Bull. Chem. Soc. Jpn., ***69***, *1023—1027 (1996)*

Synthesis and Properties of Naphthopyrans with a Benzothiophene Ring

Manabu Uchida,[†] **Makoto Kume, and Masahiro Irie***

Institute of Advanced Material Study, Kyushu University, Kasuga-Koen 6-1, Kasuga, Fukuoka 816

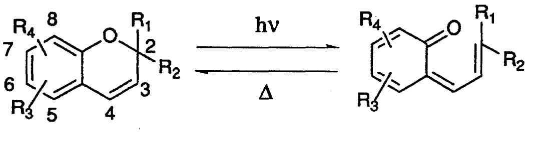
†Chisso Corporation, Ookawa, Kanazawa-ku, Yokohama, Kanagawa 236

(Received September 1, 1995)

New photochromic benzochromene derivatives condensed with a benzothiophene ring were synthesized. The condensation positions of the thiophene ring influenced the photochromism. 7a-Methyl-7a*H*-benzo[*f*][1]benzothieno-[2,3-*b*]chromene (**1**) underwent a two-photon two-step photochromism, while 7a-methyl-7a*H*-benzo[*f*][1]benzothieno-[3,2-*b*]chromene (**2**) showed an ordinary chromene-type photochromic reaction. The yellow color of **1** disappeared upon irradiation with 405 nm light, and a thermally stable oxabicyclo[3.1.0]hexene isomer was reversibly produced. On the other hand, compound **2** turned orange upon irradiation with 366 nm light, and the orange color quickly returned to the original pale yellow in the dark. Upon irradiation with both 366 and >420 nm light compound **2** isomerized to an oxabicyclo[3.1.0]hexene form.

Photochromic compounds that reversibly change their physical and chemical properties upon light irradiation are potentially applicable to various photoactive devices.[1] Although a great number of photochromic molecular systems or devices have been proposed, the compounds used in these systems are very few: They are for example spiropyrans,[2] azobenzenes,[3] fulgides,[4] and diarylethenes.[5] Among them, spiropyran derivatives are most widely used owing to their dramatic color and dipole-moment changes. Chromenes belong to spiropyran families.

Photochromic chromenes change color form colorless to yellow or orange upon UV irradiation.[6]



(1)

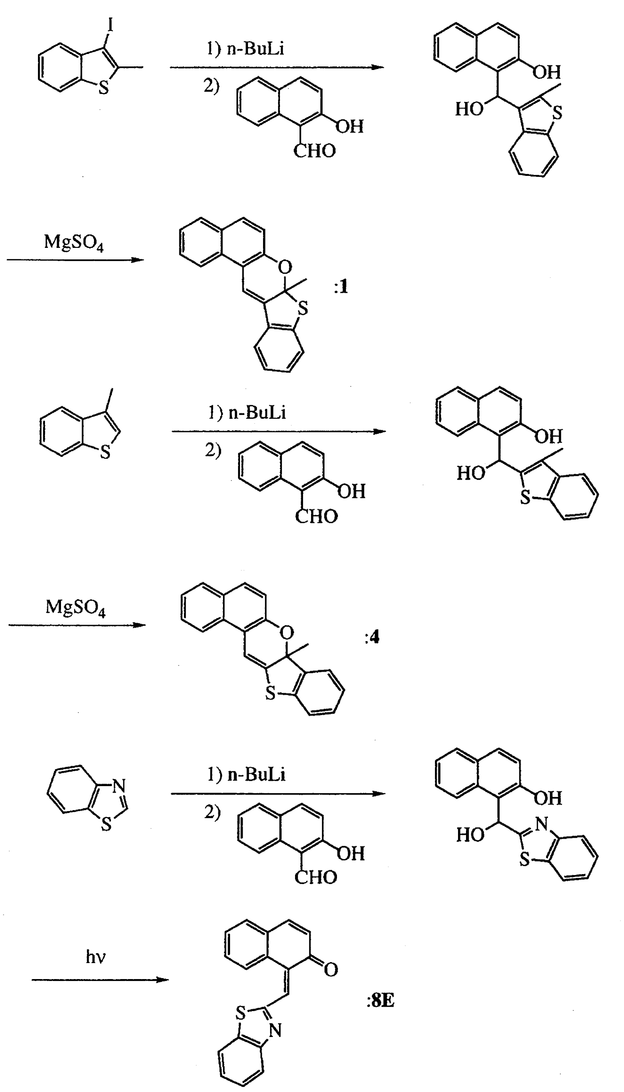
This color change, however, can be detected only at low temperature because of the poor thermal stability of the colored forms.[7] It is required to introduce bulky or aromatic substituents into the 2-position of the pyran ring in order to gain reasonable stability of the colored forms.[6,7] 5,6- or 7,8-benzo-condensation of the chromene was also reported to be effective to increase the stability.[6,7] We took the way to introduce a benzothiophene ring at the 2,3-position of the pyran ring. The open *o*-quinonoid form has an aromatic moiety, and is expected to become stable. In this paper we report on novel photochromic reactivities of the chromene derivatives condensed with a benzothiophene ring.[8]

Results and Discussion

Synthesis. The synthetic routes of chromenes condensed with a benzothiophene ring are shown in Scheme 1. 7a-Methyl-7a*H*-benzo[*f*][1]benzothieno[2,3-*b*]chromene (**1**) and 7a-Methyl-7a*H*-benzo[*f*][1]benzothieno[3,2-*b*]chromene (**4**) were prepared by condensating 3- or 2-lithio-1-benzothiophene and 2-hydroxy-1-naphthalenecarbaldehyde, respectively. 3-Lithio-2-methyl-1-benzothiophene was prepared via 3-iodo-2-methylbenzo[*b*]thiophene, while 2-lithio-3-methyl-1-benzothiophene was directly prepared from 3-methyl-1-benzothiophene with butyllithium. Each intermediate diol formed was dehydrated with anhydrous magnesium sulfate to give **1** and **4**, respectively. The dehydration reactions proceeded under mild conditions.

2-(2′-Oxo-1′-naphthylidene)methyl-1-benzothiazole (**8E**) was obtained by the condensation of benzothiazole with 2-hydroxy-1-naphthalenecarbaldehyde. The dehydration reaction was carried out in a heptane solution by irradiation with UV light ($250 < \lambda < 400$ nm). Only a trace amount of geometric isomer **8Z** was obtained. Compound **8E** was thermally stable and a closed-ring isomer **7** was not obtained.

Photochromic Properties. Figure 1 shows the absorption spectrum of a hexane solution of chromene **1**. The solution was yellow and the absorption maxima were observed at 386 and 406 nm. Upon irradiation with visible light ($\lambda = 405$ nm) at room temperature, the yellow color disappeared and the solution turned colorless. This behavior is different from that of ordinary chromenes. Ordinary chromene solutions change from colorless to yellow or orange. The photo-product gave the NMR spectrum, which can be assigned to the oxabicyclo[3.1.0]hexene structure **3**. The methyl and methine protons were observed at 1.14 and 2.97 ppm, respectively. The high field shift of these signals indicates the formation of a cyclopropane ring. The chemical shifts of the methyl and methine protons agree well with the reported values of the oxabicyclo[3.1.0]hexene derivatives.[9] The blue-shift of the absorption spectrum also supports this structure. The yellow color appeared again upon irradiation with 334 nm light. The photochromic behavior is similar

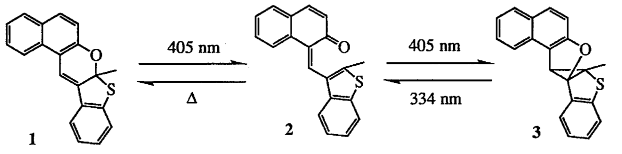


Scheme 1. Synthetic routes of the chromene derivatives.

to that of the naphthopyran derivative, which undergoes a two-step two-photon reaction via a thermally unstable keto form.[10]

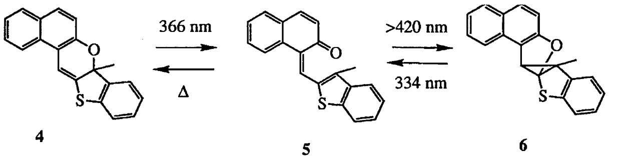
Compound **1** underwent two-photon photochromism, as confirmed by the light-intensity dependence of the photochromic reaction (Fig. 2). The disappearance rate of the absorption at 405 nm increased in proportion to the square of the light intensity, clearly indicating that two photons are required for the bleaching process. The absence of a chromene-type photochromic reaction is due to the very short lifetime of the keto form **2** at room temperature.

When a methyltetrahydrofuran solution containing **1** was irradiated with low-intensity light at −70 °C, the yellow color of the solution changed to dark orange. The dark-orange color, however, quickly disappeared, even at such a low temperature in the dark. Although the dark-orange color is considered to be due to the keto form **2**, its confirmation by NMR was impossible because of its short lifetime.



(2)

When the geometry of the benzothieno annulation to the benzochromene moiety was reversed, such as pyran **4**, the absorption spectrum and photoreactivity dramatically changed. The conjugation length of **4** is shorter than that of **1**. Therefore, the absorption maxima of **4** in a hexane solution shifted to shorter wavelengths at 365 and 379 nm. We previously reported that **4** undergoes an ordinary chromene-type photochromic reaction at room temperature upon irradiation with 366 nm light,[8] in which the colorlation is due to the keto isomer **5**. The keto form had an absorption maximum at 452 nm, and the color disappeared in the dark. The thermal decoloration reaction took place within about 9 s in hexane at room temperature. The lifetime of **5** is much longer than that of **2**.



(3)

The difference in the thermal stability between the keto forms, **2** and **5**, can be interpreted as follows. When the benzothiophene ring is connected with a 2-oxo-1-naphthilidenemethyl group at the 2-position, such as the keto form **5**, the π-electron is delocalized throughout the whole molecule. The delocalized form is considered to be more stable than the keto form **2**, in which the π-electron is localized in the *o*-quinonoid moiety, and does not extend to the benzothiophene ring. In addition to the increase in thermal stability, compound **5** shows the absorption at longer wavelengths than compound **2** (the absorption maximum was shorter than 420 nm) due to an extension of the π-cojugation.

When compound **4** was irradiated at two wavelengths (λ =366 nm and >420 nm) in hexane, a completely different photochromic reaction was observed. The absorption at 453 nm was no longer detected, and the absorptions at 365 and 379 nm disappeared, as shown in Fig. 3. The shorter wavelength absorption is considered to be due to a bicyclohexene form. The NMR spectrum of the photo-product showed methyl and methine protons at 1.07 and 2.61 ppm, which are similar to compound **3**. Apparently, the oxabicyclo[3.1.0]hexene **6** was produced from **5** with >420-nm light. This system is thus regarded as being a two-step two-photon process, as described above, in which the conversion from **4** to **6** requires two energetically different photons.[11] This reaction system is ideal for a non-destructive readout for optical recording media, in which the readout is carried out with 366 nm light, while erasing with 366 nm and λ >420 nm light. Irradiation with 366 nm light does not bleach out the absorption band at 365 and 379 nm, because the photo-

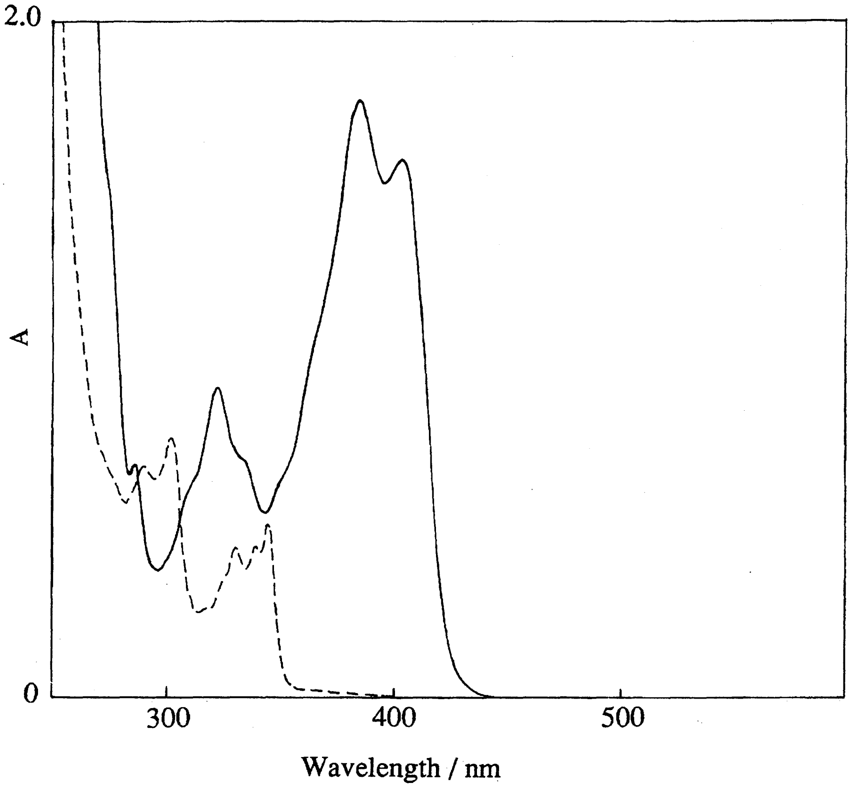


Fig. 1. Spectral change of **1** in hexane (1.0×10^{-4} mol dm^{-3}). (—): Before photoirradiation, (····): After irradiation with 405 nm light.

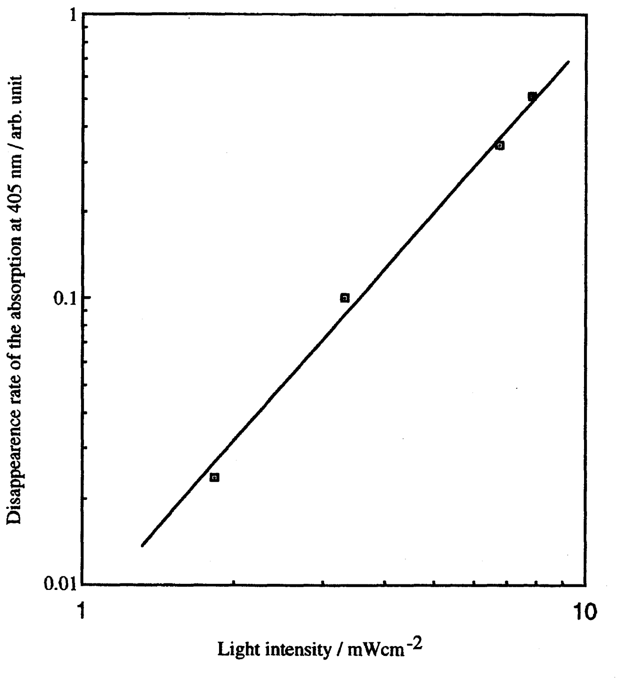
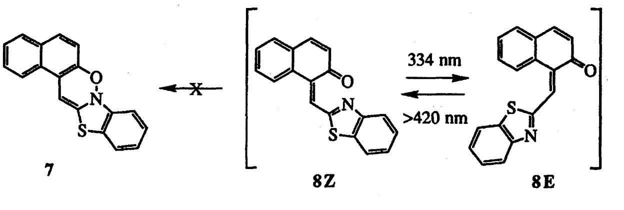


Fig. 2. Light intensity dependence of relative bleaching rate of **1**.

generated keto form **5** returns to the pyran form in the dark,[8] and the light is scarcely absorbed by the keto form **5**. The initial pyran form was reproduced from **6** by irradiation with 334-nm light, though the conversion was limited to 70%.

To investigate the effect of the structure on the stability of the intermediate keto form, we attempted to prepare compound **7**, which has a nitrogen atom at the 7a-position. However, we obtained only the keto forms **8** instead of **7**. Figure 4 shows the absorption spectral change of compound **8E** at room temperature in hexane. The hexane solution was orange and the absorption maximum was at 410 nm. The orange color changed to yellow upon irradiation with visible light (λ >420 nm), and the absorption maximum shifted to a shorter wavelength (λ_{max}=399 nm). The solution again returned to orange upon irradiation with UV light (λ =334 nm). It was confirmed by an NMR spectroscopic analysis before and after irradiation that the spectral change by UV-vis light exposure arises from a structural transformation between the *E* and *Z* geometric isomers. The closed-ring form **7** was not produced by photo-irradiation as well as by heating. In contrast with compound **5**, neither the N–O-bond-formed compound nor the oxabicyclo[3.1.0]hexene derivative was discerned. When we compared the heat-of-formation values of **7** with that of **8Z** obtained by the PM3 semiempirical MO method, that of **7** was ca. 100 kJ mol^{-1} larger than that of **8Z**. This result can explain the absence of a ring-closure reaction.



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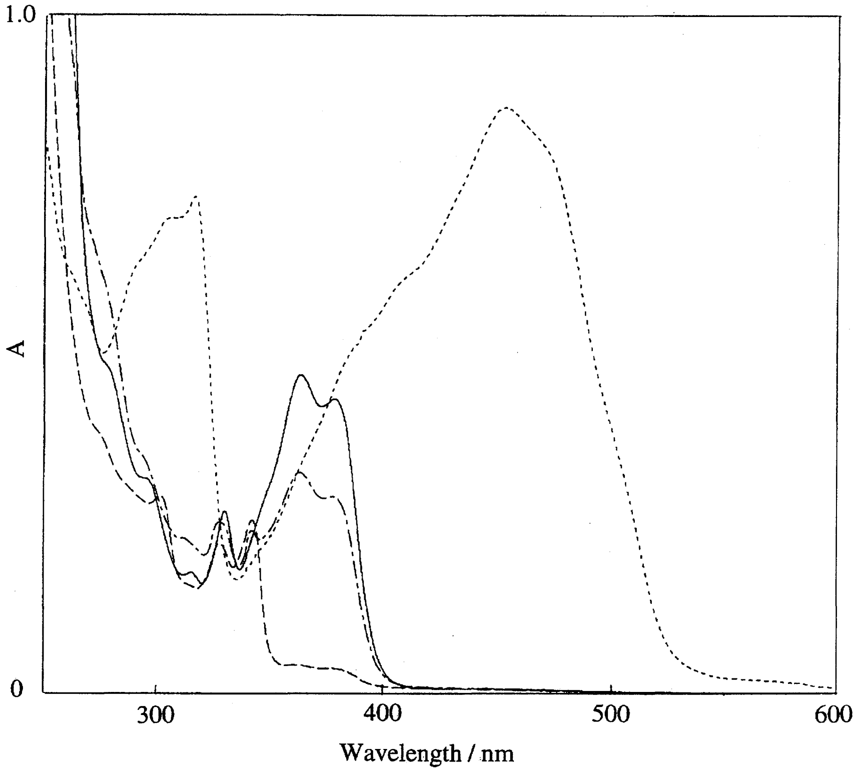

Fig. 3. Spectral change of **4** in hexane (7.6×10^{-5} mol dm^{-3}). (——): Before photoirradiation, (····): After irradiation with 366 nm light, (- - -): After irradiation with 366 and >420 nm light, (– · · –): After irradiation of the preirradiated sample with 334 nm light.

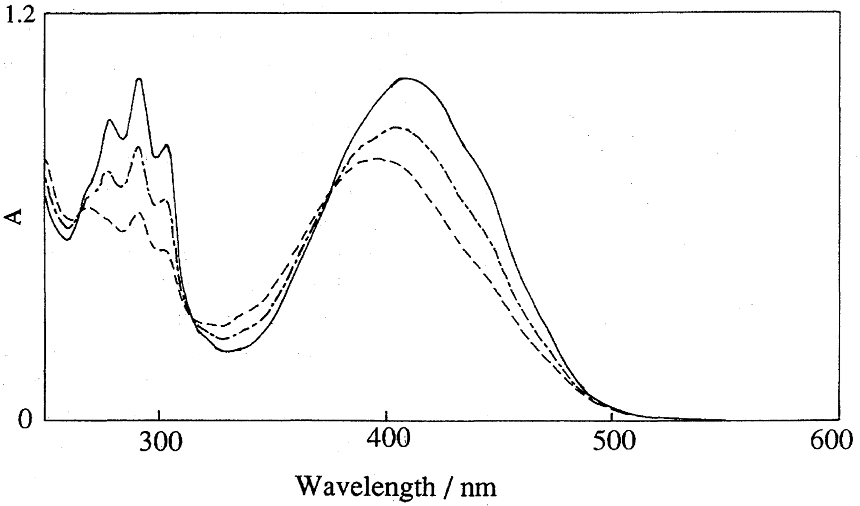

Fig. 4. Spectral change of **8E** in hexane (1.0×10^{-5} mol dm^{-3}). (——): Before photoirradiation, (- - -): After irradiation with visible light (>420 nm), (– · · –): After irradiation of the preirradiated sample with 334 nm light.

Experimental

General. The absorption spectra were measured using a Hitachi U-3410 spectrometer and NMR measurements were carried out with JEOL-GSX270 and JEOL-GSX400 NMR spectrometers. The melting points were recorded with a Metller hot-stage apparatus.

For photoisomerization, a xenon-arc lamp (Ushio, 500 W) and a mercury lamp (Ushio, 500 W and 250 W) were used as light sources. The wavelengths of irradiated light were selected by passing the light through a monochrometer (Ritsu MC-10N, Nikon P250) and glass filters (Toshiba, UV-31, UV-D35, L-39, L-42, TND).

Materials. 7a-Methyl-7a*H*-benzo[*f*][1]benzothieno[2,3-*b*]-chromene (1). To a solution of 3-iodo-2-methyl-1-benzothiophene (548 mg, 2.0 mmol) in THF (10 ml) was slowly added *n*-BuLi (1.6 mol dm^{-3} in hexane, 1.3 ml) at −50 °C; the mixture was then stirred for 30 min, followed by the addition of 2-hydroxy-1-naphthalenecarbaldehyde (172 mg, 1.0 mmol) in THF (10 ml). After the reaction mixture was stirred overnight at room temperature, the reaction was stopped with water. The products were extracted with ether, the extract was washed with saturated NaCl aqueous solution, dried over Na_2SO_4, and the solvent was evaporated. Purification by column chromatography (silica gel, hexane/ethyl acetate=5/1) afforded a diol as white crystals (220 mg, 69%): ^{1}H NMR ($CDCl_3$) δ=2.23 (s, 3H), 7.0—8.0 (m, 13H).

To a solution of the diol (100 mg, 0.3 mmol) and *p*-toluenesulfonic acid (trace) in ethyl acetate (10 ml) was added anhydrous $MgSO_4$ (100 mg). The mixture was heated at 60 °C for 1 h and the precipitate was removed by filtration. After evaporation of the solvent, purifications by column chromatography (hexane/ethyl acetate=7/1) and then recrystallization from a hexane–AcOEt solution gave yellow crystals **1** (25 mg, 26%): Mp 143—146 °C; UV (hexane) λ_{max} (log ε) 286 (3.83), 323 (3.95), 386 (4.23), 406 (4.20) nm; ^{1}H NMR ($CDCl_3$) δ=1.71 (s, 3H), 7.0—8.2 (m, 11H). Found: C, 79.77; H, 4.81%. Calcd for $C_{20}H_{14}OS$: C, 79.44; H, 4.67%.

7a-Methyl-7a*H*-benzo[*f*][1]benzothieno[3,2-*b*]chromene (4). To a solution of 3-methyl-1-benzothiophene (741 mg, 5 mmol) and *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (581 mg, 5 mmol) in ether (20 ml) was slowly added *n*-BuLi (1.6 mol dm^{-3} in hexane, 3.7 ml) at −20 °C. The reaction mixture was stirred overnight at room temperature, followed by the addition of 2-hydroxy-1-naphthalenecarbaldehyde (344 mg, 2 mmol) in THF (10 ml). The mixture was worked up in the same manner as described above to give a diol (260 mg, 41%): ^{1}H NMR ($CDCl_3$) δ=2.40 (s, 3H), 6.8—7.7 (m, 13H).

To a solution of the diol (100 mg, 0.3 mmol) in benzene (10 ml) was added anhydrous $MgSO_4$ (100 mg). The mixture was heated at 60 °C for 5 h and then cooled to room temperature. The precipitate was removed by filtration. The filtrate was worked up in the same manner as described above to give **4** (40 mg, 42%). UV (hexane) λ_{max} (log ε) 331 (3.79), 364 (4.03), 379 (4.00) nm; ^{1}H NMR ($CDCl_3$) δ=1.54 (s, 3H), 7.0—8.0 (m, 11H). Found: C, 79.57; H, 4.78%. Calcd for $C_{20}H_{14}OS$: C, 79.44; H, 4.67%.

2-(2′-Oxo-1′-naphthylidene)methyl-1-benzothiazole (8). To a solution of 1-benzothiazole (1.22 g, 9 mmol) in THF (20 ml) was slowly added *n*-BuLi (1.6 mol dm^{-3} in hexane, 6.2 ml) at −50 °C. After stirring for 1 h at ambient temperature, 2-hydroxy-1-naphthalenecarbaldehyde (517 mg, 3 mmol) in THF (15 ml) was added. The mixture was worked up in the same manner as described above to give a diol (212 mg, 23%): ^{1}H NMR ($CDCl_3$) δ=6.00 (bs, 1H), 7.16 (s, 1H), 7.20 (d, 1H, *J*=8.8 Hz), 7.33—7.38 (m, 2H), 7.43—7.49 (m, 2H), 7.73 (dd, 1H, *J*=8.0, 0.8 Hz), 7.80—7.85 (m, 3H), 8.03 (dd, 1H, *J*=7.6, 0.8 Hz), 9.48 (bs, 1H).

A heptane solution (200 ml) of the diol (100 mg, 0.33 mmol) was irradiated for 5 h with UV light (300W Xe lamp, Toshiba UV-31 and UV-D35 glass filters). The solvent was evaporated and the product was purified by column chromatography (heptane/ethyl acetate=3/1). Recrystallization from a heptane/ethyl acetatesolution gave orange crystals **8** (30 mg, 32%): Mp 144—146 °C; UV (hexane) λ_{max} (log ε) 278 (4.12), 291 (4.19), 303 (4.10), 410 (4.22) nm; ^{1}H NMR ($CDCl_3$) δ=6.55 (d, 1H, *J*=10.4 Hz), 7.4—7.6 (m, 6H), 8.03 (dd, 1H, *J*=8.0, 0.8 Hz), 8.10 (d, 1H, *J*=8.0 Hz), 8.15 (dd, 1H, *J*=8.0, 0.8 Hz), 8.55 (s, 1H). Found: C, 74.83; H, 3.99; N, 4.91; S, 10.87%. Calcd for $C_{18}H_{11}NOS$: C, 74.72; H, 3.83; N, 4.84; S, 11.08%.

Photoirradiation of Compound 1. The C_6D_{12} solution (0.6 ml) of **1** (0.8 mg) was irradiated with >420 nm light for 40 min in an NMR tube. The peaks due to the pyran **1** were completely lost, and new peaks which can be assigned to oxabicyclo[3.1.0]hexene **3** appeared.

3: UV (hexane) λ_{max} (log ε) 290 (3.83), 302 (3.88), 331 (3.64), 340 (3.64), 346 (3.71) nm; ^{1}H NMR (C_6D_{12}) δ=1.14 (s, 3H), 2.97 (s, 1H), 7.00—7.14 (m, 3H), 7.16 (d, 1H, *J*=8.8 Hz), 7.25 (m, 1H), 7.3—7.5 (m, 2H), 7.62 (d, 1H, *J*=9.2 Hz), 7.73 (d, 1H, *J*=8.8 Hz), 7.78 (d, 1H, *J*=8.0 Hz).

Photoirradiation of Compound 4. The C_6D_{12} solution (0.6 ml) of **4** (0.8 mg) was irradiated with 366 and >420 nm light for 3 h in an NMR tube. The peaks due to the pyran **4** were completely lost, and new peaks which can be assigned to oxabicyclo[3.1.0]hexene **6** appeared.

6: ^{1}H NMR (C_6D_{12}) δ=1.07 (s, 3H), 2.61 (s, 1H), 7.0—7.2 (m, 4H), 7.26 (m, 1H), 7.3—7.4 (m, 2H), 7.60 (d, 1H, *J*=8.8 Hz), 7.7 (m, 2H).

Photoirradiation of Compound 8. The $CDCl_3$ solution (0.6 ml) of the synthetic product **8** (0.8 mg) was irradiated with >420 nm light for 10 min in an NMR tube. The peaks before the irradiation decreased and new peaks appeared. The vinyl proton peak at 8.55 ppm (s, 1H) shifted to 7.92 ppm upon photoirradiation. This result indicates that the synthetic product is the *E*-form, and that the photoproduct is the *Z*-form.

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