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Synthesis and Photochromic Behavior of 5-Substituted Indolylfulgides

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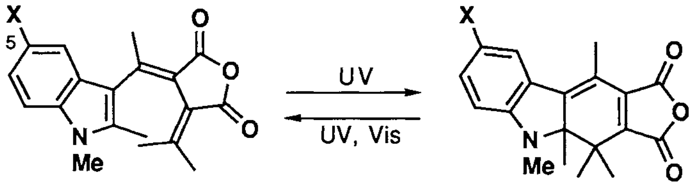
1,2-Dimethylindolylfulgides with 5-methylthio, 5-methoxy, or 5-dimethylamino group on the indole ring were synthesized and their photochromic properties were examined. Electron donating substituents lengthened the absorption maximum of the colored form and decreased the quantum yields of the photoreactions. The colored form of the dimethylaminoindolyl-substituted fulgide has λ_{max} at 673 nm, the longest absorption maximum wavelength ever known as that of a fulgide.

In order to realize a practical rewritable organic photomemory, several difficulties shown below have to be overcome;1) (1) quantum yields of the photochromic reactions should be high, (2) the colored form should have a certain amount of absorption at 780 nm, the diode laser region, (3) both colored and colorless forms should be thermally stable, (4) no side reactions should occur by light irradiation. In our previous study, we were able to give solutions to the problem (1)2,3) by introducing bulky alkyl groups on both arylmethylidene and alkylidene moiety. We here report our recent results concerning the problem (2), *i. e.*, a trial of lengthening the absorption maximum of the colored form of fulgides.1,4,5)

We chose the fulgide **1**, having 1,2-dimethylindolyl group as the aryl group, for the starting compound because it was reported to be highly fatigue-resistant and its colored form **1C** has the absorption maximum at 584 nm,5) about 90 nm longer than that of the well-known furylfulgides. According to PPP-CI calculations,6) introduction of an electron donating group onto the position five of the indole ring was suggested to lengthen the absorption maximum of the colored form. We therefore undertook to synthesize 5-methylthio-, 5-methoxy-, and 5-dimethylaminoindolylfulgides (**2** - **4**).

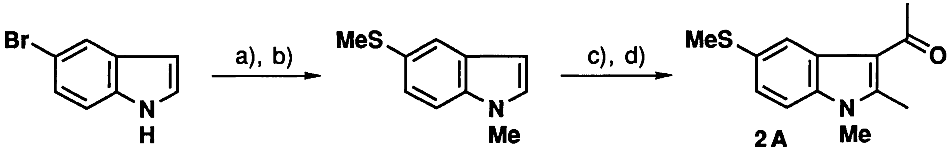


	X		X
1E	H	1C	H
2E	MeS	2C	MeS
3E	MeO	3C	MeO
4E	Me_2N	4C	Me_2N

Synthesis of the fulgides with a 5-substituted indole ring was performed by Stobbe condensation of the corresponding 3-acetyl-1,2-dimethyl-(5-substituted)indole (**A**) with diethyl isopropylidenesuccinate followed by hydrolysis and intramolecular acid anhydride formation processes. In the Stobbe condensation, lithium enolates of the isopropylidenesuccinate formed by lithium diisopropylamide (LDA) did not react well with the ketones. Cerium (III) enolates,[7] however, produced the corresponding lactones (**B**) in acceptable yields.

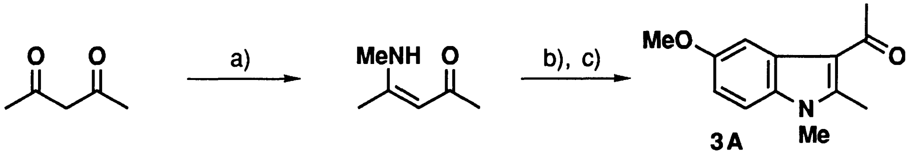
Syntheses of the 3-acetylindoles (A) and the corresponding fulgides were carried out as follows.

3-Acetyl-1,2-dimethyl-5-methylthioindole (**2A**)



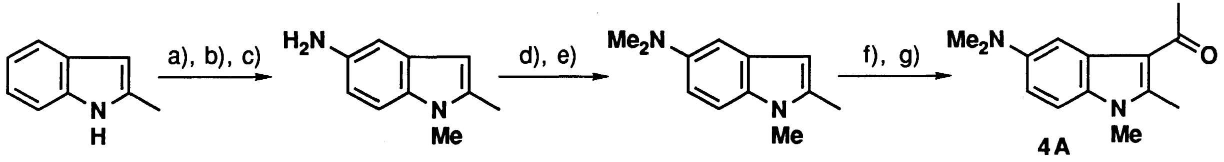
a) NaH, MeI; THF (100%). b) BuLi, MeSSMe; THF (92%).
c) BuLi, MeI; THF (93%). d) Ac_2O, AcONa (70%).

3-Acetyl-5-methoxy-1,2-dimethylindole (**3A**)



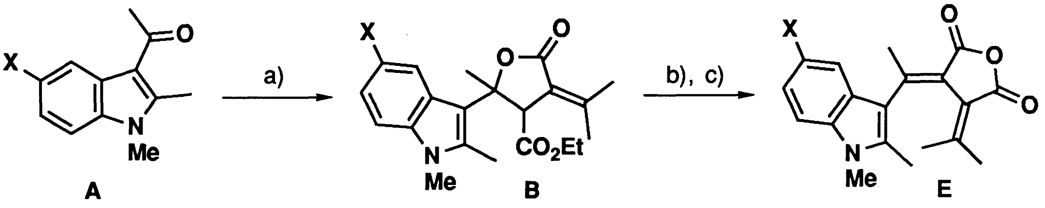
a) aq. $MeNH_2$; ethanol (84%). b) *p*-quinone; acetone (26%).
c) NaH, MeI; THF-DMF (64%).

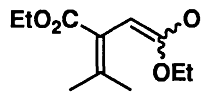
3-Acetyl-5-dimethylamino-1,2-dimethylindole (**4A**)



a) $NaNO_3$, H_2SO_4 (86%). b) NaH, MeI; THF (94%). c) Pd/C, H_2(15kg/cm^2); ethyl acetate (96%).
d) NaH, MeI; THF. e) ethanolamine (97% for two steps). f) Br_2; THF (78%).
g) BuLi; $CeCl_3$; freshly distilled $(CH_3CO)_2O$; THF (72%).

Fulgides with a 1,2-Dimethyl-(5-substituted)indole ring (**2E** - **4E**)



a)


; THF. b) KOH; ethanol. c) Ac_2O.

Lactones (**B**) were obtained as single diastereomers in 36 to 53% yield. During the subsequent hydrolysis, significant amount of 3-acetylindoles (**A**) were recovered by way of the base-promoted retro-aldol reaction. The combined yield of hydrolysis and acid anhydride formation was 14 to 26%. Different from the case of furylfulgides,[2,3] Z isomers were not detected for all of the indolylfulgides.

To a 10^{-4} mol dm^{-3} solution of the indolylfulgide in toluene, 403- or 608-nm light was irradiated at room temperature, and the change in component concentration was monitored by HPLC.[2] In the case of **4**, component ratio was determined by the combination of UV-Vis spectroscopy and 270 MHz ^1H NMR because both **4E** and **4C** did not come out of the HPLC column owing to their high polarity.

Absorption spectral data and quantum yields of the indolylfulgides thus obtained are shown in Tables 1 and 2.

Table 1. Absorption spectral data of indolylfulgides in toluene

	X	$\lambda_{max}(E)$/nm	$\varepsilon_{max}(E)/M\ cm^{-1}$ [a]	$\lambda_{max}(C)$/nm	$\varepsilon_{max}(C)/M\ cm^{-1}$ [a]	$\varepsilon_{780}(C)/M\ cm^{-1}$ [a]
1	H	385	8150	584	6810	0
2	MeS	387	8750	600	7090	80
3	MeO	393	9530	625	7060	230
4	Me_2N	404	8040	673	6200	2780

a) 1 M = 1 mol dm^{-3}.

Table 2. Quantum yields of the photoreaction of indolylfulgides[a]

	X	$\Phi_{EC}(403)$	$\Phi_{CE}(403)$	E/C(403)[b]	$\Phi_{CE}(608)$
1	H	0.040	0.067	40/60	0.051
2	MeS	0.028	0.027	32/68	0.011
3	MeO	0.024	0.024	30/70	0.012
4	Me_2N	0.015	0.001	3/97	0.00004

a) In toluene at room temperature.
b) Ratio of E-form and C-form at the photostationary state of 403-nm light irradiation.

The λ_{max} of both E- and C-forms became longer when electron donating ability of the aromatic ring increased. This result is in good agreement with the previously reported observation.[5] This also supports the concept that in the excited states of both E- and C-forms, the molecule polarizes with the electron movement from the aromatic ring toward the acid anhydride group.[5] Interestingly, while the order of the electron donating substituents to lengthen λ_{max} of both E- and C-forms, *i. e.*, H, MeS, MeO, and Me_2N, was the same as the order of increase of λ_{max} of substituted thioindigo derivatives,[8] it is different from the generally accepted order of electron donating ability, $H<MeO<MeS<Me_2N$,[9] as seen in the order of the λ_{max} of 1-substituted anthraquinones and 4-substituted azobenzenes.[10]

The quantum yields of the photoreactions decreased, again in the order of H, MeS, MeO, and Me_2N (Table 2). The C-forms of 5-dimethylamino-substituted indolylfulgide were highly resistant toward the bleaching reaction. At the photostationary state of 403-nm light irradiation in toluene-d_8, **4E**/**4C** ratio determined by 270 MHz ^1H NMR, was 3/97.

The reason why an increase in the electron-donating ability of the substituent decreases the quantum yields of the photoreactions is not clear at this stage. For Φ_{EC}, the sum of the free valences of the bond-forming carbon atoms had been reported to be in proportion to the coloring quantum yield.11) Although this relationship had fit well for phenylfulgides, it did not for indolylfulgides. For Φ_{CE}, the electronic state of the breaking single bond and the electronic structure of the excited molecule should be taken into consideration.12)

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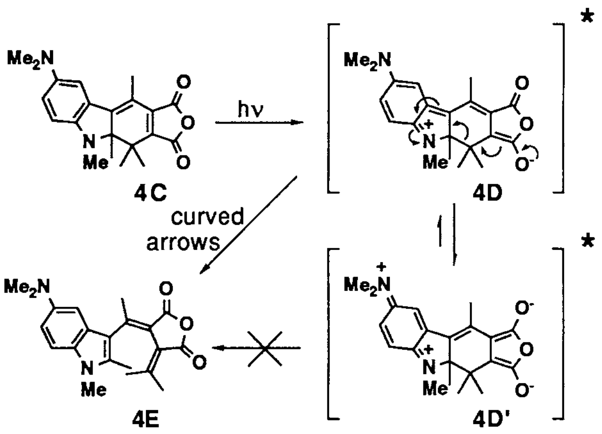
12) One possible explanation is that the photoexcited **4D** has a tendency to polarize as **4D'** because of the strong electron-donating ability of the dimethylamino group, from which direct conversion to **4E** is impossible. To the contrary, electron rearrangement depicted by arrows on **4D** could give **4E**. In fact, a PPP-CI calculation indicated that the bond order of all the double bonds in **4D'** was considerably larger than those of other indolylfulgides studied here.



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