Fulgenolides.
Thermally Irreversible Photochromic Lactones with Large Quantum Yields of Photoreactions

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Three new photochromic lactones closely related to an indolylfulgide were synthesized. While the lactones with the carbonyl group adjacent to the isopropylidene group have large quantum yields of photoreactions, the isomer with the carbonyl adjacent to the indolylethylidene group showed poor photochromic properties. The absorption maxima of the colored forms of the lactones are shorter than that of the indolylfulgide.

Fulgides such as **1** are the representative thermally irreversible organic photochromic compounds, and they have been regarded as a potential candidate to be applied to photon mode erasable optical memory media.[1,2] As one of the efforts to improve the photochromic properties of fulgides, we have been continuing to clarify the role of the acid anhydride moiety. We have recently reported that fulgenates, the diester derivatives of fulgides such as **2**, are also photochromic, though the conversion to the colored form upon irradiation of UV light was about 10%.[3] Apparently the five-membered succinic anhydride moiety is quite important for effective photochromic reactions: it controls the cyclization of the triene moiety by maintaining the planarity of bismethylidenesuccinic anhydride part. In this communication, we report the synthesis and photochromic properties of compounds with a five-membered lactone **3** - **5** that are closely related to the indolylfulgide **1**. The photochromic lactones **3** - **5** are divided into two structural types: **3** and **4**; the *E*-form possesses a carbonyl group conjugating with the isopropylidene group, **5**; the *E*-form possesses a carbonyl group conjugating with the indolylethylidene group.

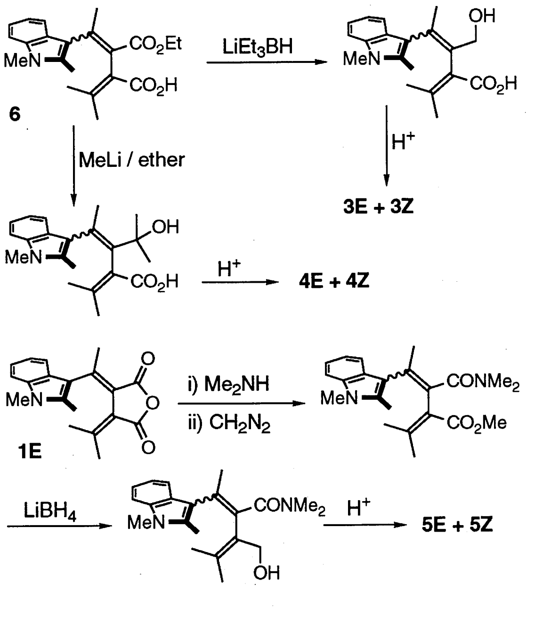
Syntheses of **3** - **5** were carried out as depicted in Scheme 1. The fulgenolides **3** and **4** were synthesized in 43% and 17% yields, respectively, from **6**. The yield of fulgenolide **5**, obtained from the fulgide **1**, was at best 8%, because **5** was quite unstable. As **5** was obtained as a 67:33 mixture of *E*- and *Z*-forms (determined by ^{1}H NMR), photoreactions were started with the mixture. Although **3E** and **3Z**, and **4E** and **4Z**, respectively, were inseparable by column chromatography, they were separated from the other isomer by iterative recrystallization. Identification of *E* and *Z* geometry was done based on ^{1}H NMR and the behavior of photoreaction. Photoreactions of **3** and **4**, however, were carried out by starting with the *E/Z* mixtures.

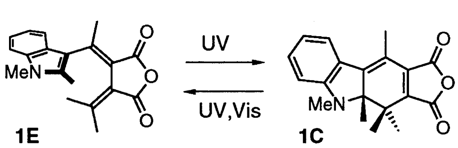
Photoreactions of **3** - **5** were done with 366-nm light of high pressure mercury lamp for coloring and 446-nm light taken out with filters from xenon lamp for bleaching. The change in concentration of the isomers was monitored by high pressure liquid chromatography and UV-Vis spectroscopy, and was analyzed to give the quantum yields of the photoreactions.[4]

The change of absorption spectra of **3**, **4**, and **5** according to the time of 366-nm light irradiation were shown in Figures 1, 2, and 3. As the photochromic properties of fulgenolide **5** are quite poor and the compound itself is labile, neither the absorption maximum wavelength of the colored form nor quantum yields of photoreactions were determined. To the contrary, photochromic properties of fulgenolides **3** and **4** were excellent. Irradiation of 366-nm light to the hexane solution of a mixture of **3E** and **3Z** (97/3) afforded a mixture of **3E**, **3Z**, and **3C** (**3C**: λ_{max} 462 nm, ε_{max} 9800 mol^{-1} dm^3 cm^{-1}). The molar ratio of components **3E/3Z/3C** when the concentration of **3C** reached the maximum was 33/5/62. As **3Z** requires long time to reach the equilibrium concentration, the molar ratio at the photostationary state (PSS) between the three isomers was not determined. Irradiation of 446-nm light to the resultant solution induced entire transformation from **3C** to **3E**.

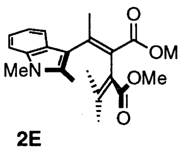
Photoreaction of **4** was carried out similarly. Irradiation of 366-nm light to the hexane solution of a mixture of **4E** and **4Z**

Scheme 1.

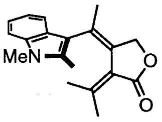




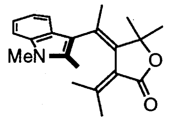
1E **1C**



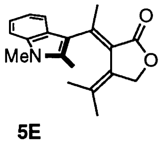
2E



3E



4E



5E

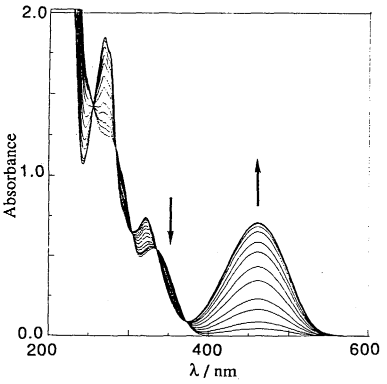


Fig.1. Spectral change of **3** (1.15 x 10^{-4} mol dm^{-3} (**3E**/**3Z** = 97/3 at t = 0)) in hexane with 366-nm light (0.48 mW cm^{-2}). Irradiation time/min: 0, 0.5, 1, 2, 3, 5, 7, 10, 13, 18, 24, 30, 40.

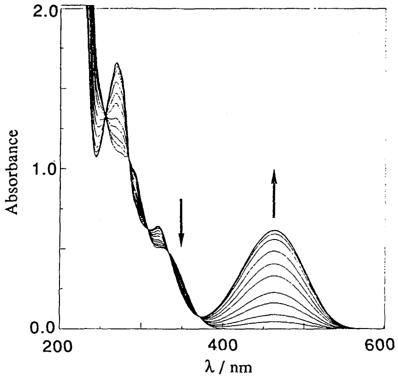


Fig.2. Spectral change of **4** (1.20 x 10^{-4} mol dm^{-3} (**4E**/**4Z** = 87/13 at t = 0)) in hexane with 366-nm light (0.51 mW cm^{-2}). Irradiation time/min: 0, 0.5, 1, 2, 3, 5, 7, 10, 15, 20, 30, 45, 60.

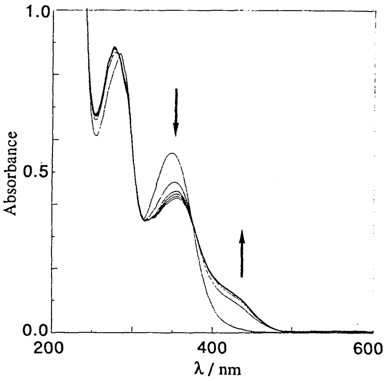


Fig.3. Spectral change of **5** (1.15 x 10^{-4} mol dm^{-3} (**5E**/**5Z** = 67/33 at t = 0)) in hexane with 366-nm light (2.94 mW cm^{-2}). Irradiation time/min: 0, 0.5, 1, 1.5, 2.5, 4.

Table 1. Quantum yields of photochromic reactions of fulgenolides **3** and **4** in hexane

	366-nm light irradiation					446-nm light irradiation
	Φ_{EC}	Φ_{CE}	Φ_{EZ}	Φ_{ZE}	*E*:*Z*:*C*[a]	Φ_{CE}
3	0.35	0.41	0.004	0.03	33:5:62	0.23
4	0.39	0.40	0.011		32:16:52	0.20
1[b]	0.045	0.16	0.040	0.072	35:9:56	0.051
2[c]	0.065	0.40	0.054	0.10	39:51:10	0.27

[a] Ratio of components at PSS (photostationary state) of UV irradiation; **1**, **2**: At PSS between E, Z, and C. **3**, **4**: At PSS between E and C when the concentration of C reached its maximum, starting from an E/Z mixture. [b] In toluene with 405-nm light for coloring and 608-nm light for bleaching. [c] In hexane with 313-nm light for coloring and 446-nm light for bleaching. See Ref. 4.

gave a mixture of **4E**, **4Z**, and **4C** (**4C**: λ_{max} 464 nm, ε_{max} 11000 mol^{-1} dm^3 cm^{-1}). Different from **3Z**, **4Z** does not have absorption at 366 nm, therefore **4Z** is the *cul-de-sac* of this photochromic system. This implies that the ratio of **4E**/**4Z**/**4C** at PSS should be 0/100/0. However, as Φ_{EZ} is substantially small compared to Φ_{EC}, the ratio of **4E**/**4Z**/**4C** when the concentration of **4C** reached the maximum was 32/16/52. Quantum yields of photoreactions are summarized in Table 1.

In order to explain the difference of photochromic properties of the two structural types of fulgenolides (**3** and **4** *vs.* **5**),[5] PM3 molecular orbital calculations[6] to obtain the most stable conformation of the *excited states* of **1E**, **3E**, and **5E** using the "Excited singlet" option was carried out, although the parameters had been prepared for the calculations of ground-state molecules. The bond-forming two carbon atoms of the most stable excited-state conformation of **1E** and **5E**, which have the carbonyl group adjacent to the indolylethylidene group, are remoter than those of the most stable ground-state conformation, as the result of nearly rectangular twisting of the double bond between the acid anhydride and the indole. On the other hand, those of the most stable excited-state conformation of **3E** are closer than those of the ground-state conformation because the double bond does not twist at the excited state, and the two carbon atoms could form a single bond very easily. Further insights for this result by calculation chemists should be necessary.

References and Notes

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