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Photochromic Chromene Derivatives with a Thiophen Moiety

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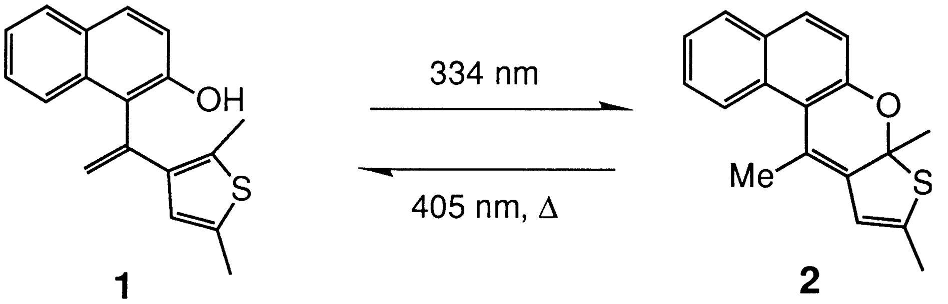
A Chromene derivative with a thiophene ring underwent a photochromic reaction at room temperature. The bond structure of the thiophene moiety influenced the photochromic reaction.

One of typical photochromic reactions is a reversible ring-opening of a substituted pyran ring as observed in spirobenzopyrans1) or chromenes.2) Becker et al. reported that 2H-chromene and its derivatives underwent photochromic reactions from colorless to yellow-orange by UV irradiation at low temperature.3) The photochromic reaction, however, was not observed at room temperature except for the benzochromene derivative with a methoxy group, lapachenol, because of thermal instability of the colored form. The photochromic behavior depends on the aryl group attached to the chromene. We have synthesized a new type of chromene derivatives with a thiophene moiety, **3** and **5**, and found that **5** underwent the photochromic reaction at room temperature.4)

In a previous paper,5) we have shown that a vinylnaphthol derivative **1** underwent a reversible color change and the colored form had a chromene structure, **2**. In contrast with 2H-chromene, the chromene



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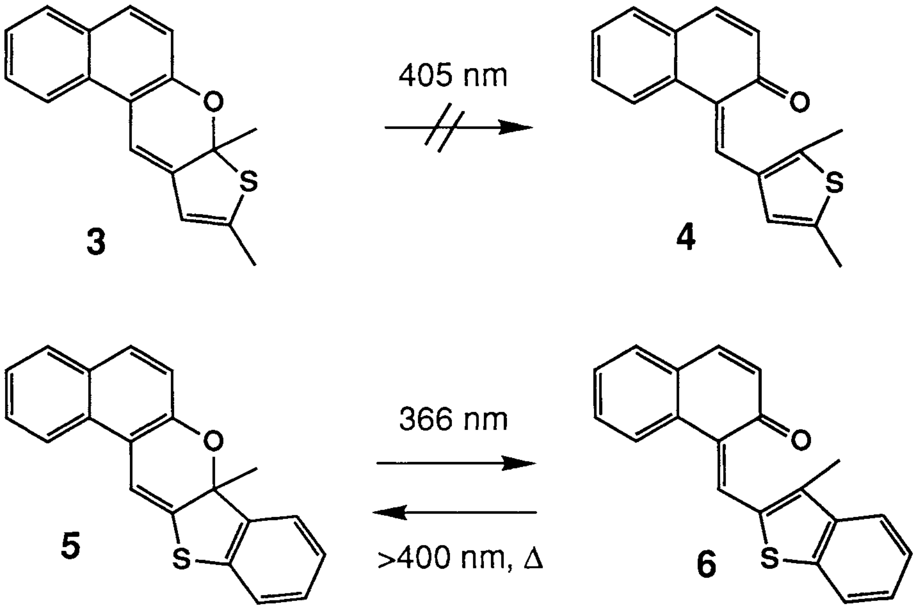
structure was thermally unstable and returned to the open-ring form upon heating above 60 °C. In order to gain access to a thermally stable chromene derivative with a thiophene moiety, we synthesized compound **3** and **5**, derivatives of compound **2**. Compound **3** had an absorption maximum at 381 nm, which is close to the maximum of **2**. Although the chemical structure of **3** is very similar to **2** except that **3** has no methyl group at 4-position, **3** did not show any spectral change at room temperature even when the compound was irradiated in hexane with 405 nm light. A methyl group at 4-position is indispensable for the derivative to undergo the photochromic reaction.



On the other hand, **5** underwent the photochromic reaction as shown in Fig.1. The hexane solution containing **5** turned yellow upon UV irradiation (λ = 366 nm) and a new absorption band appeared at 452 nm. In the dark at room temperature the yellow color disappeared. The bleaching time was accelerated by irradiation with visible light ($\lambda > 400$ nm). The photochemical behavior is similar to lapachenol.

Figure 2 shows the decay behavior of the colored form at room temperature in acetonitrile. The decay did not obey a simple first order kinetics. Two components, fast and slowly decaying processes, were observed. Table 1 summarizes the fast decay rate constants, the absorption maxima of the open-ring forms, and the ratio of the fast decaying component to the slowly one in various solvents. The fast decay rate increased with the decreasing solvent polarity. In acetonitrile the life time of the open-ring form was 36 sec, while it decreased to 9 sec in hexane. The open-ring keto form was stabilized in polar solvents. The absorption maxima of the open ring forms, however, remained almost constant regardless of the solvents. These results suggest that the open-ring form has not a zwitterionic property but a keto structure **6**.

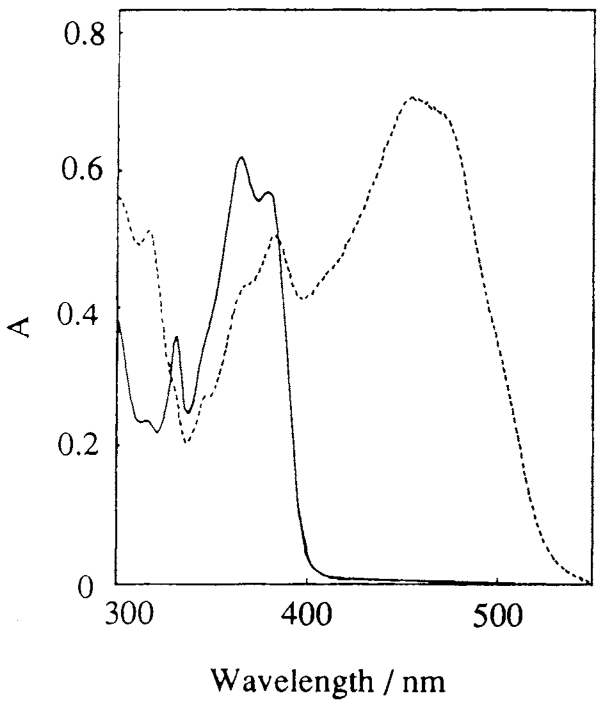


Fig.1. Absorption spectral change of **5** (1.0×10^{-4} mol dm^{-3}) in hexane. -----, **5**
- - -, under irradiation with 366 nm light.

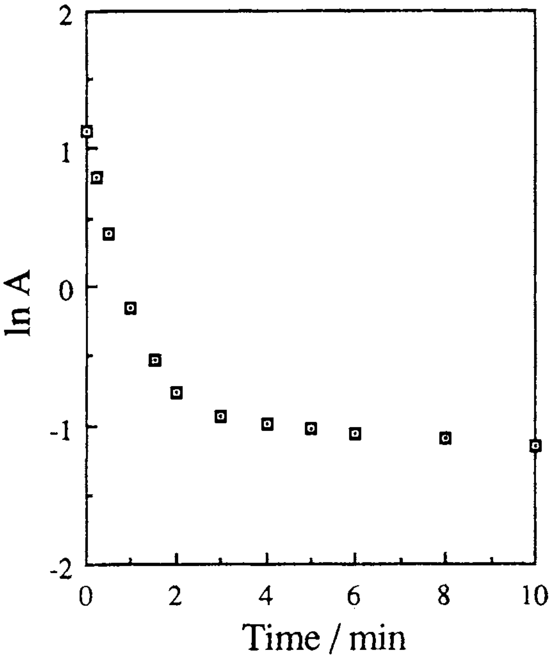


Fig.2. Thermal decay of the colored form **6** in acetonitrile.

The ratio of the two components was dependent on solvents. The slowly decaying component decreased in medium polar solvents, ethyl acetate and dichrolomethane. The fraction was only 8%. In non-polar hexane and polar acetonitrile it was more than 10%.

The structural difference between **3** and **5** is the position of a sulfur atom, whether it sits at the neighbor of the carbon at 2-position of chromene or of the double bond. The difference influenced the photochromic reaction. The open-ring form **6** is reasonably stabilized by the π-conjugation, but the extension of π-conjugation is not enough for **4**. This could explain the different reactivity between **3** and **5**. **3** and **5** have a possible reaction path

Table 1. Solvent effects of absorption maximum, the decay rate constants of the colored forms, and the ratio of the fast decaying component and the slowly one

Solvent	Absorption maxima (nm)	$k/\ s^{-1}$	F(fast) / F(slow)
hexane	452	7.5×10^{-2}	7.3
benzene	467	5.5×10^{-2}	6.7
ethyl acetate	458	3.6×10^{-2}	11.5
dichloromethane	459	2.0×10^{-2}	11.5
acetonitrile	458	1.9×10^{-2}	7.3

to produce β-naphthol derivatives by the 1,7-sigmatropic hydrogene shift. The photoreaction, however, was not observed.

References

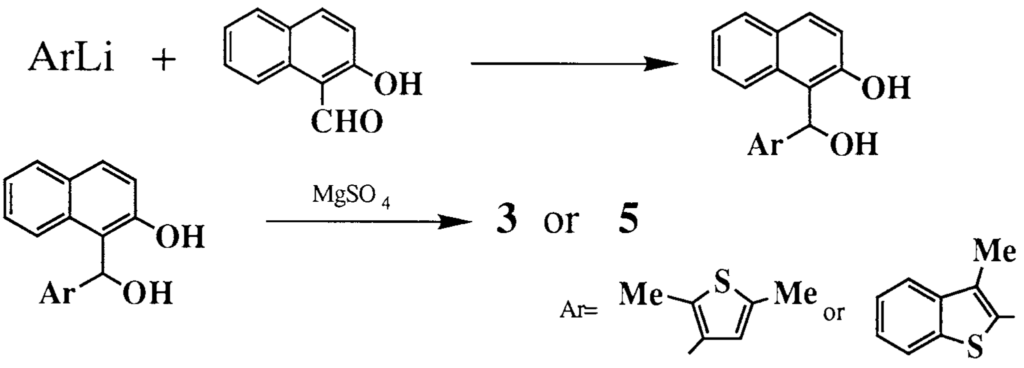
1) S.Tamura, N.Asai, and J.Seto, *Bull. Chem. Soc. Jpn.*, **62**, 358(1989).

2) A.Padwa, A.Au, G.A.Lee, and W.Owens, *J. Org. Chem.*, **40**, 1142(1975).

3) R.S.Becker and J.Michl, *J. Am. Chem. Soc.*, **88**, 5931(1966).

4) Synthesis of **3** and **5** were carried out as shown below.

The dehydration of diol proceeded under mild conditions. Spectral data of **3** and **5**. **3**: ^{1}H NMR δ 1.63(s,3H), 2.19(broad s,3H), 6.00(s,1H), 6.96(broad s, 1H), 7.00-8.00(m,6H); IR 3060, 2920, 1620, 1470, 1220 cm^{-1}. Anal. Found: C, 76.18; H, 5.15%. Calcd for $C_{20}H_{14}OS$: C, 76.65; H, 5.30%. **5**: ^{1}H NMR δ 1.55(σ,3H), 7.00–8.00(m,11H); IR 3050, 2910, 1590, 1460, 1230 cm^{-1}. Anal. Found: C, 79.57; H, 4.78%. Calcd for $C_{20}H_{14}OS$: C, 79.44; H, 4.67%.



5) M.Uchida and M.Irie, *Chem. Lett.*, **1991**, 2159.

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