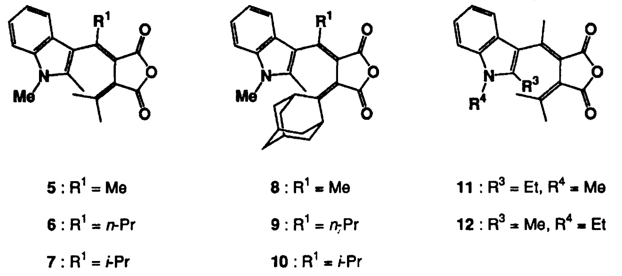


Chart 2.

ter, obtained from the condensation of a diethyl alkylidenesuccinate and an indolyl ketone, was hydrolyzed, and the resulting dibasic acid was dehydrated to afford the indolylfulgide. Purification was carried out by column chromatography and recrystallization (CH_2Cl_2/hexane). The yield of fulgides based on the indolyl ketone decreased along with an increase in the steric bulkiness of R^1.

Different from furylfulgides, only the E-isomer of indolylfulgides were obtained as crystals by the purification procedures described above. A measurement of the ^{1}H NMR spectroscopy showed the E-methyl group of the isopropylidene group, or an allylic methine proton located on the E-carbon atom of the adamantylidene group, resonated at higher fields than expected to appear, because of a shielding effect of the indole ring, as had been previously interpreted.[11)] As discussed later, the photoirradiation of UV-light to a toluene solution of the E-form affords the Z-form as well as the C-form; the Z-form could be detected only by ^{1}H NMR, and not by an HPLC apparatus equipped with a silica-gel column. We believe that the thermodynamically less stable Z-form, produced during the synthetic procedures, isomerized to the more stable E-form, probably during column chromatographic purification using a slightly acidic silica gel.

Photoreaction of Indolylfulgides. Photoreactions of the E-form of indolylfulgides in toluene (about 1×10^{-4} mol dm^{-3}) were monitored by a UV/Vis spectrophotometer and an HPLC apparatus. Independent reactions were carried out to monitor the change in the concentration by ^{1}H NMR in toluene-d_8. When 405-nm light was irradiated to a toluene solution of the E-form indolylfulgide, the absorption of the C-form appeared at about 580 nm. Although indolylfulgides, like **7**, having an isopropyl group as R^1, showed isosbestic points on the absorption spectral changes with time of 405-nm light irradiation (Fig. 1a), fulgides like **11**, having a methyl group as R^1, did not show isosbestic points (Fig. 1b).[12)] Consequently, the photoreactions of indolylfulgides with an isopropyl group as R^1 undergo photoreactions between E- and C-forms, and the photoreactions of indolylfulgides with a methyl group as R^1 involve the E-, Z-, and C-forms. This observation was confirmed by ^{1}H NMR during 405-nm light irradiation on **11** in toluene-d_8. Before 405-nm light irradiation, only the signals of the E-form appeared (Fig. 2a). The irradiation of 405-nm light on the solution brought about the appearance of two new sets of peaks along with a decrease in the intensity of the E-form (Fig. 2b). When 608-nm light was irradiated to the resulting toluene solution, one of the two new sets disappeared along with an increase in the intensity of the set of the E-form, while the other new set did not change (Fig. 2c). The disappeared set was that of the C-form, and the unchanged one was that of the Z-form, concluded by an analogy with the photochromic behavior of furylfulgides.

The relative amount of the Z-form at the photostationary state of 405-nm light irradiation (PSS(405)) decreased as the steric bulkiness of the alkyl group R^1 increased. When R^1 was isopropyl (**7** and **10**), the Z-form was not detected at PSS(405) (Table 1).

We also used HPLC to follow the photoreaction. The number of peaks of the components appearing on the chromatograms were always two. For example, although fulgide **11** underwent a three-component pho-

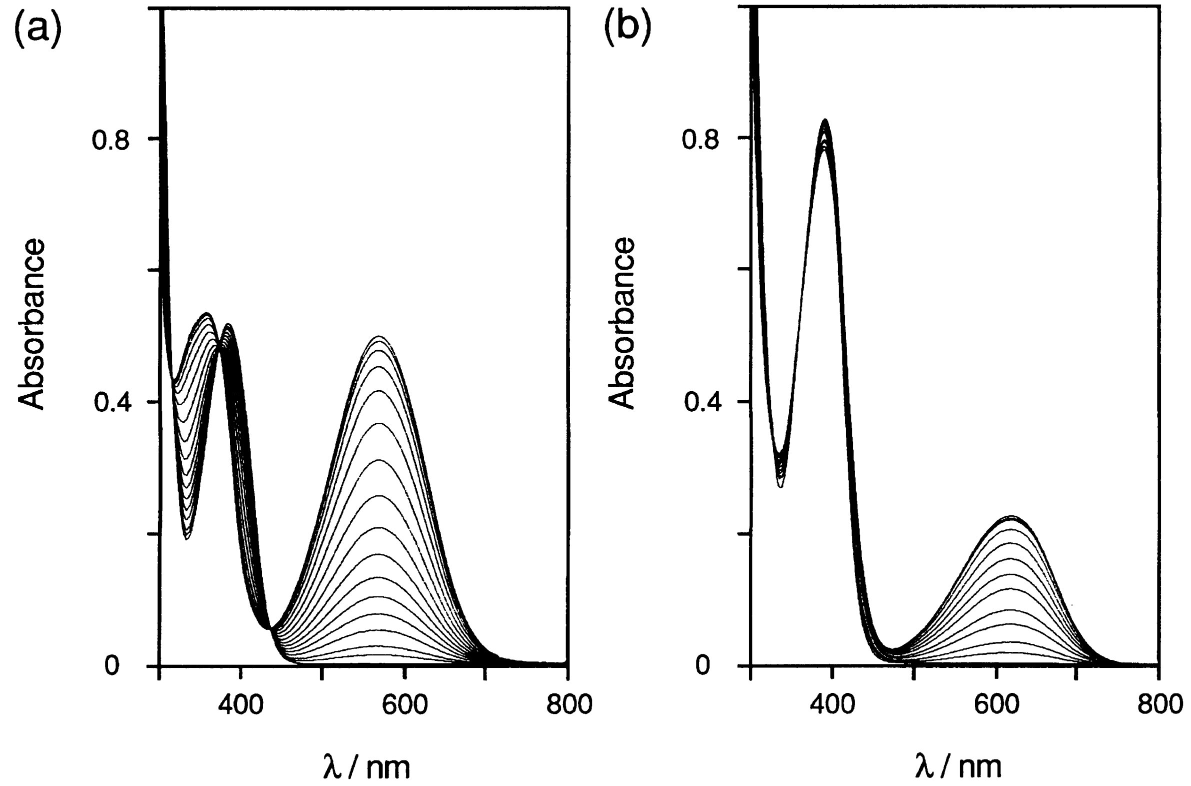


Fig. 1. (a) Absorption spectral changes of coloring of **7** in toluene. Concentration: 8.42×10^{-5} mol dm^{-3}, irradiation light: 405 nm, light intensity: 2.67×10^{-8} einstein min^{-1} cm^{-2}, irradiation time/min: 0, 0.5, 1.0, 2.0, 3.0, 4.2, 5.6, 7.4, 9.8, 13, 17, 23, 31, 42, 55, 71, 91 (PSS). (b) Absorption spectral changes of coloring of **11** in toluene. Concentration: 1.00×10^{-4} mol dm^{-3}, irradiation light: 405 nm, light intensity: 1.54×10^{-7} einstein min^{-1} cm^{-2}, irradiation time/min: 0, 0.5, 1, 2, 3, 5, 7, 10, 15, 23, 35, 55 (PSS).

Table 1. Quantum Yields of Photoreactions of Indolylfulgides with Bulky Alkyl Substituents in Toluene

	Φ_{EC}[a]	Φ_{CE}[a]	Φ_{EZ}[a]	Φ_{ZE}[a]	$[E]/[Z]/[C]$[b]	Φ_{CE}[c]
5	0.045	0.16	0.040	0.072	35/ 9/56	0.051
6[d]	0.14	0.12	—	—	20/ -/80	0.049
7[e]	0.23	0.31	0	—	19/ 0/81	0.054
8	0.037	0.52	0.11	0.063	51/36/13	0.42
9[d]	0.054	0.22	—	—	64/ -/36	0.33
10[e]	0.066	0.91	0	—	77/ 0/23	0.42
11	0.023	0.087	0.057	0.042	39/31/30	0.066
12	0.095	0.23	0.048	0.059	22/10/67	0.049

a) 405-nm light irradiation. b) PSS(405). c) 608-nm light irradiation. d) Z-form was neglected. e) Z-form was not detected at PSS(405) by ^{1}H NMR in toluene-d_8.

toreaction (confirmed by ^{1}H NMR) with 405-nm light irradiation, the HPLC chromatogram suggested that only two components were involved in the reaction. Taking the result of ^{1}H NMR into account, we realized that the Z-form isomerized to the E-form in the HPLC silica-gel column, although furylfulgides never isomerized between the E- and Z-forms in this HPLC column.

Quantum Yields of Photoreactions of Indolylfulgides. The quantum yields of the photochromic reactions are summarized in Table 1. For propyl-substituted fulgides **6** and **9**, Φ_{EZ} and Φ_{ZE} could not be obtained, because the concentrations of the Z-forms of them at PSS(405) were too low to accurately determine by ^{1}H NMR. Therefore, the quantum yields of 405-nm light irradiation for **6** and **9** were calculated while neglecting the concentration of the corresponding Z-forms. Changes in component concentration with the time of light irradiation of other indolylfulgides were determined based on the UV/vis absorption spectra, ^{1}H NMR and HPLC measurements, and the quantum yields were calculated as previously reported.[6,10]

When the alkyl substituent on the indolylmethylidene group was replaced by a sterically more demanding group, such as an isopropyl or a propyl, the coloring quantum yield increased and the E-to-Z isomerization quantum yield decreased. This was in good accordance with the observation for furylfulgides. The coloring quantum yield of **7**, with an isopropyl group, was five-times as large as that of **5**.

Different from furylfulgides, the C-forms of indolylfulgides have an absorption band at about 380 nm as well as one at about 580 nm. Since the UV-range absorption band of the C-form overlaps with the absorption of the E-form, irradiation of 405-nm light causes

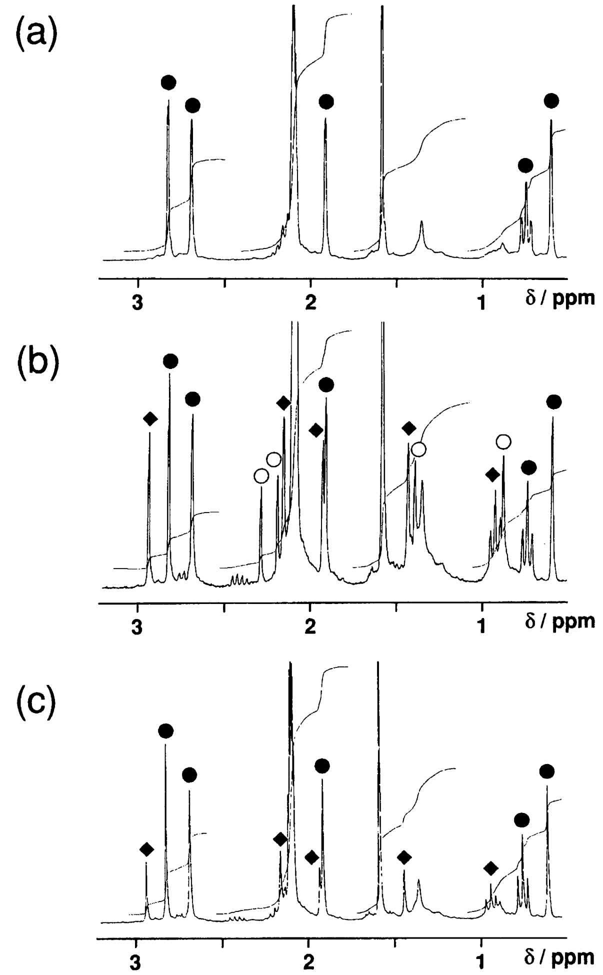


Fig. 2. ^{1}H NMR spectral changes of **11** by photoirradiation in toluene-d_8. Symbols: ●;*E*-form, ◆;*Z*-form, ○;*C*-form. (a) Before 405-nm light irradiation. (b) Photostationary state of 405-nm light irradiation. (c) Photostationary state of 608-nm light irradiation on (b).

bleaching of the *C*-form. As a result of this process, the relative ratio of the *C*-form at PSS(405) is lower than that of furylfulgides, the latter being between 92 and 100%. A tendency that an increase in the bleaching quantum yield of the *C*-form under UV-light irradiation along with an increase in the bulkiness of R^1 was also observed.

Substitution of the isopropylidene group of **5** with an adamantylidene group increased the bleaching quantum yield of 608-nm light irradiation. As previously reported, steric effects of R^1 and R^2 on the photochromism of furylfulgides worked independently; while a bulky R^1 worked to increase the coloring quantum yield of UV-light irradiation, a bulky R^2 worked to increase the bleaching quantum yield of Vis-light irradiation. Furylfulgide **3** with an isopropyl group as R^1 and an adamantylidene group as R^2 has large coloring and bleaching quantum yields, and the ratio of the *C*-form at PPS(UV) is 92%. However, this finding does not apply to the case of indolylfulgides, as exemplified by the following two cases: (1) Whereas the coloring quantum yield is 0.23 for an isopropyl-substituted indolylfulgide **7**, the coloring quantum yield is 0.066 for the isopropyl- and adamantylidene-substituted fulgide **10**. In the latter, the isopropyl group did not work to increase the coloring quantum yield effectively. (2) Although the bleaching quantum yield of Vis-light irradiation of **8**, having an adamantylidene group, was 8.2-times as large as that of **5**, the bleaching quantum yield upon UV-light irradiation also increased, and the ratio of the *C*-form of **8** at PSS(405) is much smaller than that of **5**. Namely, the effect of the isopropyl group for **8** was offset by the adamantylidene group. This tendency, although not so apparent as in the present case, has been reported for thienylfulgides.[13]

The substitution of the 2-methyl group of the indole ring of **5** with an ethyl group decreased $\Phi_{\mathrm{EC}}(405)$ and increased $\Phi_{\mathrm{EZ}}(405)$. Since the carbon atom of the 2-position of the indole ring forms a C–C bond upon UV-light irradiation, an increase in the bulkiness of the substituent is unfavorable to cause a ring closure.

The photochromic properties of indolylfulgide **12**, possessing an ethyl group instead of the methyl on the indole nitrogen, were almost the same as those of **5**.

Absorption Spectra. Since the light absorption of a fulgide molecule is attributed to a π–π^* transition, electronic effects on the conjugated π-system should be important. Although the change in the absorption spectra of indolylfulgides with regard to the change of alkyl and alkylidene substituents would be considered to be small, the observed changes were more than our expectation. The results are shown in Table 2.

Although the absorption maxima of the *E*-forms were not largely affected, the deviation in the absorption maxima of the *C*-forms by the steric factor from **5C** (λ_{max} 584 nm) was significant. While the introduction of a propyl group as R^1 (**6C** compared to **5C** and **9C** compared to **8C**) caused a slight bathochromic shift,

Table 2. Absorption Spectral Data of Indolylfulgides with Bulky Alkyl Substituents in Toluene

	λ_{max}/nm ($\varepsilon_{\mathrm{max}}$)		
	E-Form	*Z*-Form[a)]	*C*-Form
5	385 (8150)	397 (14300)	584 (6810)
6	385 (7300)	—[b)]	587 (7300)
7	385 (4790)	—[c)]	574 (6180)
8	384 (6980)	397 (13900)	598 (5740)
9	386 (7150)	—[b)]	600 (6240)
10	382 (4110)	—[c)]	581 (5750)
11	384 (8080)	395 (10900)	616 (7460)
12	386 (8790)	395 (17400)	589 (7960)

a) Calculated values. b) Not possible to calculate.
c) *Z*-form was not detected during the photoreaction.

the introduction of an isopropyl group (**7C** compared to **5C** and **10C** compared to **8C**) caused a hypsochromic shift by more than 10 nm. The introduction of an adamantylidene group as R^2 (**8C**, **9C**, and **10C** compared to **5C**, **6C**, and **7C**, respectively) caused about a 10-nm bathochromic shift. The absorption maximum of **11C**, replacing the R^3 methyl group with an ethyl group, was 616 nm (32-nm bathochromic shift). Since R^3 is connected to the sp^3 carbon atom, the effect might not be electronic on the conjugated system, but should be a steric effect on the planar molecular structure of the *C*-form.

The molar absorption coefficients (ε) of both the *E*- and *C*-forms were also affected by the steric bulkiness of the substituents. For the *E*-forms, ε decreased as the bulkiness of R^1 increased. This tendency is obvious for the isopropyl-substituted fulgides. A decrease in ε by introducing a bulky alkyl substituent to the arylmethylidene moiety has also been observed for furylfulgides.[4,6)]

The absorption spectrum of the *Z*-form can be calculated from the *E*/*Z*/*C* ratio at the PSS(UV) determined by ^{1}H NMR, the absorption spectra of the *E*-form and that obtained by visible-light irradiation to the PSS(UV) solution.[14)] The calculated absorption maximum wavelengths and the molar absorption coefficients of the *Z*-forms are also shown in Table 2. The apparent features are: (1) the absorption maximum wavelengths of *Z*-forms are longer than that of the corresponding *E*-forms, and (2) the molar absorption coefficients at the absorption maxima are considerably larger than that of the corresponding *E*-forms.

Conclusion

In conclusion, we have synthesized indolylfulgides with bulky substituents, and the steric effects on photochromic reactions were studied. The quantum yields of the coloring reaction of 405-nm light irradiation and the bleaching reaction of 608-nm light irradiation increased as the steric bulkiness of R^1 and R^2 increased, respectively. Both effects, however, did not work independently. Namely, an indolylfulgide having large coloring and bleaching quantum yields was not obtained. Since the *C*-form of an indolylfulgide has a second absorption band in the near-UV region, and bleaching quantum yield of UV irradiation on the *C*-form is considerably large (usually greater than that of visible-light irradiation), the conversion ratio to the *C*-form at PSS(UV) is much smaller than that of a furylfulgide with the corresponding substituents. The steric bulkiness of substituents also affected the absorption maximum and the absorption coefficient at the absorption maximum.

Experimental

General. IR spectra were measured using a Perkin–Elmer 1650 FT-IR or a JASCO A 202 IR spectrometers. ^{1}H NMR spectra were recorded with a JEOL JNM-EX-270 (270 MHz) spectrometer in $CDCl_3$ or toluene-d_8. The signals are expressed as ppm down field from tetramethylsilane, used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet; br, broad, and aromatic protons are represented as Ar. The low- and high-resolution mass spectra were taken with a JEOL JMS D-300 or a JEOL JMS AX-500 mass spectrometer. UV-vis spectra were recorded on a JASCO Ubest-50 UV-vis Spectrophotometer. Emission line of 405 nm of a 500 W high-pressure mercury lamp (Ushio Electric) was separated by glass filters (Toshiba UV-35, V-44, KL-40) and a 5-cm water filter. Monochromatic light of 608 nm was taken out from a 500 W xenon lamp (Ushio Electric) using filters (5-cm water filter and Toshiba O-58 and KL-60 glass filters). The irradiation light intensity was determined by a photometer (IL-1350, International Light Inc.) with a detector (SED038/S/W), calibrated with tris(oxalato)ferrate(III) chemical actinometer. Measurements of the concentration of components during the photoreaction were made using a high-pressure liquid chromatograph (Shimadzu LC-6A) and a detector (Shimadzu SPD-6AV) using a silica-gel column (Wako, Wakosil 5-sil, 4.6 mm×150 mm) with a mixture of ethyl acetate and hexane as an eluent. Flash column chromatography was carried out with a Merck Kieselgel 60 (230—400 mesh) with a mixture of ethyl acetate and hexane as an eluent. Analytical thin-layer chromatography was performed on Merck precoated silica gel 60 F-254, 0.25 mm thick TLC plates. All of the synthetic reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl, and diethyl ether and dichloromethane were distilled from CaH_2 immediately before use.

Synthesis of Indolylfulgides. (*E*)-3-[1-(1,2-Dimethyl-3-indolyl)butylidene]-4-isopropylidenedihydro-2,5-furandione (6E). To a solution of lithium diisopropylamide (prepared from 0.54 ml diisopropylamine and 2.3 ml hexane solution of butyllithium (1.66 mol dm^{-3}) in 2 ml THF at −78 °C) was added a solution of diethyl isopropylidenesuccinate (845.9 mg in 3 ml of THF); the mixture was stirred for 90 min at −78 °C. To it was added a solution of 3-butanoyl-1,2-dimethylindole (523.5 mg in 2 ml THF) at −78 °C; the temperature of solution was allowed to gradually rise to r. t.; the solution was then stirred for 4 d. The reaction mixture was acidified with diluted hydrochloric acid. The reaction mixture was extracted with diethyl ether three times, and the combined organic layer was washed with saturated aqueous NaCl. The organic layer was dried with anhydrous Na_2SO_4, and the solvent removed in vacuo. The half acid was roughly separated by silica-gel column chromatography, and was used for the next reaction without further purification.

The impure half ester was dissolved in 20 ml ethanol; to it was added 10 ml of water and 0.68 g of potassium hydroxide. The mixture was refluxed for 40 h, and then poured into a mixture of diluted hydrochloric acid and ice. After the solution was saturated with solid NaCl, it was extracted with diethyl ether three times. The combined organic layer was washed with saturated aqueous NaCl and dried with anhydrous Na_2SO_4; the solvent was then removed in vacuo. The residue was dissolved in 20 ml of CH_2Cl_2; to it was added dicyclohexylcarbodiimide (0.33 g). The mixture was stirred for 20 min at r. t. The solvent was removed in vacuo, and the fulgide was purified by flash column chromatography and recrystallization.

Fulgide **6E** (134.4 mg, 16%): Mp. 119—120 °C; ^{1}H NMR ($CDCl_3$) δ=0.89 (3H, t, J=7.4 Hz), 0.93, 2.17, 2.18, 3.69 (each 3H, s), 1.42 (2H, dqd, J=9.0, 7.4, 6.0 Hz), 3.17 (1H, m), 3.42 (1H, m), 7.1—7.3 (3H, m), 7.42 (1H, d, J=7.6 Hz); IR (KBr) 1804, 1752, 1221, 925, 741 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 337 (M^+, 56), 145 (($C_{10}H_{11}N$)$^+$, 100). Found: m/z 337.1660. Calcd for $C_{21}H_{23}NO_3$: M, 337.1678.

Other fulgides were synthesized practically in the same manner.

(*E*)-3-[1-(1,2-Dimethyl-3-indolyl)-2-methylpropylidene]-4-isopropylidenedihydro-2,5-furandione (7E). Fulgide **7E** (2%): Mp 143—144 °C; ^{1}H NMR ($CDCl_3$) δ= 0.95, 2.10, 2.13, 3.68 (each 3H, s), 1.02 (3H, d, J=6.9 Hz), 1.41 (3H, d, J=6.9 Hz), 4.09 (1H, sep, J=6.9 Hz), 7.1—7.3 (3H, m), 7.44 (1H, d, J=7.6 Hz); IR (KBr) 1801, 1756, 1230, 954, 733 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 337 (M^+, 57), 145 (($C_{10}H_{11}N$)$^+$, 100). Found: m/z 337.1657. Calcd for $C_{21}H_{23}NO_3$: M, 337.1678.

(*E*)-3-[1-(1,2-Dimethyl-3-indolyl)ethylidene]-4-adamantylidenedihydro-2,5-furandione (8E). Fulgide **8E** (7%): Mp 207—208 °C; ^{1}H NMR ($CDCl_3$) δ=0.30 (1H, s), 0.92 (2H, br), 1.4—2.0 (9H, br), 2.2 (1H, br), 2.26, 3.67 (each 3H, s), 4.16 (1H, br), 7.1—7.3 (3H, m), 7.39 (1H, d, J=7.6 Hz); IR (KBr) 1799, 1758, 1230, 952, 744 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 401 (M^+, 100), 145 (($C_{10}H_{11}N$)$^+$, 60). Found: m/z 401.2040. Calcd for $C_{26}H_{27}NO_3$: M, 401.1991.

(*E*)-3-[1-(1,2-Dimethyl-3-indolyl)butylidene]-4-adamantylidenedihydro-2,5-furandione (9E). Fulgide **9E** (2%): Mp 212—213 °C; ^{1}H NMR ($CDCl_3$) δ=0.1 (1H, s), 0.8 (1H, br), 0.85 (3H, t, J=7.3 Hz), 1.3—2.0 (11H, br), 1.34 (2H, m), 2.23, 3.66 (each 3H, s), 3.03 (1H, m), 3.45 (1H, m), 4.13 (1H, br), 7.1—7.3 (3H, m), 7.40 (1H, d, J=7.9 Hz); IR (KBr) 1800, 1758, 1227, 915, 738 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 429 (M^+, 48), 145 (($C_{10}H_{11}N$)$^+$, 100). Found: m/z 429.2315. Calcd for $C_{28}H_{31}NO_3$: M, 429.2304.

(*E*)-3-[1-(1,2-Dimethyl-3-indolyl)-2-methylpropylidene]-4-adamantylidenedihydro-2,5-furandione (10E). Fulgide **10E** (2%): Mp 212—213 °C; ^{1}H NMR ($CDCl_3$) δ=−0.33 (1H, br), 0.53 (1H, br), 0.92 (3H, d, J=6.9 Hz), 1.17, 3.66 (each 3H, s), 1.2—1.9 (10H, br), 1.36 (3H, d, J=7.2 Hz), 2.32 (1H, br), 4.08 (1H, br), 4.11 (1H, sep, J=6.9 Hz), 7.1—7.3 (3H, m), 7.39 (1H, d, J=7.9 Hz); IR (KBr) 1802, 1758, 1224, 942, 743 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 429 (M^+, 36), 145 (($C_{10}H_{11}N$)$^+$, 100). Found: m/z 429.2301. Calcd for $C_{28}H_{31}NO_3$: M, 429.2304.

(*E*)-3-[1-(2-Ethyl-1-methyl-3-indolyl)ethylidene]-4-isopropylidenedihydro-2,5-furandione (11E). Fulgide **11E** (9%): Mp 166—167 °C; ^{1}H NMR ($CDCl_3$) δ=0.96, 2.13, 2.78, 3.74 (each 3H, s), 1.21 (3H, t, J=7.6 Hz), 2.71 (2H, q, J=7.6 Hz), 7.1—7.3 (4H, m); IR (KBr) 1804, 1754, 1225, 924, 739 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 323 (M^+, 100), 294 ($M-C_2H_5$)$^+$, 95). Found: m/z 323.1469. Calcd for $C_{20}H_{21}NO_3$: M, 323.1521.

(*E*)-3-[1-(1-Ethyl-2-methyl-3-indolyl)ethylidene]-4-isopropylidenedihydro-2,5-furandione (12E). Fulgide **12E** (9%): Mp 161—162 °C; ^{1}H NMR ($CDCl_3$) δ=0.93, 2.20, 2.20, 2.81 (each 3H, s), 1.34 (3H, t, J=7.2 Hz), 4.16 (2H, q, J=7.2 Hz), 7.1—7.3 (3H, m), 7.41 (1H, d, J=7.6 Hz); IR (KBr) 1803, 1752, 1415, 1227, 925, 744 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 323 (M^+, 100), 159 (($C_{11}H_{13}N$)$^+$, 73). Found: m/z 323.1480. Calcd for $C_{20}H_{21}NO_3$: M, 323.1521.

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12) Although the absence of isosbestic points is not apparent on Fig. 1b (**11**), an expanded chart showed it clearly. Fig. 1a (**7**) showed isosbestic points when expanded.

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14) The values of absorption maximum wavelengths and molar absorption coefficients of *Z*-forms shown in Table 2 were obtained from the spectra of *E*/*Z* mixtures, obtained after 608-nm light irradiation to the PSS(UV), by subtracting the spectra of *E*-forms.