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Fulgenates. A New Class of Fulgide-Related Thermally Irreversible Photochromic System

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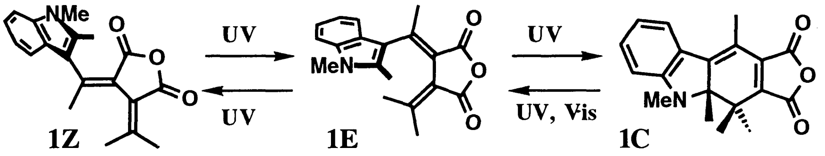
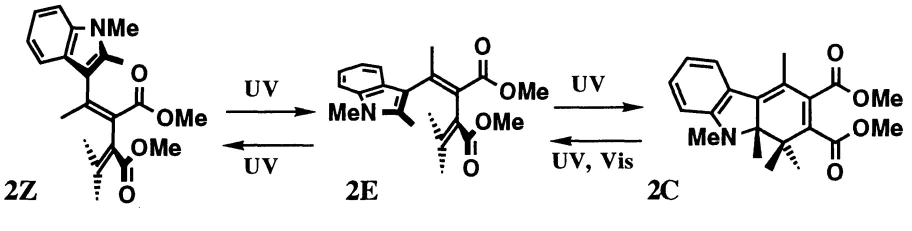
Thermally irreversible photochromic properties of indolylfulgenates, *i.e.* 2-alkylidene-3-[1-(1,2-dimethyl-3-indolyl)alkylidene]succinate esters were examined. A large indolylalkylidene group reduced the relative ratio of the colored species at the photostationary state of UV irradiation. Introduction of an adamantylidene group increased the bleaching quantum yield. The absorption maximum wavelengths of the colorless and colored species were shorter than those of the corresponding indolylfulgide.

Fulgides such as **1** are the representative thermally irreversible organic photochromic compounds. This class of compounds was discovered by Stobbe at the beginning of this century.1) A number of research groups have concerned with the photochromism of fulgides,2) and now some fulgides are given with splendid properties from the viewpoint of application to the rewritable photon-mode optical memory, such as diode laser sensitivity,3) non-destructive readout ability,4) high light sensitivity,5,6) and thermal stability.7) One drawback of the fulgides had been the relatively low fatigue resistivity, while this has been highly improved by changing the aromatic ring structure7) and addition of UV-stabilizers.8) Now, the anhydride moiety may be regarded as the "Achilles' heel" for fulgides, to be hydrolyzed9) by protic species such as water, alcohols, or amines.

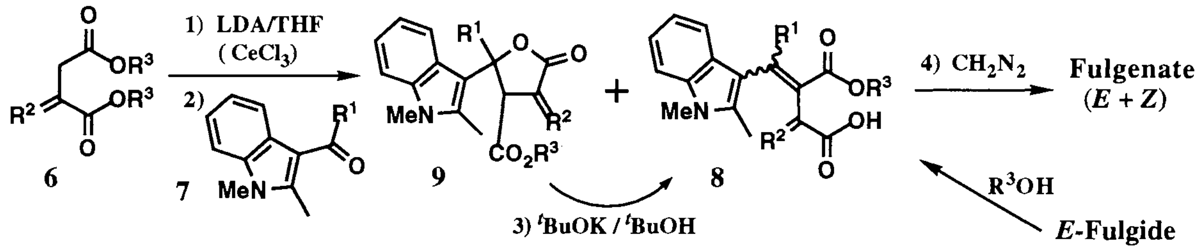


We here report the synthesis and photochromism of the compounds such as **2**, the diester analog of fulgides, which is supposed not to react with protic solvents under neutral conditions. Because Stobbe named the aryl-substituted bismethylenesuccinic acid as "Fulgensäure" in German1) and the translation of it into English must be "fulgenic acid,"10) we would like to call the corresponding ester derivative as "fulgenate" hereafter.



Syntheses of the *E*- and Z-fulgenates (**2** – **5**) were performed in either of the two ways; (i) modified Stobbe condensation[3,5] of the 2-alkylidenesuccinates (**6**) with the 3-acyl-1,2-dimethylindole (**7**) followed by esterification of the half acid (**8**), obtained directly from the condensation reaction or after the dehydrative hydrolysis of the lactone (**9**); (ii) alcoholysis of the fulgide[11] followed by the esterification with diazomethane.

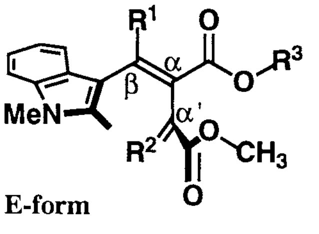
Separation of the olefinic isomers was performed by flash column chromatography or semi-preparative HPLC. The *E*-*Z* geometry of the arylalkylidene moiety of the isolated fulgenates was assigned from the result of the photoreaction; an electrocyclic photobleaching reaction of the colored form gives only the *E*-form.



Photoreactions of fulgenates (**2** – **5**) were carried out by using 313-nm light (coloring) of a 500 W high-pressure mercury lamp and 446-nm light (bleaching) taken out from a 500 W xenon lamp, and the concentration of the three isomeric species (*E*-, *Z*-, and *C*-forms) observed during the photoirradiation was determined by an HPLC apparatus.[5] The absorption spectral properties are listed in Table 1, and the quantum yields of the photoreactions are shown in Table 2, together with the data of the indolylfulgide **1**.[3,7,12]

	R^1	R^2	R^3
2	Me	IPD	Me
3	Me	IPD	Et
4	Pr	IPD	Me
5	Me	ADD	Me

IPD: isopropylidene ADD:adamantylidene



E-form

The difference of the structural features between fulgides and fulgenates must be considered before the detailed discussion. For fulgides, the change in conformation of both *E*- and Z-forms is induced only by the rotation of the C-C single bond between the aromatic ring and the β-carbon of the adjacent α,β-unsaturated carbonyl group,[13] whereas fulgenates have many additional freedom of rotation of C-C single bonds; the central C_α-$C_{\alpha'}$ bond between the two α,β-unsaturated ester groups, two C-C single bonds which are connecting the carbonyl carbon atoms with C_α and $C_{\alpha'}$ carbon atoms, and rotation of four C-O single bonds in the two ester groups. Modro *et al.* reported that the dihedral angle composed of two carbonyl carbon atoms and the central C_α-$C_{\alpha'}$ bond of (*E*,*E*)-2,3-bisbenzylidenesuccnic acid was 88.8°, determined by X-ray crystallographic analysis.[14] The similar, almost rectangular twist might also have occurred for fulgenates.

For *C*-forms of fulgides, the conjugation is quite effective because of the planarity of the molecule. For fulgenates, however, both of the two ester groups have freedom of rotation. Therefore the conjugation between the rigid tricyclic chromophore and carbonyl groups of the diester functionalities is not effective.

The freedom of internal rotation of *E*-, *Z*-, and *C*-forms of fulgenates mentioned above caused some serious differences between fulgenates and the fulgide in spectroscopic as well as photochromic properties.

Table 1. Absorption spectral data of indolylfulgenates in hexane

	E	*Z*	*C*
	λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})[a]	λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})[a]	λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})[a]
2	293 (11500)	285 (9300)	437 (7100)
2[b]	284 (9800)	286 (8200)	446 (6000)
3	293 (11500)	285 (9000)	437 (7100)
4	293 (11300)	285 (8900)	445 (7600)
5	293 (12300)	285 (9400)	451 (6900)
1[c]	385 (6800)	——[d]	585 (7100)

a) 1M = 1 mol dm^{-3}. b) In methanol. c) In toluene. d) **1Z** not ever isolated.

First, the absorption spectral properties are discussed. (1) All the absorption maxima of fulgenate isomers are shorter than that of the corresponding fulgide **1**. This is caused by the vast freedom of the internal rotation of fulgenates. (2) In methanol, the absorption maximum of *E*-form of **2** is a little shorter than in hexane, and that of *C*-form a little longer than in hexane. The latter phenomenon, together with the fact that the absorption coefficients of the *C*-forms are 6000 - 7600, implies that the absorption band in the visible-light region of the *C*-forms are attributable to the π–π* excitation. (3) As seen for **4** and **5**, the *C*-forms of fulgenates with the bulkier alkyl substituents as R^1 or R^2 have somewhat longer absorption maxima. This was also observed for indolylfulgides.[12)] To the contrary, for the colorless *E*- and *Z*-forms, the bulkiness of alkyl substituent did not affect the absorption maximum. (4) As expected, the minor change in size of the ester moiety, from methyl in **2** to ethyl in **3**, did not influence the absorption characters.

Table 2. Quantum yields of photochromic reactions of indolylfulgenates in hexane

	313-nm light irradiation					446-nm light irradiation
	Φ_{EC}	Φ_{CE}	Φ_{EZ}	Φ_{ZE}	*E*:*Z*:*C*[a]	Φ_{CE}
2	0.065	0.40	0.054	0.10	39:51:10	0.27
2[b]	0.052	0.38	0.042	0.062	41:52:7	0.26
3	0.060	0.32	0.044	0.10	40:48:12	0.32
4	0.043	0.37	0.050	0.030	16:81:3	0.31
5	0.071	0.51	0.050	0.10	39:49:12	0.40
1[c]	0.045	0.16	0.040	0.072	35:9:56	0.051

a) Ratio of components at photostationary state of UV-light irradiation. b) In methanol. c) Carried out in toluene with 403-nm light for coloring and 608-nm light for bleaching.

Next, the photochromic properties are discussed as follows. (1) The relative ratio of the *C*-form at the photostationary state is generally lower than for fulgides, owing to the large Φ_{CE}(313). For fulgenate **4** with a propyl group for R^1, the relative ratio of the colored form at the photostationary state is particularly low. This is mainly due to the small Φ_{ZE}(313). As the result, the ratio of Z-form is high at the photostationary state for **4**. For fulgides, the increase in size of R^1 worked to increase Φ_{EC}(UV).[5)] For fulgenates, the central C-C single bond can rotate freely, therefore the increased steric congestion did not work well to fix the conformation suitable for the cyclization. (2) The minor change in size of the ester group is not so significant in photochromism, as seen for **2** and **3**. (3) The bleaching quantum yield of fulgenates, Φ_{CE}(446), is much larger than that of fulgide **1**. Particularly, that of **5**, with an adamantylidene group, is remarkable. This is in good agreement with the previous observation for fulgides.[6)] (4) As shown in Table 2, **2** exhibited the stable photochromic properties even in methanol. Under the similar conditions where this photoreaction was carried out, a fulgide was solvolyzed to afford a half ester.[9b)]

In summary, we have synthesized fulgenates, a new class of thermally irreversible photochromic compounds closely related to fulgides. Their longest absorption maxima of the colored and colorless forms are shorter than those of fulgides. The ratio of the colored species at the photostationary state of UV irradiation is smaller and the bleaching quantum yield is greater than those of fulgides. Although the photochromic properties of fulgenates seem to be inferior to those of fulgides, fulgenates are more stable than fulgides in protic environments. Moreover, it should be emphasized that the two ester groups offer the ability to append two cooperatively working functional groups to a *thermally irreversible* photochromic molecule. As the activity of the functional groups may be controllable with the photoirradiation because the structural change accompanying with the photochromic reaction is large, this type of molecules will be regarded as a photo-switchable molecular devices. Research to pursue this possibility is now under way.

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11) It should be noted that a nucleophilic attack of an alcohol molecule to **1E** occurred exclusively on the carbonyl carbon atom proximate to the aromatic ring. The *E*- and Z-fulgenates obtained by the ethanolysis of **1E** followed by diazomethane treatment were identical with the *E*- and Z-fulgenates **3**, respectively, obtained by the Stobbe condensation of diethyl isopropylidenesuccinate **6** and the indolylketone **7** (R^1 = Me) followed by diazomethane esterification.
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