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Fulgides as Efficient Photochromic Compounds. Role of the Substituent on Furylalkylidene Moiety of Furylfulgides in the Photoreaction

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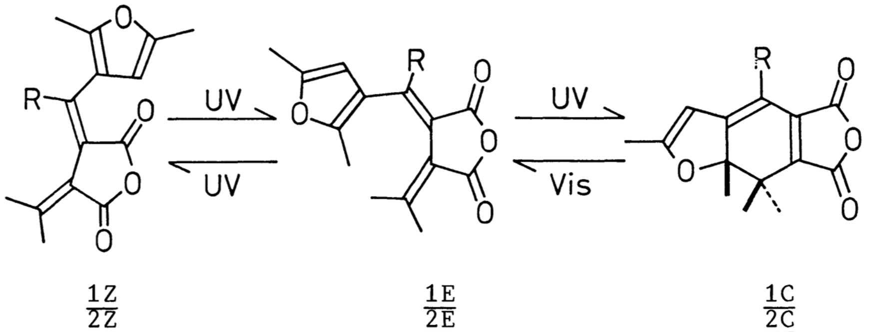
Quantum yields of photoreactions of furylfulgides having Me, Et, n-Pr, or i-Pr on the furylalkylidene moiety were measured. The E-Z isomerization was greatly suppressed and the cyclization was accelerated when the alkyl group (R) became bulkier. When R was i-Pr, no E-Z isomerization was observed and the quantum yield of the colorizing cyclization was 0.62.

Although the photochromic nature of fulgides was discovered more than eighty years ago,1) intensive studies have not been done until very recently.2) In 1981, Heller and co-workers reported (E)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (1E) as a highly efficient photochromic compound3) which showed (1)high stability to the thermal decoloration which included the prototropic photoisomerization of the colored form to photochemically unreactive colorless forms, (2)high quantum yield of the coloration process, (3)possibility of increasing the absorption maximum wave length of the colored form by modifying the substituents, the aromatic ring, and/or the succinic anhydride moiety. Along this line, remarkable efforts have been continued to get better fulgides which would be applicable to the erasable photomemory.4)

In order to materialize an ideal photochromic system, both the coloration and decoloration processes should be fast and the system should contain only the desired coloration and decoloration processes. Here we report the effect of the



R= Me	1Z	1E	1C
R= Et	2Z	2E	2C
R=n-Pr	3Z	3E	3C
R=i-Pr	4Z	4E	4C

substituent on the furylalkylidene moiety of the fulgides, and the first observation of a highly efficient photochromic fulgide with no E-Z isomerization.5)

Fulgides 1E, 1Z, 2E, and 2Z were prepared according to the method of Heller. Although the condensation of (2,5-dimethyl-3-furyl)propylketone or (2,5-dimethyl-3-furyl)isopropylketone with diethyl isopropylidenesuccinate according to the procedure in the literature had failed, use of lithium diisopropylamide as base successfully gave an E,Z-mixture of desired products, and was transformed to 3E and 3Z, or 4E and 4Z, respectively, as usual.6) Fulgides were purified by flash column chromatography7) using hexane/ethyl acetate as the eluting solvent, and were recrystallized three times from the hexane/ether mixture. Their structures were fully characterized by the spectroscopic methods and the elemental analysis.

Each E fulgide was weighed and dissolved into spectral grade chloroform to make a 1.0×10^{-4} mol dm^{-3} solution. Each solution of the colored form (C-fulgide) was prepared from the corresponding E-fulgide by the irradiation of 366 nm light till it became the photostationary state, and the purity of which was confirmed to be 100% by the high pressure liquid chromatography (HPLC).

Photoreactions were carried out in a capped quartz cell having 1 cm cell length with continuous stirring with a teflon-coated spinning bar.

A 250 W high pressure mercury lamp was used as the UV source, to which were fitted a quartz cell of 1 cm length containing aqueous $CuSO_4 \cdot 5H_2O$ (50 g dm^{-3}), Toshiba UV-35, and D-35 glass filters, to obtain 366 nm light.8) A 500 W xenon lamp, associated with a 5 cm water filter, Toshiba IRA-25S, Y-47, and KL-50 glass filters, was used to take out 492 nm light.9) Potassium iron(III) oxalate actinometer was used to determine the intensity of the light.10)

Photoreaction was monitored by the HPLC with a UV detector.11) Concentration of the fulgides E, Z, and C were calculated directly from the chromatogram of the solution and the molar absorption coefficient of each component at 366 nm, the detecting wave length. The change in component concentration with light irradiation time were analyzed by means of the least squares method to give the quantum yields of the cyclization ϕ_{EC}, the E-to-Z isomerization ϕ_{EZ}, the Z-to-E isomerization ϕ_{ZE}, and the ring opening decoloration ϕ_{CE}.

Table 1 shows the λ_{max} and the ε_{max} of the fulgides, and Table 2 shows the quantum yields ϕ_{EC}, ϕ_{EZ}, ϕ_{ZE}, and ϕ_{CE}.

From Table 1, it is obvious that the ε_{max} of 4E and 4Z are significantly smaller than those of the E and Z isomers of other fulgides, despite that all of the E isomers and Z isomers, respectively, have almost the same λ_{max}.12) This fact suggests that the conformation of 4E and 4Z in solution are quite different from those of 1, 2, and 3 because of the bulkiness of the isopropyl group. On the other hand, 1C, 2C, 3C, and 4C have the same λ_{max} and the same order of ε_{max}.

Table 2 tells us some valuable information. First, ϕ_{EC} becomes greater and ϕ_{EZ} becomes smaller when R becomes bulkier. This result is understandable that because the E-Z isomerization is prohibited by the repulsion between the alkyl group and the isopropylidene moiety when R is bulky, the quantum yield of the cyclization increases. In the case of 4E in which R was i-Pr, ϕ_{EC} was 0.62 and ϕ_{EZ} was zero. Together with the fact that the ε_{max} of 4E is small, this suggests thst

Table 1. Absorption maximum and molar absorption coefficient of fulgidesa)

		E		Z		C	
	R	λ_{max} / nm	ε_{max} / $dm^3 mol^{-1} cm^{-1}$	λ_{max} / nm	ε_{max} / $dm^3 mol^{-1} cm^{-1}$	λ_{max} / nm	ε_{max} / $dm^3 mol^{-1} cm^{-1}$
1	Me	347	6780	358	8900	510	9690
2	Et	349	6690	358	8480	510	10270
3	n-Pr	348	6210	358	7460	510	9590
4	i-Pr	347	4080	360	4700	510	9320

a) In $CHCl_3$ at room temperature.

Table 2. Quantum yields of the photoreaction of fulgidesa)

	R	ϕ_{EC} b)	ϕ_{EZ} b)	ϕ_{ZE} b)	ϕ_{CE} c)
1	Me	0.19	0.13	0.11	0.035
2	Et	0.34	0.06	0.12	0.027
3	n-Pr	0.45	0.04	0.10	0.044
4	i-Pr	0.62	0.00	0.06d)	0.040

a) In $CHCl_3$ at room temperature. b) Determined by 366 nm light irradiation to the corresponding E-fulgides. c) Determined by 492 nm light irradiation to the corresponding C-fulgides prepared from E-fulgides by 366 nm light irradiation. d) Determined by 366 nm light irradiation to 4Z.

4E takes a different conformation from other E-fulgides, which might be in favor of the photocyclization. The value 0.62 for the ϕ_{EC} is, to our knowledge, the largest one for that of the photocoloration of fulgides. That ϕ_{EZ} is zero implies that during the photoreaction starting from 4E, no undesired E-Z isomerization occurs.13)

Second, the sum of ϕ_{EC} and ϕ_{EZ} (i.e. the fraction of photon used for photoreactions) becomes greater when the substituent R becomes larger. Because this result is not in agreement with the observation of Ilge et al. that additional substituents increased the chance of radiationless deactivation,14) we presume that the bulky alkyl group facilitates the cyclization much more than to prevent the E-Z isomerization and than to increase the deactivation.

Third, the quantum yield of photodecoloration does not seem to depend much on the size of R. It probably depends on the repulsion between the adjacent alkyl groups on the position 7 and 7a (benzofuran numbering) of the colored form.15)

In conclusion, a new and efficient furylfulgide 4E was synthesized, which showed no E-Z isomerization and cyclized with ϕ_{EC}=0.62 in $CHCl_3$. Efforts to obtain more useful fulgides with high decoloration quantum yield, with longer wavelength of absorption maximum of the colored form, and/or with functional groups to attach them to polymer chains, are currently under investigation.

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6) Either fulgides with R=t-Bu or R=2,5-dimethyl-3-furyl could not be obtained in our hands. Although the E-fulgide with R=H was synthesized, it was highly unstable against the 366 nm light irradiation.
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11) Condition of HPLC analysis is as follows: HPLC; Shimadzu LC-6A: Detector; Shimadzu SPD-6AV at 366 nm: Data Processor; Shimadzu C-R5A: Column; Yamamura Chemical Lab. Co., A-002 SIL (silica gel), 4.6 mm x 150 mm: Elution; hexane/benzene = 1/3: Flow rate; 1 ml/min or 2 ml/min.
12) UV-Vis spectra of 4E at several different concentration did not show any evidence of its aggregation.
13) While 1E was reported as a convenient chemical actinometer in Ref. 3 despite its nature of E-Z isomerization, 4E might be a better one because of its simple photoreaction character and high quantum yield.
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15) A fulgide with the adamantylidene group instead of the isopropylidene group in 1E recorded ϕ_{CE}=0.38,4) which is ca. ten times larger than that of the fulgides C described here.

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