

## Oxazolyfulgides as Yellow Photochromic Dyes

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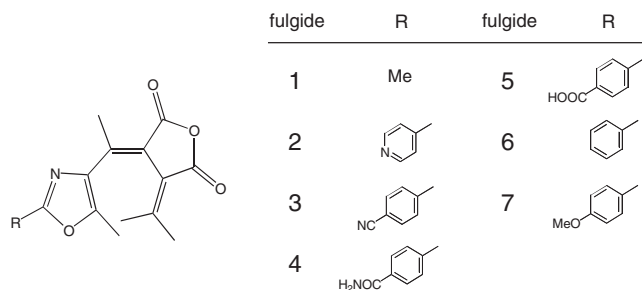
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A series of substituted oxazolyfulgides have been prepared as photochromic compounds which color in the yellow region on irradiation with UV light. Some of them exhibit favorable features as photochromic yellow dyes in polymer film with fairly good photochemical reversibility, coloration quantum yields, and thermal stability.

Photochromic compounds have been extensively studied for use mostly as optical switches and photon-mode rewritable memory devices,<sup>1-3</sup> but little has been studied as rewritable printing materials. Although monochrome rewritable paper using leuco dye has been developed recently,<sup>4</sup> a full-color rewritable paper is also desirable. In order to realize a photon-mode rewritable full-color print, the three primary colors (yellow, magenta, and cyan) are needed. While photochromic compounds which color in magenta<sup>5,6</sup> and cyan<sup>7,8</sup> have been well studied, those which color yellow have been least studied so far, excepting for some fulgides,<sup>9-11</sup> diarylethenes,<sup>12</sup> and chromene derivatives.<sup>13</sup> This paper reports on the photochromic properties of some oxazolyfulgides (Scheme 1) which color in the yellow region on irradiation with UV light.

Fulgides **1**, **2**, **6** and **7** were prepared from the corresponding



Scheme 1. Substituted oxazolyfulgides.

2-substituted derivatives of 4-acetyl-5-methyloxazole<sup>14</sup> by the Stobbe condensation reaction with diethyl isopropylidenesuccinate, followed by the hydrolysis and dehydration steps according to the literatures method.<sup>15-20</sup> Similarly, fulgide **5** was prepared starting from 4-acetyl-2-(4-carbomethoxyphenyl)-5-methyloxazole, while both fulgides **3** and **4** were prepared from 4-acetyl-2-(4-cyanophenyl)-5-methyloxazole by controlling the conditions of base-catalytic hydrolysis. The <sup>1</sup>H NMR, IR, and MS spectra are summarized in Table 1. The presence of the cyano group in fulgide **3** is confirmed by its strong IR band at 2227 cm<sup>-1</sup>

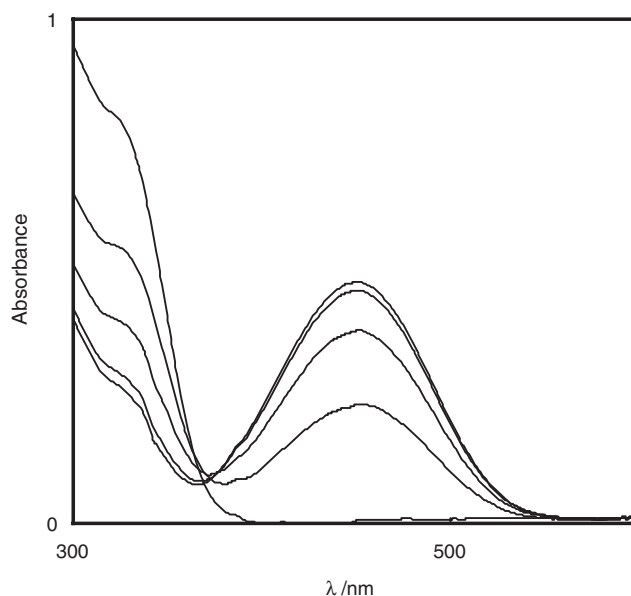


Figure 1. Photochemical coloration of fulgide **2** (2 wt%) in PMMA film upon irradiation with 313-365 nm light. Irradiation times were 0, 30, 90, 210, 330 s, from the bottom.

Table 1. Physical constants of oxazolyfulgides

Fulgide	mp °C	<sup>1</sup> H NMR (CDCl <sub>3</sub> , 60 MHz)	IR (KBr) ν cm <sup>-1</sup>	MS m/z
		δ		
<b>1</b>	115-117	1.97 (3H, s), 2.23 (6H, s), 2.42 (6H, s)	1805, 1759	261
<b>2</b>	147-149	1.99 (3H, s), 2.30 (3H, s), 2.38 (3H, s), 2.45 (3H, s), 7.82 (2H, d, <i>J</i> = 5.4 Hz), 8.69 (2H, d, <i>J</i> = 5.4 Hz)	1809, 1755	324
<b>3</b>	198-202	2.04 (3H, s), 2.31 (3H, s), 2.38 (3H, s), 2.47 (3H, s), 7.68 (2H, d, <i>J</i> = 7.8 Hz), 8.06 (2H, d, <i>J</i> = 7.8 Hz)	2227, 1809, 1757	a
<b>4</b>	192-193	2.00 (3H, s), 2.27 (3H, s), 2.36 (3H, s), 2.41 (3H, s), 3.21 (H <sub>2</sub> O), 3.34 (2H, s), 7.24-8.24 (4H, m) <sup>b</sup>	3421, 1809, 1755, 1670	366
<b>5</b>	217-220	1.84 (3H, s), 1.95 (3H, s), 2.20 (3H, s), 2.33 (3H, s), 8.01 (4H, s) <sup>b</sup>	2987, 1811, 1760, 1689	367
<b>7</b>	148-151	2.00 (3H, s), 2.33 (6H, s), 2.45 (3H, s), 3.83 (3H, s), 6.90 (2H, d, <i>J</i> = 9.0 Hz), 7.90 (2H, d, <i>J</i> = 9.0 Hz)	1809, 1755, 1504	a

<sup>a</sup>Not determined. <sup>b</sup>Measured in DMSO-d<sub>6</sub>.

**Table 2.** Spectral properties of oxazolyfulgides in ethyl acetate

Fulgide	E-form		C-form <sup>a</sup>	
	$\lambda_{\max}/\text{nm}$	$\epsilon_{\max}/10^4\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\max}/\text{nm}$	$\epsilon_{\max}/10^4\text{M}^{-1}\text{cm}^{-1}$
<b>1</b>	262	0.81	434	0.30
	326	0.75		
<b>2</b>	280	1.9	444	0.75
<b>3</b>	311	2.0	451	0.98
<b>4</b>	296	1.9	455	0.91
<b>5</b>	300	2.4	455	1.2
<b>6</b>	278	2.1	455	0.92
	333	0.97		
<b>7</b>	284	2.8	467	1.2
	342	0.9		

<sup>a</sup>Each  $\epsilon_{\max}$  of the C-form estimated assuming total conversion into colored form at the photostationary state.

characteristic of the CN stretching.

Figure 1 illustrates photochemical coloration ( $\lambda_{\max}$  451 nm) of fulgide **2** in spin-coated PMMA film upon irradiation with UV light. In a dilute ethyl acetate solution, the color band maximum shifted to the blue (444 nm) demonstrating pure yellow color. Table 2 lists the absorption spectral properties of the colored (c-form) and erased (E-form) forms in solution. Fulgide **1** shows significantly more blue-shifted bands of both colored and erased forms, though their absorption coefficients are considerably smaller. Thus, fulgides **1-6** can be candidates for photochromic yellow dyes though their actual colors vary with the medium properties. The colored forms were decolorized upon irradiation with 436 nm light. The coloration and decoloration quantum yields ( $\phi_{\text{EC}}$  and  $\phi_{\text{CE}}$ ) of fulgide **2** were 0.25 at 313 nm and 0.070 at 436 nm, respectively, in ethyl acetate. These are comparable with those of the furylfulgide (0.20 and 0.073).<sup>7,16</sup> Table 3 lists the quantum yields of oxazolyfulgides in ethyl acetate.

**Table 3.** Quantum yields  $\phi_{\text{EC}}$  and  $\phi_{\text{CE}}$  in solution

Fulgide	$\phi_{\text{EC}}$		$\phi_{\text{CE}}$	
	Toluene	Ethyl acetate	Toluene	Ethyl acetate
<b>1</b>	0.38	0.43	0.46	0.42
<b>2</b>	0.26	0.25	0.091	0.070
<b>3</b>	0.25	0.23	0.036	0.041
<b>4</b>	0.26	0.27	0.047	0.046
<b>5</b>	0.23	0.21	0.039	0.026
<b>6</b>	0.22	0.21	0.052	0.054
<b>7</b>	0.23	0.22	0.039	0.031

While fulgide **1** exhibits higher values, all other fulgides exhibit almost similar values of  $\phi_{\text{EC}}$  and  $\phi_{\text{CE}}$ .

Fulgides **2-7** showed fairly good photochemical reversibility toward repeated coloration–decoloration cycles at room temperature, as previously reported with **6** which showed relatively low fatigues (below 10% after 500 cycles in toluene solution while 40% after 50 cycles in PMMA film).<sup>17,18</sup> In the present study, the photochromic fatigues of **2-7** were less than 10% after 20 repeated cycles in PMMA under the air without any protection from oxidative degradations by atmospheric oxygen. The photochemical fatigues could be substantially depressed by sealing the

film to keep air-tight.<sup>21,22</sup> Upon heating at 80 °C for 100 h in the dark, both the colored and erased forms of fulgides **2-7** showed good thermal stability (degradations less than 15%) in PMMA film, reflecting improved stability of the oxazole ring which is highly resistant to oxidative degradations as compared with the furan ring. As such, they are one of the candidates for a photon-mode rewritable dyes for a temporary document, but not suitable for a permanent document which needs a high readout stability toward visible light.

In summary, some oxazolyfulgides exhibit favorable features for photochromic yellow dyes with fairly good photochemical reversibility, quantum yields, and thermal stability.

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