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Electronic Effects of Substituents on Indole Nitrogen on the Photochromic Properties of Indolylfulgides

Soichi Uchida,# Yasushi Yokoyama,* Jitsuo Kiji,*,† Tamon Okano,†
and Hitoshi Kitamura†

Department of Materials Chemistry, Faculty of Engineering, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama 240

†Department of Materials Science, Tottori University, Tottori 680

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The attempt to synthesize *N*-*p*-tolylsulfonylindolylfulgide by Stobbe condensation was unsuccessful because hydrolysis of the Stobbe-condensation product eliminated the sulfonyl moiety to give, after several steps, the *N*-unsubstituted fulgide. Pd(II)-catalyzed carbonylation of 2-butyne-1,4-diol derivative bearing the *N*-*p*-tolylsulfonylindole, however, afforded the desired *N*-*p*-tolylsulfonylindolylfulgide. A comparison of absorption spectroscopic and photochromic properties of these fulgides with those of the known *N*-methylindolylfulgide gave the following results. The electron-withdrawing substituent on nitrogen (i) shortened the absorption maximum of the colored form, (ii) suppressed thermal *E*–*Z* isomerization, and (iii) enlarged quantum yields of photochromic reactions.

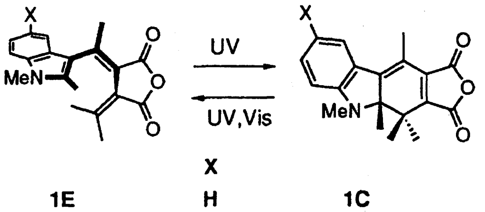
Indolylfulgides such as **1** are fatigue resistive and thermally stable among the fulgides reported so far.[1)] We (the Yokohama group) have already reported the effects of substituents on 5-position of the indole ring on absorption spectroscopic and photochromic properties of indolylfulgides **2**—**4** (Chart 1).[2)] An electron-donating substituent on 5-position of the indole ring lengthened the absorption maximum of the colored form and decreased the coloring and bleaching quantum yields. Based on these findings, an indolylfulgide with a dimethylamino group (**4**) has become a candidate for photon-mode rewritable optical recording media which have non-destructive readout ability.[3,4)] Thus we intended to obtain more information about the relationship between the steric[5,6)] and electronic[2)] effects of substituents of indolylfulgides and their photochromic properties.

Syntheses of fulgides have generally been done by way of Stobbe condensation[7)] since the beginning of this century, though important improvements have been reported.[8,2,6)] Recently we (the Tottori group) have developed a new and efficient method of synthesis of fulgides, by way of the palladium(II)-catalyzed carbonylation of 2-butyne-1,4-diol derivatives[9)] (Scheme 1). We have already reported the synthesis and photochromic reactions of furyl- and thienylfulgides with a *t*-butyl group (**5** and **6**) with this method (Chart 2);[10)] such compounds have never been synthesized by the Stobbe-condensation method.[11)]

In this article, we report (i) application of the carbonylation method to the synthesis of indolylfulgides, and (ii) analysis of the electronic effects of substituents on the nitrogen atom of indolylfulgides.

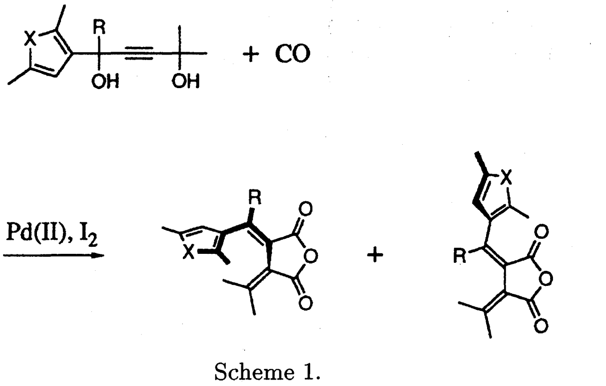
Results and Discussion

Application of Stobbe-Condensation Method



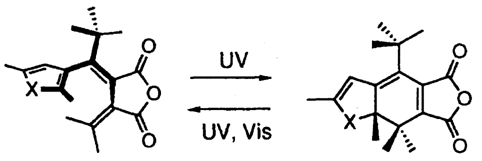
	X	
1E	**H**	**1C**
2E	**SMe**	**2C**
3E	**OMe**	**3C**
4E	**NMe$_2$**	**4C**

Chart 1.



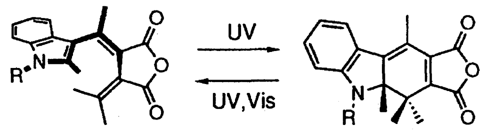
Scheme 1.

#JSPS Predoctoral Research Fellow.



	X	
5E	**O**	**5C**
6E	**S**	**6C**

Chart 2.



	R	
1E	**Me**	**1C**
10E	**H**	**10C**
11E	**Ts**	**11C**

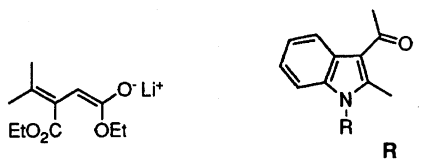
Chart 4.

to the Synthesis of an Indolylfulgide with an Electron-Withdrawing Substituent on Indole Nitrogen. A Stobbe condensation of the lithium enolate of diethyl isopropylidenesuccinate (**7**) (generated by lithium diisopropylamide (LDA)) with 3-acetyl-1,2-dimethylindole possessing an electron-donating substituent on 5-position did not proceed smoothly. This can be attributed to the weakened polarization of the carbonyl group.[2] As 5-unsubstituted 3-acetyl-1,2-dimethylindole (**8**) reacted smoothly, we expected that the introduction of an electron-withdrawing substituent on the indole nucleus might accelerate the condensation reaction. It would naturally be better that the electron-withdrawing substituent could be replaced after the condensation reaction, to obtain a broader range of fulgide derivatives. We therefore carried out a condensation reaction of 3-acetyl-2-methyl-1-*p*-tolylsulfonylindole (3-acetyl-2-methyl-1-*p*-Ts-indole, **9**) with the enolate **7** (Chart 3).

As had been expected, condensation proceeded smoothly to give, after the usual work-up, two geometrically isomeric half esters in 44 and 16% yields based on the ketone. The major half ester was subjected to hydrolysis with potassium hydroxide in refluxing aqueous ethanol. The dibasic acid obtained was treated, without further purification, with trifluoroacetylimidazole, to afford the unexpected *N*-unsubstituted indolylfulgide **10** instead of **11** (Chart 4). Apparently the sulfonamide group was hydrolyzed together with the ester group upon treatment with potassium hydroxide. The fulgide **10E** was obtained in 54% for the major half ester. Contrary to our expectation, however, introduction of substituents to the indole nitrogen of **10** (e.g., *p*-Ts group with *p*-tolylsulfonyl chloride and LDA in tetrahydrofuran (THF)) was not successful.

Application of Carbonylation Method to the Synthesis of Indolylfulgides. The effectiveness of the palladium(II)-catalyzed carbonylation method has been proved by the syntheses of furyl- and thienylfulgides[9] including **5** and **6** having a *t*-butyl group on the arylmethylene moiety.[10] As the extension of application of this method, we tried to synthesize indolylfulgides. Reaction of the *N*-methyl indolyl ketone **8** with the lithium acetylide of 3-methyl-1-butyn-3-ol (**12a**), however, did not give the desired addition product in a sufficient yield. Replacement of the lithium cation with cerium(III)[2,12] was not effective. As the polarization of the carbonyl of **8** is weakened by the electron-donation from the indole ring, the acetylide carbanion could not react efficiently. In order to reduce the electron donation from the indole nitrogen, addition of the cerium(III) acetylide **12b** to the *N*-Ts-indolyl ketone **9** was carried out (Chart 5). The reaction proceeded to give the desired acetylenic diol derivative **13** in 25% yield after column chromatographic purification. Treatment of **13** with palladium(II) acetate in benzene under an atmosphere of carbon monoxide (7.1 MPa) at 90 °C for 6 h afforded a mixture of the *E*- and *Z*-isomers of desired *N*-*p*-Ts-indolylfulgide **11** in 31% yield. Column chromatographic separation followed by recrystallization (EtOAc/hexane for **11E** and Et_2O for **11Z**) gave pure **11E** and **11Z**.

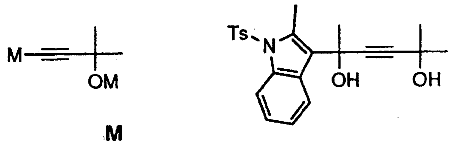
Unlike other indolylfulgides and similarly to furylfulgides, *E*- and *Z*-forms of **11** did not isomerize to each other during column chromatographic separation.[5] A reduction of the electron-donating ability of the aromatic ring decreased the contribution of the charge-separated resonance structure such as **14** (Chart 6), which is supposed to undergo the ground-state *E*–*Z* isomerization. This is the first example of an indolylfulgide in which *Z*-form is isolated and characterized. The *Z*-forms of indolylfulgides **1**—**4**, **10**, and other indolylfulgides reported so far[5] could not be isolated. As the *Z*-forms, if generated by syntheses, isomerized to the corresponding *E*-forms during the silica-gel column chromatographic purification,[5] they could only be de-



7

	R
8	**Me**
9	**Ts**

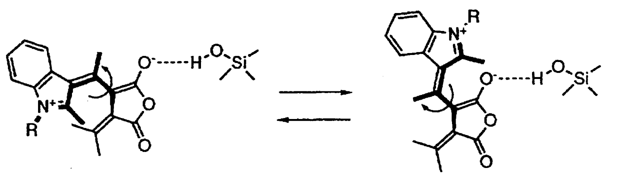
Chart 3.



	M
12a	**Li**
12b	**$CeCl_2$**

13

Chart 5.



14E **14Z**

Chart 6.

tected by ^{1}H NMR during UV-light irradiation. The *Z*-forms of **2**—**4** isomerized to the corresponding *E*-forms in toluene quickly at room temperature because of the enhanced electron-donating power of the aromatic ring. The precise concentration ratios of the *E*- and *Z*-isomers during the photoirradiation were therefore not determined either by HPLC[5] or by ^{1}H NMR. For that reason, the quantum yields of photoreactions of **2**—**4** had been calculated without considering the existence of small amounts of corresponding *Z*-forms.[2]

Electronic Effects of Substituents of Indole Nitrogen on Absorption Spectroscopic Properties of Indolylfulgides. As fulgides **1**, **10**, and **11** have substituents on indole nitrogen with different degrees of electron-donating or -withdrawing effects (Me, H, *p*-Ts), such effects appeared directly in their absorption spectra. As shown in Table 1, absorption maximum wavelengths of both *E*- and *C*-forms shortened in the decreasing order of electron-donating ability of the substituent. This is in good accord with the observation for 5-substituted indolylfulgides[2] and fulgides with different aromatic rings.[1] It is worth noting that the change of electron-transition energy associated with the change of the substituents on the indole nitrogen is larger than that associated with the change of the substituents on the 5-position of the indole nucleus. The differences of electron-transition energy are also shown in Table 1. While the lone pair on nitrogen can participate in the conjugation of the diene- (*E*-form) and triene-conjugated (*C*-form) carbonyl functionality as the electron donor, the group on the 5-position cannot participate in the conjugation. Therefore the transition energy is more affected by the substituents on indole nitrogen than by the substituents on 5-position.

Electronic Effects of Substituents of Indole Nitrogen on Photochromic Properties of Indolylfulgides. Photochromic reactions were carried out as previously reported for furylfulgides[6] and indolylfulgides.[5] The change in absorption spectra of **11** as the time of photoirradiation continued is shown in Fig. 1. The results of photochromic reactions are summarized in Table 2.

All the quantum yields except Φ_{ZE}(UV) decreased

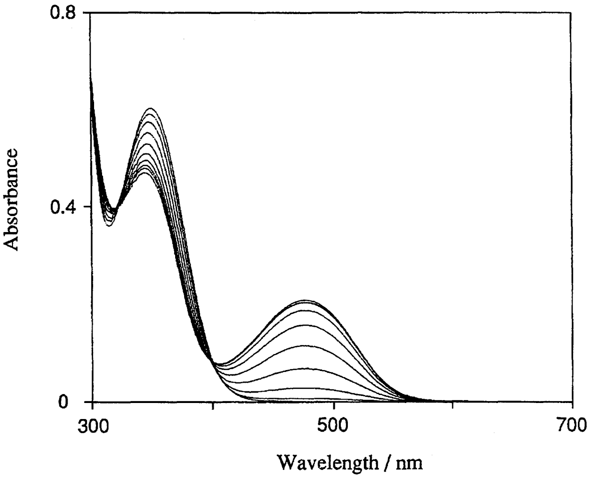


Fig. 1. Absorption spectral changes of coloring of **11** in toluene. Concentration: 1.01 × 10^{-4} mol dm^{-3}, Irradiation light: 366 nm, Light intensity: 2.31 mW cm^{-2}, Irradiation time/min: 0, 0.5, 1.2, 2.2, 3.5, 5.2, 7.4, 11, 15, 25 (PSS).

Table 2. Quantum Yields of Photoreactions of Indolylfulgides with Different Substituents on Indole Nitrogen in Toluene

	Φ_{EC}[a]	Φ_{CE}[a]	Φ_{EZ}[a]	Φ_{ZE}[a]	[*E*] / [*Z*] / [*C*][b]	Φ_{CE}[c]
11	0.19	0.44	0.11	0.083	39 / 33 / 28	0.27
10	0.14	0.23	0.074	0.15	23 / 3 / 74	0.092
1	0.045[d]	0.16[d]	0.040[d]	0.072[d]	35 / 9 / 56	0.051[e]

a) 366-nm light irradiation. b) PSS (UV). c) 495-nm light irradiation. d) 405-nm light irradiation. e) 608-nm light irradiation.

Table 1. Absorption Spectral Data of Indolylfulgides with Electron-Withdrawing and -Donating Substituents in Toluene

	E-Form		*Z*-Form		*C*-Form			
	λ_{max}/nm	(ε_{max})[a]	λ_{max}/nm	(ε_{max})[a]	λ_{max}/nm	(ε_{max})[a]	TE/kJ mol^{-1} [b]	
11	340	(4980)	351	(5970)	479	(7120)	250	(+46)
10	375	(7800)	383	(13400)[c]	535	(7400)	223	(+19)
1	385	(8150)	397	(14300)[c]	584	(6810)	204	(0)
2	387	(8750)	—[d]		600	(7090)	199	(−5)
3	393	(9530)	—[d]		625	(7060)	191	(−13)
4	404	(8040)	—[d]		673	(6200)	178	(−26)

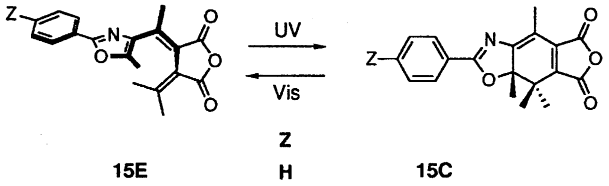
a) ε_{max}/mol^{-1} dm^3 cm^{-1}. b) Electronic transition energy of *C*-forms. Values in parentheses are the deviation from **1**. c) Calculated values. d) Could not be determined (see text).

as the electron-donating ability increased. We have previously reported similar effects of electron-donating groups on 5-position of the indole ring of indolylfulgides on the quantum yields of photoreactions.[2)] To the contrary, Tomoda et al. reported that increase in the electron-donating ability of substituents on heteroaromatic ring of fulgides (i) increased the coloring quantum yield and (ii) decreased the bleaching quantum yield.[13)] Although the latter trend is consistent with our observations, the former is not consistent with ours. For example, the coloring quantum yield of an oxazolylfulgide (**15**, Z=H) increased (0.18 to 0.26) and bleaching quantum yield decreased (0.054 to 0.0091) when the electron-donating group was substituted on the *p*-position of the phenyl ring (**16**, Z=NMe$_2$) (Chart 7). The electronic factors governing the quantum yields are thus ambiguous. The differences may have come from the electronic nature of the aromatic rings of not only the ground states but also the excited states, the latter being more important. Unfortunately, because no effective and reliable calculation methods to evaluate the electronic properties of the excited states of complex molecules such as fulgides are available, further discussion is not possible at the present time.[14)]

The relationship between the conversion ratio to the *C*-form at the photostationary state of UV-irradiation (PSS(UV)) and the electronic nature of the substituents is not simple for the present case. The ratio of *C*-form at PSS(UV) increased as the electron-donating ability of the substituents increased for 5-substituted indolylfulgides **2**—**4**, because the decrease in bleaching quantum yield of UV-light irradiation (Φ_{CE}(UV)) is larger than the decrease in coloring quantum yield (Φ_{EC}(UV)). To the contrary, the percentage of *C*-form at PSS(UV) for **10** is the largest in the **1**, **10**, and **11** series. This is attributed to the drastic decrease of Φ_{EC} (UV) from **10** to **1** (0.14 to 0.045).

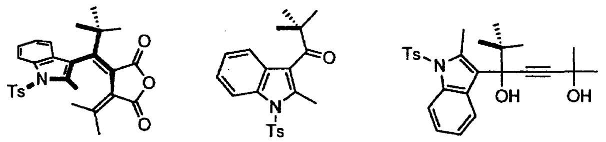
***N*-*p*-Ts-Substituted Indolylfulgide with a 2,2-Dimethylpropylidene Group.** Using the carbonylation methodology, we obtained the *t*-butyl-substituted *N*-*p*-Ts-indolylfulgide **17** by way of the indolyl ketone **18** and the acetylenic diol **19** (Chart 8). Examination of the steric effect of the indolylalkylidene moiety on spectroscopic and photochromic properties of *N*-*p*-Ts-indolylfulgides is possible by comparing those of **11** with those of **17**.

The absorption spectroscopic data and quantum yields of photochromic reactions of **11** and **17** are listed in Tables 3 and 4. The absorption maximum wavelength of **17E** in the UV region is shorter than that of **11E**. This absorption band is shaped like a shoulder (Fig. 2(a)). This is because (i) the absorption maximum wavelength shortened, and (ii) its molar absorption coefficient decreased, so that the absorption band merged into the absorption end of the large absorption of the shorter wavelength. A similar tendency has been observed for furylfulgides.[6,10,11)]



15E H **15C**
16E NMe$_2$ **16C**

Chart 7.



17E **18** **19**

Chart 8.

The absorption band of **17C** in the visible region

Table 3. Quantum Yields of Photoreactions of the *N*-*p*-Ts-Indolylfulgide with a *t*-Butyl Group in Toluene

	Φ_{EC}[a)]	Φ_{CE}[a)]	Φ_{EZ}[a)]	Φ_{ZE}[a)]	[*E*] / [*Z*] / [C][b)]	Φ_{CE}[c)]
11	0.19	0.44	0.11	0.083	39 / 33 / 28	0.27
17[d)]	0.34	0.34	—	—	57 / — / 43	0.25

a)366-nm light irradiation. b) PSS (366). c) 495-nm light irradiation. d) *Z*-form was neglected.

Table 4. Absorption Spectral Data of *N*-*p*-Ts-Indolylfulgides with *t*-Butyl Group in Toluene

	E-Form	*Z*-Form		*C*-Form	
	λ_{max}/nm ($\varepsilon_{\mathrm{max}}$)[a)]	λ_{max}/nm ($\varepsilon_{\mathrm{max}}$)[a)]		λ_{max}/nm ($\varepsilon_{\mathrm{max}}$)[a)]	
11	340 (4980)	351[b)]	(5970)[b)]	479	(7120)
17	333 (2350) (sh)	—[c)]		459	(4770)

a) $\varepsilon_{\mathrm{max}}$/mol^{-1} dm^3 cm^{-1}. b) Calculated values. c) Could not be determined (see text).

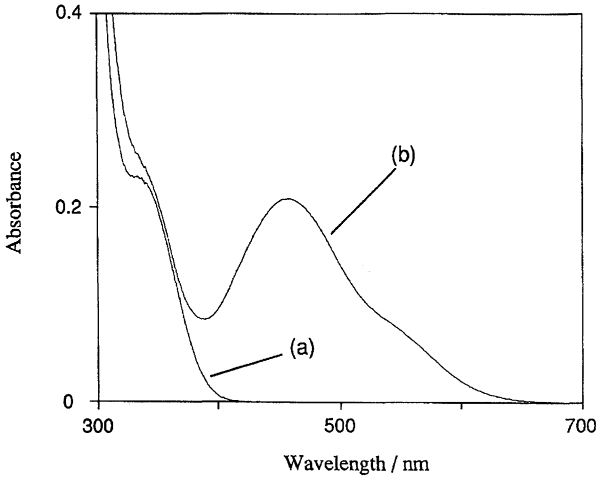


Fig. 2. Absorption spectra of **17** in toluene (1.01 × 10^{-4} mol dm^{-3}). (a) *E*-Form. (b) Photostationary state of 366 nm-light irradiation on (a).

is composed of two ill-distinguished bands (Fig. 2(b)). That **17C** has these two absorption bands was confirmed from the facts that (i) the absorption changed proportionally during the photoreaction, and (ii) the HPLC chromatogram showed only two components (**17E** and **17C**) during photoirradiation. The absorption maximum wavelength of the major band of the *t*-butyl-substituted **17C** (459 nm in toluene) is shorter than that of the methyl-substituted **11C** (479 nm in toluene), while that of the smaller one of **17C** (about 550 nm) locates at a longer wavelength in the visible region than that of **11C**. The absorption end of **17C**, therefore, reaches 650 nm, while that of **11C** is about 610 nm. The molar absorption coefficient of the absorption maximum of **17C** is considerably smaller than that of **11C**.

Different from the furyl- and thienylfulgides **5** and **6** with a *t*-butyl group, the photochromic reaction of **17** was shown, by ^{1}H NMR in toluene, to involve the *Z*-form. However, because the amount of the *Z*-form is small and the *Z*-form was not isolated, quantum yields were calculated by neglecting the *Z*-form. As shown in Table 3, the coloring quantum yield increased when the substituent changed from methyl to *t*-butyl (0.19 to 0.34). This tendency is the same that for the photochromism of *t*-butyl-substituted furyl- and thienylfulgides **5** and **6**.

As **17C** has two absorption bands, irradiation of the light of the wavelength in each absorption band is interesting. If irradiation of one of the bands causes bleaching while the other does not, it is conceptually possible to construct a system having a non-destructive readout of memory when it is applied to the optical memory media. Bleaching quantum yields of **17C** with 495-nm light (in the major absorption band) and 608-nm light (in the smaller absorption band), however, were both 0.25. In addition, these values are almost the same as that of **11C** (0.27).

Conclusion

Although it was not effective to prepare *N*-methylindolylfulgide **1**, the Pd(II)-catalyzed carbonylation method was successful to prepare *N*-Ts-indolylfulgides **11** and **17**. Electronically influential substituents on the indole nitrogen atom affected both absorption spectroscopic and photochromic properties of indolylfulgides more than the substituents on 5-position of the indole ring. The $\lambda_{\max}$ of the *C*-form became shorter when the electron-withdrawing nature of the substituent on the indole nitrogen increased. Almost all of the quantum yields increased as the electron-withdrawing ability increased. The *t*-butyl-substituted *N*-Ts-indolylfulgide exhibited a large coloration quantum yield.

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 and m: multiplet. 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. The emission line of 366 nm of a 500 W high-pressure mercury lamp (Ushio Electric) was separated by filters (Toshiba UV-35, UV-D35, a 1-cm thick aqueous $CuSO_4$ (50 g dm^{-3}), and a 5-cm water filter). Monochromatic light beams of the visible region were taken out from a 500 W xenon lamp (Ushio Electric) using filters (495 nm; 5-cm water filter and Toshiba Y-47, IRA-25S, and KL-50 glass filters. 608 nm; 5-cm water filter and Toshiba O-58, IRA-25S, and KL-60 glass filters). The irradiation light intensity was determined by a photometer (IL-1350, International Light Inc.) with detectors (SED038 for 495- and 608-nm lights and SED400 for 366-nm light), 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. Silica-gel column chromatography was carried out with a Merck Kieselgel 60 (230—400 mesh) with a mixture of ethyl acetate and hexane as an eluent, unless otherwise noted. 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 Fulgides. 3-Acetyl-2-methyl-1-(4-tolylsulfonyl)indole (9). A THF solution (70 ml) of oily NaH (ca. 60%, 0.25 g, ca. 6.3 mmol) and 3-acetyl-2-methylindole (1.00 g, 5.77 mmol) was stirred at room temperature for 30 min. To it was added, at that temperature, *p*-tolylsulfonyl chloride (1.33 g, 6.98 mmol) in THF (5 ml), and the resulting solution was stirred for 2 h. Methanol (0.5 ml) was added to quench the reaction, followed by addition of sat. aq NaCl. The solution was extracted with ethyl acetate, the organic layer was washed with aq NaCl, dried with anhydrous Na_2SO_4, and the solvent was removed in vacuo. The residue was chromatographed to give **9**.

9 (1.35 g, 71%): ^{1}H NMR ($CDCl_3$) δ=2.36, 2.63, 2.89 (each 3H, s), 7.25 (2H, d, J=8.57 Hz), 7.3—7.4 (2H, m), 7.71 (2H, d, J=8.68 Hz), 7.9 (1H, m) 8.3 (1H, m); IR (KBr) 1670, 1381, 1176, 722 cm^{-1}.

(*E*)-3-Isopropylidene-4-[1-(2-methyl-3-indolyl)ethylidene]-3,4-dihydro-2,5-furandione (10). To a solution of lithium diisopropylamide (prepared from 0.85 ml diisopropylamine and 3.1 ml hexane solution of butyllithium (1.63 mol dm^{-3}) in 15 ml THF at −78 °C) was added a solution of diethyl isopropylidenesuccinate (1.08 g in 5 ml of THF), and the mixture was stirred for 1 h at −78 °C. To this was added a solution of **9** (1.11 g in 5 ml THF) at −78 °C. The temperature of this solution was allowed to gradually rise to r.t., and the solution was then stirred for 2 d.

The reaction mixture was acidified with diluted hydrochloric acid. The reaction mixture was extracted with ethyl 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 two isomers of half acid were roughly separated by silica-gel column chromatography (major isomer 745 mg, and minor isomer 264 mg), and were used for the next reaction without further purification.

The impure major half acid (745 mg) was dissolved in 15 ml ethanol; to this mixture were added 15 ml of water and 3.1 g of potassium hydroxide. The mixture was refluxed for 18 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 ethyl acetate three times. The combined organic layer was washed with saturated aqueous NaCl, dried with anhydrous Na_2SO_4, and the solvent was then removed in vacuo. The residue was dissolved in 30 ml of THF, and to it was added 1-trifluoroacetylimidazole (0.25 ml). The mixture was stirred for 1 h at r.t. To the mixture was added saturated aqueous NaCl and the mixture was extracted with ethyl acetate three times. The combined organic layer was washed with saturated aqueous NaCl and dried with anhydrous Na_2SO_4. The solvent was removed in vacuo, and the fulgide **10** was purified by flash column chromatography and recrystallization (CH_2Cl_2/hexane).

Fulgide 10E (241.6 mg, 24%): Mp 214—215 °C; ^{1}H NMR ($CDCl_3$) $\delta=1.00$, 2.22, 2.24, 2.81 (each 3H, s), 7.1—7.4 (4H, m), 8.21 (1H, s); IR (KBr) 1801, 1747, 1458, 1229, 929, 742 cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel intensity) 295 (M^+; 100), 131 ($C_9H_9N^+$; 34). Found: *m*/*z* 295.1173. Calcd for $C_{21}H_{23}NO_3$: M, 295.1208.

5-Methyl-2-[2-methyl-1-(4-tolylsulfonyl)-3-indolyl]-3-hexyne-2,5-diol (13). Indolyl ketone **9** (2.56 g, 7.8 mmol) and $CeCl_3 \cdot 7H_2O$ (13.0 g), which was dried beforehand under vacuum at 140 °C for 8 h, were stirred in THF (70 ml) at room temperature for 3 h. An acetylide solution was prepared by addition of butyllithium (hexane solution, ca. 32 mmol) to a THF solution (20 ml) of 2-methyl-3-butyn-2-ol (1.6 ml, ca. 16 mmol), and this was added to the above solution of **9** at −78 °C. The resulting solution was stirred at −78 °C for 3 h and was then warmed slowly to room temperature while stirring overnight. Aqueous NH_4Cl was added and the product was extracted with ether. The ether solution was dried over Na_2SO_4. Concentration gave crude **13** (2.50 g) as dark oil. The product (1.65 g) was chromatographed on Wakogel C-200 with benzene, benzene/chloroform (2/1), and methanol. The eluate with methanol was collected and concentrated to give **13** (0.79 g) as a dark brown solid.

Carbonylation of 13. Synthesis of 3-Isopropylidene-4-{1-[2-methyl-1-(4-tolylsulfonyl)-3-indolyl]ethylidene}-3,4-dihydro-2,5-furandione (11). The combined crop of **13** (1.05 g, 2.55 mmol), $Pd(OAc)_2$ (20 mg, 0.1 mmol), I_2 (24 mg, 0.1 mmol), and benzene (10 ml) were charged in a 40 ml stainless steel autoclave. The air was purged with carbon monoxide. The autoclave was pressurized at 7.1 MPa and heated at 90 °C for 6 h with magnetic stirring. After the reaction, the benzene solution was filtered through a short silica gel column. Benzene was evaporated under reduced pressure to give a brown solid (ca. 0.8 g), which was chromatographed on Wakogel C-200 with hexane/benzene (1/1), benzene, and chloroform (2/1—1/1). The eluate with benzene gave **11** as a light brown solid (0.33 g, 31%). Repeated silica-gel column chromatographic purification followed by recrystallization (ethyl acetate/hexane for *E*-form and ethyl ether for *Z*-form) afforded pure isomers.

Fulgide 11E: Mp 188—189 °C; ^{1}H NMR ($CDCl_3$) $\delta=0.73$, 2.04, 2.33, 2.39, 2.65 (each 3H, s), 7.3 (4H, m), 7.4 (1H, m), 7.73 (2H, d, $J=8.25$ Hz), 8.32 (1H, d, $J=8.25$ Hz); IR (KBr) 1810, 1759, 1380, 1225, 1178, 934, 752 cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel intensity) 449 (M^+; 65), 294 ($(M-C_7H_7O_2S)^+$; 100). Found: *m*/*z* 449.1324. Calcd for $C_{25}H_{23}NO_5S$: M, 449.1297.

Fulgide 11Z: Mp 192—193 °C; ^{1}H NMR ($CDCl_3$) $\delta=2.10$, 2.14, 2.34, 2.49, 2.54 (each 3H, s), 7.2 (5H, m), 7.69 (2H, d, $J=8.57$ Hz), 8.10 (1H, dd, $J=9.25$, 0.66 Hz); IR (KBr) 1812, 1761, 1377, 1223, 1172, 928, 750 cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel intensity) 449 (M^+; 78), 294 ($(M-C_7H_7O_2S)^+$; 100). Found: *m*/*z* 449.1323. Calcd for $C_{25}H_{23}NO_5S$: M, 449.1297.

3-(2,2-Dimethylpropanoyl)-2-methyl-1-(4-tolylsulfonyl)indole (18). 2-Methylindole (9.71 g, 74 mmol) in ether (50 ml) was added to a Grignard solution, which was prepared by addition of ethyl bromide (6.8 ml, ca. 80 mmol) to magnesium (2.18 g, 90 mmol) in ether (80 ml). 2,2-Dimethylpropanoyl chloride (9.7 ml, ca. 80 mmol) in ether (10 ml) was added to the above solution and the resulting solution was stirred at room temperature for 1.5 h. Aqueous $NaHCO_3$ was added to the solution. Extracting with ethyl acetate, washing with aq NaCl, and drying with anhydrous Na_2SO_4 gave red brown oily liquid (15.36 g; Yield, 96.5%). This product (14.7 g, 68 mmol) was subjected to the synthesis of **18** in a similar manner to that of **9** (giving 22.9 g of **18**).

2,6,6-Trimethyl-5-(2-methyl-1-(4-tolylsulfonyl)-3-indolyl)-3-heptyne-2,5-diol (19). This compound was prepared from **18** (2.70 g, 7.25 mmol) in a similar manner to the synthesis of **13**, giving 2.75 g of **19**.

Carbonylation of 19. Synthesis of 3-{2,2-Dimethyl-1-[2-methyl-1-(4-tolylsulfonyl)-3-indolyl]propylidene}-4-isopropylidene-3,4-dihydro-2,5-furandione (17). Carbonylation was performed in a similar manner to that of **13**. The crude, dark brown solid (1.61 g) thus obtained was chromatographed repeatedly to give the *E*-isomer of fulgide **17** in 22% yield (0.34 g). It was recrystallized from Et_2O/hexane. Mp 138—139 °C. ^{1}H NMR ($CDCl_3$) $\delta=0.84$, 1.75, 2.33, 2.37 (each 3H, s), 1.28 (9H, s), 7.2—7.4 (5H, m), 7.67 (2H, d, $J=8.24$ Hz), 8.27 (1H, d, $J=7.92$ Hz); IR (KBr) 1817, 1770, 1176 cm^{-1}. MS (EI, 70 eV) *m*/*z* (rel intensity) 449 (M^+; 65), 294 ($(M-C_7H_7O_2S)^+$; 100). Found: *m*/*z* 449.1324. Calcd for $C_{28}H_{29}NO_5S$: 449.1297.

References

1) A. Kaneko, A. Tomoda, M. Ishizuka, H. Suzuki, and R. Matsushima, *Bull. Chem. Soc. Jpn.*, **61**, 3569 (1988).

2) Y. Yokoyama, T. Tanaka, T. Yamane, and Y. Kurita, *Chem. Lett.*, **1991**, 1125.

3) Y. Yokoyama, T. Yamane, and Y. Kurita, *J. Chem. Soc., Chem. Commun.*, **1991**, 1722.

4) F. Matsui, H. Taniguchi, Y. Yokoyama, K. Sugiyama, and Y. Kurita, *Chem. Lett.*, **1994**, 1869.

5) S. Uchida, S. Yamada, Y. Yokoyama, and Y. Kurita, *Bull. Chem. Soc. Jpn.*, **68**, 1677 (1995).

6) Y. Yokoyama, T. Inoue, M. Yokoyama, T. Goto, T. Iwai, N. Kera, I. Hitomi, and Y. Kurita, *Bull. Chem. Soc. Jpn.*, **67**, 3297 (1994).

7) H. Stobbe, *Ber. Dtsch. Chem. Ges.*, **37**, 2232 (1904); **38**, 3673 (1905).

8) W. S. Johnson and G. H. Daub, *Org. React.*, **6**, 1 (1951).

9) J. Kiji, H. Konishi, T. Okano, S. Kometani, and A. Iwasa, *Chem. Lett.*, **1987**, 313.

10) J. Kiji, T. Okano, H. Kitamura, Y. Yokoyama, S. Kubota, and Y. Kurita, *Bull. Chem. Soc. Jpn.*, **68**, 616 (1995).

11) Y. Yokoyama, T. Goto, T. Inoue, M. Yokoyama, and Y. Kurita, *Chem. Lett.*, **1988**, 1049.

12) T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, and Y. Kamiya, *J. Am. Chem. Soc.*, **111**, 4392 (1989).

13) A. Tomoda, A. Kaneko, H. Tsuboi, and R. Matsushima, *Bull. Chem. Soc. Jpn.*, **66**, 330 (1993).

14) Y. Yokoyama, T. Serizawa, S. Suzuki, Y. Yokoyama, and Y. Kurita, *Chem. Lett.*, **1995**, 17.