One Pot Synthesis of Photochromic Maleic Anhydride Derivatives

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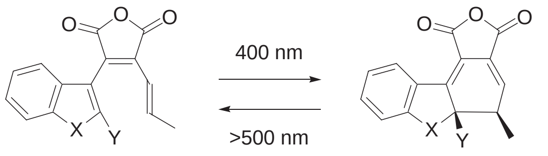
Photochromic 2-aryl-3-(1-propenyl)maleic anhydride derivatives were synthesized by one pot synthesis and their photochromic performance was examined in solution.

Photochromism has attracted considerable attention because of its potential application in molecular devices, such as optical memories and switches.[1,2] Among various thermally irreversible photochromic compounds, diarylethene derivatives are the most promising compounds because of their fatigue resistant property.[3] Recently, 1-aryl-1,3-butadiene derivatives[4,5] and bis(2,3′-benzothienyl) derivatives[6] have been reported to show thermally irreversible photochromic reactions.

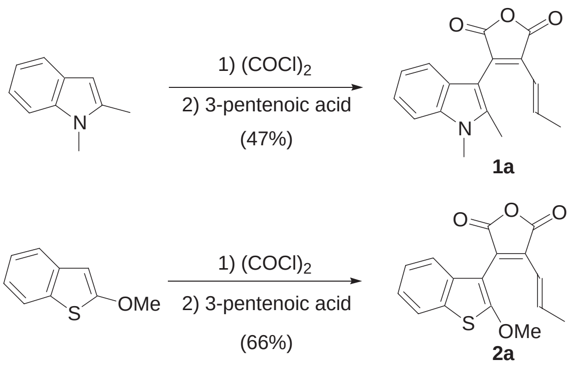
2,3-Diarylmaleic anhydrides are thermally irreversible photochromic compounds.[7,8] They undergo cyclization as well as cycloreversion reactions upon irradiation with visible light. Here, we report on the one pot synthesis of diarylmaleic anhydride analogues.



1a: X=NCH$_3$; Y=Me
2a: X=S; Y=OMe

1b: X=NCH$_3$; Y=Me
2b: X=S; Y=OMe

Compounds **1a** and **2a** were synthesized as shown in Scheme 1. 1,2-Dimethylindole and 3-pentenoic acid were purchased from Tokyo Kasei and used without purification. To a dry dichloromethane solution (7 mL) containing 600 mg (4.1 mmol) of 1,2-dimethylindole, 0.36 mL (4.1 mmol) of oxalyl chloride was added at 5 °C. The mixture was stirred for 10 min at 5 °C. To the flask, 10 mL of a dichloromethane solution containing 410 mg (4.1 mmol) of 3-pentenoic acid and 1.2 mL of triethylamine were added dropwise at 5 °C. The reaction mixture was stirred for 1.5 h, and the solution was evaporated in vacuo. The residue was purified by column chromatography (eluent:chloroform) to give **1a** in 47% yield.[10] **2a** was synthesized by similar procedures.[11]



1a

2a

Scheme 1.

Figure 1 shows the photoinduced absorption spectral change of **1a** in hexane. In the photostationary state upon irradiation with 400-nm light, 35% of the open-ring isomer (**1a**) was trans-

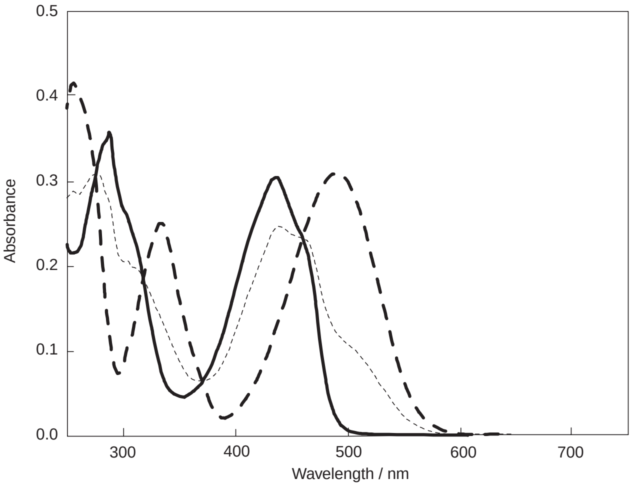


Figure 1. Absorption spectra of **1a** (solid line) and **1b** (dashed line) in hexane (4.4×10^{-5} mol L^{-1}) and in photostationary state (broken line) upon irradiation with 400-nm light.

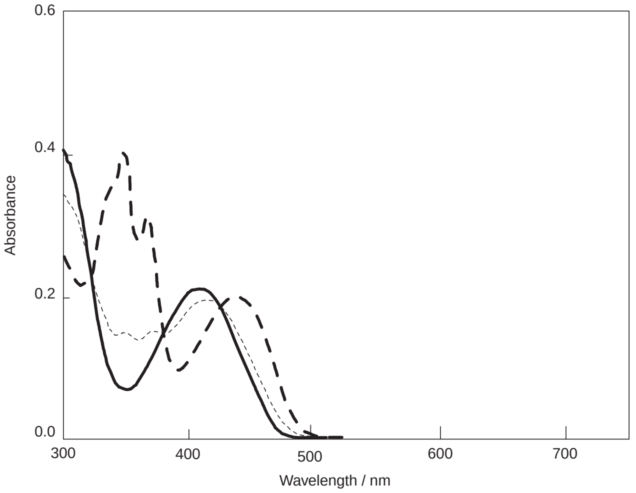


Figure 2. Absorption spectra of **2a** (solid line) and **2b** (dashed line) in hexane (4.4×10^{-5} mol L^{-1}) and in photostationary state (broken line) upon irradiation with 400-nm light.

formed into the closed ring isomer (**1b**). Upon irradiation with >500-nm light, the closed-ring isomer returned to its original form **1a**. The photogenerated isomer was thermally stable at 80 °C for more than 1 day in decaline. **1** could repeat the cyclization/cycloreversion cycle more than 10 times.

As in the case of **1a**, **2a** underwent photochromism upon irradiation with UV–vis light in a hexane solution. Upon irradiation with 400-nm light, **2a** converted to **2b** but the conversion rate was only 26% in the photostationary state. The low conversion rate is due to the overlapping of the absorption spectra of the open- and closed-ring isomers. The photogenerated isomer was thermally stable at 80 °C for more than 1 day in decaline. The conversion rate further decreased to 9% when the irradiation wavelength was shifted to 450 nm. The photoresponsive behavior of **2** is inferior to that of **1**.

Table 1 summarizes the absorption maxima and molar absorption coefficients of the open- and closed-isomers in hexane. Cyclization and cycloreversion quantum yields are also shown in Table 1. The cyclization quantum yield (Φ_{OC}) of **1** was 0.10 in hexane, which is close to that of 2,3-bis(2,4,5-trimethylthiophen-3-yl)maleic anhydride **3a** (0.12) in hexane.[12] The obtained cycloreversion quantum yield (Φ_{CO}) of **1** was 0.32, which is larger than that of **3b** (0.16).[12]

Single crystals of **1a** and **1b** were obtained by recrystallization from chloroform and from a mixed solution of hexane and ethyl acetate, respectively, and analyzed by X-ray crystallographic analysis. The ORTEP drawings of (a) **1a** and (b) **1b** are shown in Figure 3. **1a** contains indole and (*E*)-ethene moieties and has a hexatriene structure. The distance between the reactive carbons is 0.462 nm, which is too long for the molecule to undergo the photocyclization reaction in the crystal. In fact, the single crystal of **1a** did not show any photochromism in the crystalline phase. Compound **1b** has a cyclohexadiene structure, which indicates that the photocyclization reaction of this compound proceeds in the conrotatory mode.

We have prepared new photochromic compounds (**1a** and **2a**) having a maleic anhydride unit by one pot synthesis. The starting materials for **1a** are commercial reagents, and the coupling reaction is completed in 2 h. The photogenerated closed-ring isomers are thermally stable at 80 °C for more than 1 day in decaline, and the cyclization/cycloreversion cycle can be repeated more than 10 times.

Table 1. Absorption characteristics and photoreactivity of **1** and **2** in hexane

Compound	$\varepsilon/10^3$ dm^3 mol^{-1}cm^{-1}		Quantum yield	
	a	**b**	Cyclization	Cycloreversion
1	7.18 (436 nm)	7.31 (492 nm)	0.10 (400 nm)	0.32 (492 nm)
2	4.86 (411 nm)	4.40 (438 nm)	0.035 (400 nm)	0.23 (450 nm)

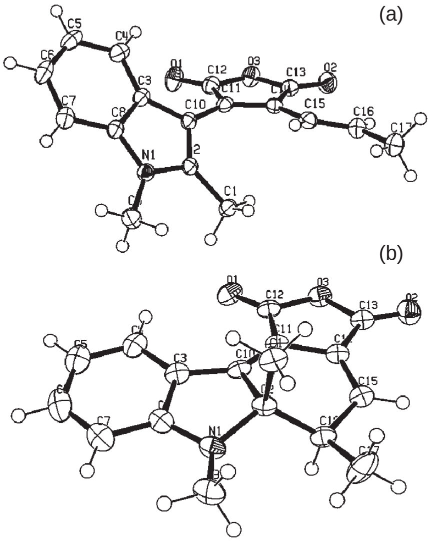


Figure 3. ORTEP drawings of (a) **1a** and (b) **1b** showing 50% probability displacement ellipsoids.

References and Notes

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10 **1a**: orange crystals; mp 199–200 °C; ^{1}H NMR (200 MHz) δ 1.90–1.94 (m, 3H), 2.44 (s, 3H), 3.77 (s, 3H), 6.20 (m, 1H), 6.28 (m, 1H), 7.18–7.38 (m, 4H). Anal. Calcd. for $C_{17}H_{15}NO_3$: C 72.58, H 5.37, N 4.98%. Found: C 72.52, H 5.41, N 5.04%. MS–FAB *m*/*z*: [M$^+$] 282.
11 **2a**: orange crystals; mp 112–113 °C; ^{1}H NMR (200 MHz) δ 1.91–1.94 (m, 3H), 4.08 (s, 3H), 6.16–6.23 (m, 1H), 7.18–7.35 (m, 3H), 7.69–7.73 (m, 1H). EIMS *m*/*z* 300 (M$^+$); Anal. Calcd. for $C_{16}H_{12}O_4S$: C 63.99, H 4.03%. Found: C 63.94, H 4.06%.
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13 Crystal data for **1a**: $C_{17}H_{15}NO_3$, $M_r = 281.30$, monoclinic, space group $P2_1/c$, $a = 11.132(4)$ Å, $b = 7.341(3)$ Å, $c = 17.308(6)$ Å, $\alpha = 90°$, $\beta = 101.366(5)°$, $\gamma = 90°$, $V = 1386.6(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.347$ g cm^{-3}, $R_1 = 0.0422$ for 1702 observed reflections with $I > 2\sigma(I)$ from 2007 unique reflections. CCDC deposition number: 254323.
14 Crystal data for **1b**: $C_{17}H_{15}NO_3$, $M_r = 281.30$, monoclinic, space group $P2_1/n$, $a = 8.0219(19)$ Å, $b = 17.056(4)$ Å, $c = 9.822(2)$ Å, $\alpha = 90°$, $\beta = 93.761(4)°$, $\gamma = 90°$, $V = 1340.9(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.393$ g cm^{-3}, $R_1 = 0.0446$ for 1529 observed reflections with $I > 2\sigma(I)$ from 1916 unique reflections. CCDC deposition number: 254324.

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