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# Photochromism of Heterocyclic Fulgides. IV. Relationship between Chemical Structure and Photochromic Performance

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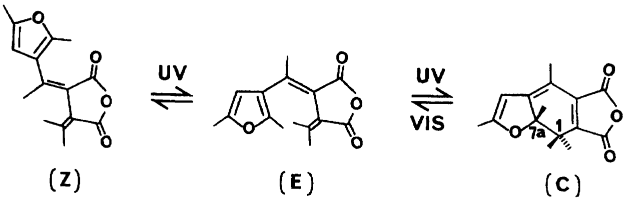
**Synopsis.** The absorption spectra and quantum yields of various heterocyclic fulgides were measured. The absorption maxima of the colored photocyclization products of fulgides were dependant upon the structure of heterocyclic rings and the substituent; and increase of the electron-donating ability of the heterocyclic ring caused a red shift of $\lambda_{\max}$. A quantum yield measurement of the photochromic reaction of fulgides revealed that not only the steric effect, but also the electronic effect of substituent (e.g. *p*-(dimethylamino)phenyl, cyano, acetyl) introduced into the heterocycles, changed the reactivity for both coloration and bleaching.

"Fulgides" are 2,3-bis(methylene)derivatives of succinic anhydride. It had been known that some fulgides are photochromic.[1] In the 1970's Heller and co-workers reported that (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (3-furyl fulgide) exhibited excellent thermal stability of the colored form of the fulgide(Scheme 1).[2] One interesting result, which had never been observed in other common photochromic compounds, e.g. spirobenzopirans, attracted much attention because of a high possibility of fulgide being used as a rewritable recording media. For the practical utilization of fulgide as data-storage media, however, there are some other problems which must be solved, e.g. the susceptibility at the semiconductor laser oscillation wavelength, cycle-repeating fatigue resistance (photochemical stability) and high photo-responsiveness.

In previous papers[3—5] we had revealed the relationship between the structure of the heterocyclic rings and the photochromic performances of fulgides, e.g. the absorption spectra as well as the thermal and photochemical stability in poly(methyl methacrylate) thin film. This work is mainly concerned with the result of the quantum yield measurements (photoresponsiveness) of the various heterocyclic fulgides (Scheme 2).

## Results and Discussion

**Absorption Spectra and Photochromism.** A dilute toluene solution of fulgides (**1**—**4**) ($1\times10^{-4}$ mol dm$^{-3}$) was irradiated with UV light (366 nm) for coloration. When a photostationary state (pss) was acquired, e.g. no spectra change was observed, the absorption spectra was recorded. The results are shown in Fig. 1. The spectra show that $\lambda_{\max}$ of colored fulgides are bathochromic-shifted with an increase of the bulkiness of $R^2$ in the following order: methyl<ethyl<adamantylidene. On the other hand, colored fulgide **4C** containing an acetyl group on the furan ring exhibited a hypsochromic-shifted spectra. HPLC measurements of the colored solutions indicated that 80 and 86% of fulgide **1** and **2** were converted into colored forms. To the contrary, fulgide **4** exhibited a lower conversion (51%). Subsequent irradiation of visible light on the colored solutions of fulgide caused rapid bleaching.



Scheme 1. Photochromic reaction of 3-fury fulgide **1**.

On the other hand, $\lambda_{\max}$ of the colored form of fulgide (**5C**, **7C**—**9C**) was strongly dependant upon the structure of the heterocyclic rings. The absorption maxima shifted to longer wavelengths in the following order: **9C**<**5C**<**8C**<**7C**. It was obvious that an increase in the electron-donating ability of the heteroaromatic structure caused a bathochromic shift of $\lambda_{\max}$. The spectroscopic properties of fulgide (**E**) and their photocyclized form (**C**) are summarized in Table 1.

**Quantum Yield of the Photochromic Reaction.** In Table 2 the quantum yields of both the coloration and bleaching of fulgides in toluene are given. The results of

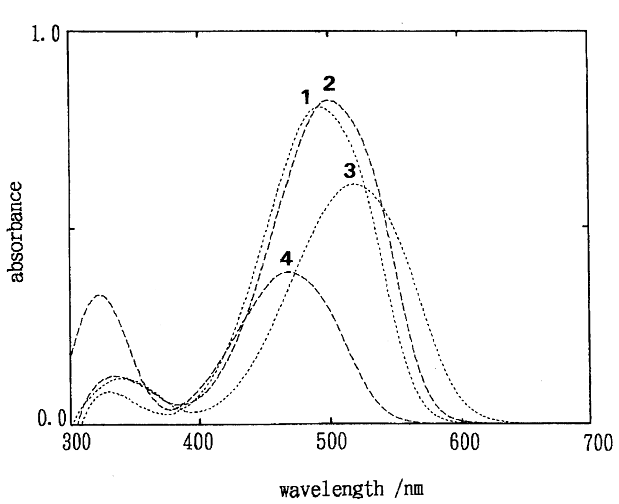


Fig. 1. Absorption spectra of photocyclized form of 3-furyl fulgides **1**, **2**, **3**, and **4** in toluene ($1\times10^{-4}$ mol dm$^{-3}$).

the bleaching reaction of 3-furyl fulgides indicate that the quantum yield ($\phi_{CE}$) increases with the bulkiness of substituent $R^2$ in the following order; methyl<ethyl<adamantylidene. Heller[10)] and Kurita[11)] had independently studied the role of substituent ($R^2$) on the photochromic reaction. They reported that the adamantylidene or cyclopropyl group as $R^2$ was effective at improving the $\phi_{CE}$ of 3-furyl fulgide (**1**), and gave the following interpretation: a bulky and rigid group, such as adamantylidene, weakened the $\sigma$ bond due to a steric repulsion between the bulky 1-substituent and 7a-methyl, thus facilitating a rupture of the bond which led to a ring-opening reaction. Our results are consistent with their observations.

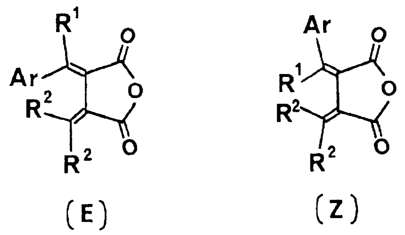
Fulgide **4C** containing an acetyl group on the furan ring, however, exhibited a higher $\phi_{CE}$ (0.39). No steric reason can be applied to **4C**. Furthermore, the high molecular extinction coefficient of **4C** means that the acetyl group causes no steric effect on the colored fulgide structure. It can thus be concluded that the high $\phi_{CE}$ of **4C** is due to the electronic effect, e.g. the electron-accepting ability of the acetyl group. To the contrarly, the quantum yield of coloration ($\phi_{EC}$) was decreased.

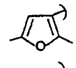
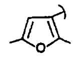
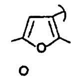
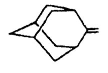
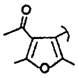
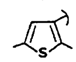
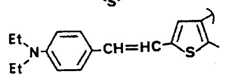
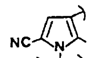
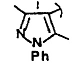
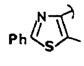
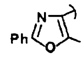
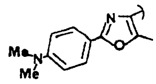
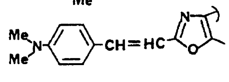
3-Pyrrolyl fulgide **7** gave high quantum yields for both reactions; the value of $\phi_{CE}$ was 0.49. Again, Heller[10)] had indicated that $\phi_{EC}$ and $\phi_{CE}$ of 3-pyrrolyl fulgide, e.g. (*E*)-2-[1-(2,5-dimethyl-1-phenyl-3-pyrrolyl)-ethylidene]-3-isopropylidenesuccinic anhydride, were 0.20 and 0.04, respectively. The structural difference between fulgide **7** and the Heller's pyrrolyl fulgide is mainly referred to the kind of substituent on the pyrrole ring (e.g. CN and methyl). The observed high $\phi_{CE}$ of fulgide **7** seems to be due to the electron-accepting ability of the CN group, just as the performance of the acetyl group of fulgide **4**.

On the other hand, 4-pyrazolyl fulgide **8** gives a high $\phi_{CE}$ and a low $\phi_{EC}$. It seemed that the colored structure of 4-pyrazolyl fulgide **8C** had some strain because of a steric repulsion between two methyl groups, e.g. the 3-methyl group of the pyrazole ring and $R^1$, and is less stable than the other photocyclized form of the fulgides. Furthermore, an electron-negative C=N bond on the pyrazole ring seemed to have an effect on $\phi$, just as an electron-accepting group.

Table 1. Spectroscopic Properties of Fulgides in Toluene

| Fulgide | E | C |
|---|---|---|
| | $\lambda_{max}$/nm ($\varepsilon_{max}$/$M^{-1}$ $cm^{-1}$) | $\lambda_{max}$/nm ($\varepsilon_{max}$/$M^{-1}$ $cm^{-1}$) |
| **1** | 345 ( 6100) | 495 ( 9200) |
| **2** | 344 ( 6300) | 500 ( 9900) |
| **4** | 318 ( 5700) | 472 ( 8300) |
| **5** | 333 ( 5100) | 520 ( 5300) |
| **6** | 382 (41400) | 595 (30500) |
| **7** | 343 ( 8400) | 569 ( 6800) |
| **8** | 335 ( 7200) | 550 ( 4800) |
| **9** | 297 (18500) | 488 ( 8200) |
| **10** | 337 (10100) | 465 (11000) |
| **11** | 325 (31800) | 510 (18300) |
| **12** | 379 (36100) | 528 (26000) |



| Fulgide | Ar | $R^1$ | $R^2$ |
|---|---|---|---|
| 1 |  | $CH_3$ | $CH_3$ |
| 2 |  | $CH_3$ | $CH_2CH_3$ |
| 3 |  | $CH_3$ |  |
| 4 |  | $CH_3$ | $CH_3$ |
| 5 |  | $CH_3$ | $CH_3$ |
| 6 |  | H | $CH_3$ |
| 7 |  | $CH_3$ | $CH_3$ |
| 8 |  | $CH_3$ | $CH_3$ |
| 9 |  | $CH_3$ | $CH_3$ |
| 10 |  | $CH_3$ | $CH_3$ |
| 11 |  | $CH_3$ | $CH_3$ |
| 12 |  | $CH_3$ | $CH_3$ |

Scheme 2. Heterocyclic fulgides.

4-Thiazolyl and 4-oxazolyl fulgide **9** and **10** exhibited nearly the same quantum yields. The structural features of the fulgides include the presence of the phenyl group and the C=N bond contained in the heterocyclic ring. Heller[10)] had studied the photochromism of 2-methyl-5-phenyl-3-thienyl fulgide, e.g. (*E*)-2-[1-(2-methyl-5-phenyl-3-thienyl)ethylidene]-3-isopropylidenesuccinic anhydride; the value of $\phi_{CE}$ (0.024) was lower than that of 2,5-dimethyl-3-thienyl fulgide (**5**). $\phi_{EC}$ and $\phi_{CE}$ of 4-thiazolyl fulgide (**9**) were 0.21 and 0.061, respectively, and the value of $\phi_{CE}$ was higher than that of the 2-methyl-5-phenyl-3-thienyl fulgide. This implies that the electronegative C=N bond on the heteroaromatic ring contributes to the recovery of $\phi_{CE}$, which is

Table 2. Quantum Yields for Photochromic Reaction of Fulgides in Toluene at Room Temperature[a]

| Fulgide | $\phi_{EC}$ | $\phi_{CE}$ |
|---|---|---|
| 1 | 0.19(311) | 0.048 (512)[b] |
| 2 | 0.08(366) | 0.19 (511) |
| 3 | 0.12(311) | 0.34 (510)[c] |
| 4 | 0.11(311) | 0.39 (477) |
| 5 | 0.16(311) | 0.14 (535)[d] |
| 6 | 0.09(366) | 0.0043 (591) |
| 7 | 0.10(366) | 0.49 (556) |
| 8 | 0.03(311) | 0.28 (556) |
| 9 | 0.21(366) | 0.061 (477) |
| 10 | 0.18(311) | 0.054 (477) |
| 11 | 0.26(366) | 0.0091 (511) |
| 12 | 0.28(366) | 0.00019(535) |

a) Values in parentheses are refer to the irradiation wavelength/nm. b) Heller[2] and Kurita[12] reported the quantum yields independently; coloration/0.20 (366 nm), 0.18 (366 nm), bleaching/0.06 (500 nm), 0.048 (502 nm), respectively. c) 0.28 (546 nm) for bleaching by Heller[11]. d) 0.20 (366 nm) and 0.14 (546 nm) for coloration and bleaching of fulgide **5** were reported by Heller.[11]

depressed by the phenyl group.

4-Oxazolyl fulgide **11** and **12** contain electron-donating *p*-(dimethylamino)phenyl and *p*-(dimethylamino)styryl group on the heterocyclic ring. Both fulgides showed rapid photo-coloration compared in fulgide **10**. Regarding bleaching, however, a significant decreases of $\phi_{CE}$ was observed.

The electronic effects on the photochromic reaction in this work were presumably caused by a changing of potential energy for the excited colored form of fulgide. As described in a previous paper,[3] the electronic transitions of colored fulgides involved an intramolecular electron migration from the heteroaromatic rings to the carbonyl groups; the resulting excited states were polar. In this work, the quantum yield for the bleaching reaction of fulgide **5** was affected by the polarity of the solvent: 0.14 in toluene to 0.052 in ethyl acetate. The electron-donating substituent on the ring also has the effect to delocalize an electron and depress the potential energy of photocyclized fulgide in the excited state. The expanded energy gap between fulgide and the photocyclized form causes a low and high reactivity for bleaching and coloration reactions, respectively. On the contrary, the electron-accepting group on the heterocyclic ring causes high and low reactivities for coloration and bleaching.

## Experimental

The UV-vis and $^1$H NMR spectra were measured with a spectrophotometer (Hitachi U-3200) as well as 60- and 90-MHz spectrometers (JEOL JNM-PMX60 and EX-90 NMR). A mercury lamp (Ushio, 250 W) and a xenon lamp (Ushio, 300 W) were used as light sources for the coloration and discoloration reactions, respectively. Mercury lines at 366 and 311 nm and visible light beams were isolated by passing the light through glass filters (UV light; 366 nm/Toshiba UV-35, U-360, and KL-37, 311 nm/Toshiba UV-31 and KUVB313, visible light; 477 nm/Toshiba IR-25, Y-50, and KL-48, 510 nm/IR-25, Y-50, and KL-50, 535 nm/IR-25, Y-50, and KL-53, 556 nm/IR-25, O-54, and KL-55, 591 nm/IR-25, O-58, and KL-58).

Both of the reactions were monitored by HPLC measurements and the molar absorption coefficients were determined by the mole ratio at pss based upon the result of the measurement. The quantum yields[6,7] of the photochromic reaction of fulgides in a toluene solution were determined by measuring the absorption spectrum change in the visible region; the intensity of the incident visible and UV light was measured with a power meter AQ2710 (ANDO) and chemical actinometer (potassium iron(II) oxalate for fulgide **1** and fulgide **1** for other fulgides), respectively.

**Materials.** **(*E*)-2-[1-(2,5-Dimethyl-3-furyl)ethylidene]-3-(1-ethylpropylidene)succinic Anhydride, Fulgide (2).**[2] A mixture of 3-acetyl-2,5-dimethylfuran (7 g, 50 mmol) and diethyl 2-(3-pentanylidene)succinate (15 g, 50 mmol) was added to a solution of NaH (60% dispersion in oil, 4.2 g) in toluene (100 ml) with stirring at 60°C. When the gas evolution ceased, the reaction mixture was poured onto crushed ice and the resulting organic layer was extracted twice with 25 ml of water. The combined aqueous extracts were acidified with 6M HCl (1M=1 mol dm$^{-3}$) and extracted with 200 ml of toluene. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed. The residue, e.g. half ester, was hydrolized with 5 wt% ethanolic potassium hydroxide. After removing the solvent the reaction mixture was acidified. The resulting dicarboxylic acid was boiled in acetic anhydride. After removing the solvent fulgide **2** was isolated in 1% yield by column chromatography on silica gel using chloroform as the eluant and recrystallization from hexane. Mp 76—80°C; $^1$H NMR ($CDCl_3$) $\delta$=0.70 (3H, s), 1.10 (3H, t), 1.87 (2H, q), 2.04 (3H, s), 2.25 (3H, s), 2.56 (3H, s), 2.73 (2H, q), 5.93 (1H, s); MS *m*/*z* 288 ($M^+$). Calcd for $C_{17}H_{20}O_4$: C, 70.82; H, 6.99%. Found: C, 70.53; H, 7.06%.

**(*Z*)-2-(4-Acetyl-2,5-dimethyl-3-furyl)ethylidene-3-isopropylidenesuccinic Anhydride, Fulgide (4).** To a solution of 1.0 g (4 mmol) of (*Z*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride, fulgide **1** and 0.34 g (4 mmol) of acetic anhydride in 10 ml benzene, 1.0 g (4 mmol) of anhydrous tin(IV) chloride[2,8] in 5 ml benzene was added dropwise with stirring at 0°C. After stirring for 2 h the reaction mixture was poured onto crushed ice and 10 ml of 6 M HCl. The organic layer was separated, washed with water and dried; the solvent was then removed. The resulting solid was recrystallized from hexane-benzene to give 0.55 g (2 mmol, 50% yield) of fulgide **4**. Mp 98—99°C; $^1$H NMR ($CDCl_3$) $\delta$=2.06 (3H, s), 2.11 (3H, s), 2.13 (3H, s), 2.38 (3H, s), 2.43 (3H, s), 2.59 (3H, s); IR $\nu_{C=O}$, 1660 cm$^{-1}$; MS, *m*/*z* 302 ($M^+$). Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00%. Found: C, 67.44; H, 6.04%.

Fulgide **1**, **3**, **5**, **6**—**12** were prepared by methods described in the literature.[2,3,5,9]

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