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# Photochemistry of Flavonoids. V.[1] Photocyclization of 2-Styryl-4H-chromen-4-ones

Ichiro Yokoe,* Kyoko Higuchi, Yoshiaki Shirataki, and Manki Komatsu

*Faculty of Pharmaceutical Sciences, Josai University, Keyakidai,*
*Sakado, Saitama, 350-02 Japan*

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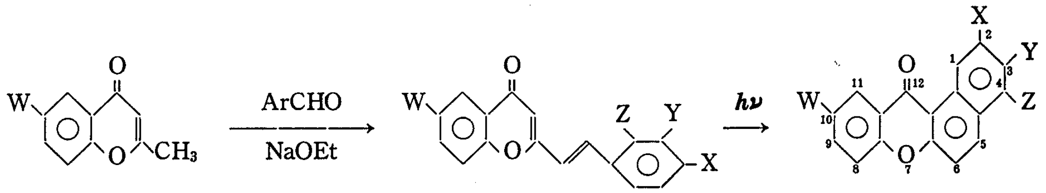
Irradiation of 2-styryl-4H-chromen-4-ones (1) with a high pressure Hg lamp at room temperature under air gave benzo[*a*]xanthones (2). The cyclization of methoxy-substituted styrylchromones occurred at the *para* position relative to the OMe group on the styryl ring, whereas 2-[$\beta$-(2-naphthyl)vinyl]chromone (3) cyclized at the $\alpha$-position of the naphthalene ring.

**Keywords**——photocyclization; 2-styryl-4H-chromen-4-ones; 12H-benzo[*a*]xanthen-12-ones; 2-[$\beta$-(2-naphthyl)vinyl]-4H-chromen-4-one; 14H-naphtho[1,2-*a*]xanthen-14-one; polyaromatic xanthene derivatives

Photocyclodehydrogenation of stilbenes and their analogs is a potential synthetic method for polycyclic aromatic compounds, and has been studied extensively.[2] As a part of our continuing interest in the photochemistry of flavonoids, we report in the present paper on the photocyclization of 2-styryl-4H-chromen-4-ones (1) to give 12H-benzo[*a*]xanthen-12-ones (2).



1

2

| | W | X | Y | Z |
|---|---|---|---|---|
| **a** | H | H | H | H |
| **b** | H | $CH_3$ | H | H |
| **c** | H | $OCH_3$ | H | H |
| **d** | H | H | $OCH_3$ | H |
| **e** | H | $OCH_3$ | $OCH_3$ | H |
| **f** | $CH_3$ | H | H | H |
| **g** | $CH_3$ | $CH_3$ | H | H |
| **h** | $CH_3$ | $OCH_3$ | H | H |
| **i** | H | H | H | Br |

Fig. 1

### Synthesis of 2-Styryl-4H-chromen-4-ones (1)

2-Styryl-4H-chromen-4-ones (1) were prepared by the treatment of 2-methyl- or 2,6-dimethyl-4H-chromen-4-one with the corresponding aromatic aldehydes in the presence of sodium ethoxide in absolute ethanol at room temperature.[3] The yields and melting points of **1** are listed in Table I. From the coupling constants of the proton magnetic resonance (PMR) spectra of **1** ($J$=15—16 Hz), the configuration of ethylenic bonds is concluded to be *trans*.

### Photolyses of 2-Styryl-4H-chromen-4-ones

2-Styryl-4H-chromen-4-one (**1a**) was irradiated in benzene under air with stirring for 15 h. The reaction mixture was chromatographed on silica gel and **2a**, mp 144—145°C, was

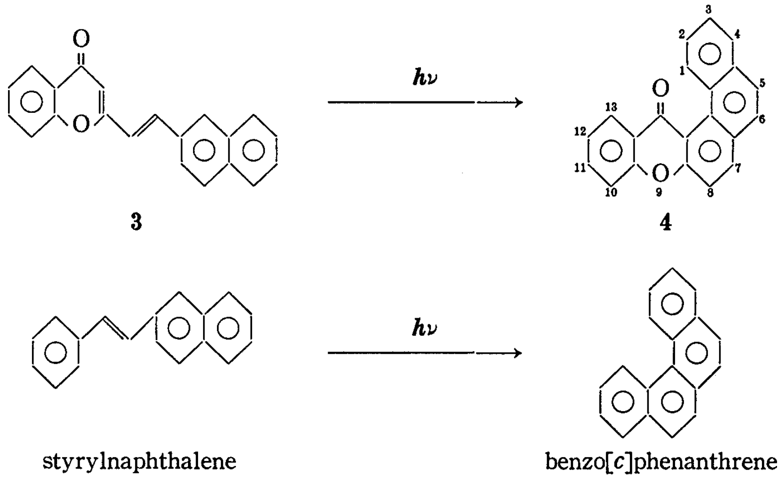
Table I. 2-Styryl-4H-chromen-4-ones (1)

| Compd. No. | Yield (%) | mp (°C) | Formula | Analysis (%) Calcd (Found) | | PMR (CDCl$_3$) δ (ppm) (Ethylene proton) |
|---|---|---|---|---|---|---|
| | | | | C | H | |
| **1a** | 80 | 141—143 | $C_{17}H_{12}O_2$ | 82.24<br>(81.97 | 4.87<br>5.02) | 6.79 (1H, d, $J=16.1$ Hz) |
| **1b** | 57 | 164 | $C_{18}H_{14}O_2$ | 82.42<br>(82.34 | 5.38<br>5.57) | 6.73 (1H, d, $J=16.1$ Hz) |
| **1c** | 43 | 139—140 | $C_{18}H_{14}O_3$ | 77.68<br>(77.23 | 5.07<br>5.00) | 6.64 (1H, d, $J=15.9$ Hz) |
| **1d** | 43 | 144—145 | $C_{18}H_{14}O_3$ | 77.68<br>(76.99 | 5.07<br>5.13) | 6.76 (1H, d, $J=15.9$ Hz) |
| **1e** | 78 | 163—164 | $C_{19}H_{16}O_4$ | 74.01<br>(73.95 | 5.23<br>5.34) | 6.65 (1H, d, $J=15.9$ Hz) |
| **1f** | 77 | 137 | $C_{18}H_{14}O_2$ | 82.42<br>(82.99 | 5.38<br>5.67) | 6.78 (1H, d, $J=16.1$ Hz) |
| **1g** | 77 | 140 | $C_{19}H_{16}O_2$ | 82.58<br>(82.55 | 5.84<br>5.97) | 6.72 (1H, d, $J=16.1$ Hz) |
| **1h** | 55 | 162—163 | $C_{19}H_{16}O_3$ | 78.06<br>(78.14 | 5.52<br>5.76) | 6.63 (1H, d, $J=16.1$ Hz) |
| **1i** | 66 | 212—214 | $C_{17}H_{11}BrO_2$ | 62.40<br>(61.93 | 3.39<br>3.55) | 6.74 (1H, d, $J=16.1$ Hz) |
| **3** | 88 | 191—192 | $C_{21}H_{14}O_2$ | 84.54<br>(84.39 | 4.73<br>4.80) | 6.89 (1H, d, $J=16.1$ Hz) |

Table II. Photocyclized Products (2 and 4)

| Compd. No. | Yield (%) | mp (°C) | Formula | Analysis (%) Calcd (Found) | | PMR (CDCl$_3$) δ (ppm) |
|---|---|---|---|---|---|---|
| | | | | C | H | |
| **2a** | 22 | 144—145 | $C_{17}H_{10}O_2$ | 82.91<br>(82.38 | 4.09<br>4.47) | 10.10 (1H, d, $J=8.5$ Hz), 8.44 (1H, d, $J=7.8$ Hz), 8.13 (1H, d, $J=9.0$ Hz) |
| **2b** | 23 | 151 | $C_{18}H_{12}O_2$ | 83.06<br>(82.66 | 4.65<br>4.84) | 9.92 (1H, s), 8.43 (1H, d, $J=7.8$ Hz), 8.07 (1H, d, $J=9.0$ Hz), 2.64 (3H, s, $-CH_3$) |
| **2c** | 1 | 154 | $C_{18}H_{12}O_3$ | 78.25<br>(78.72 | 4.38<br>4.30) | 9.71 (1H, s), 8.44 (1H, d, $J=8.3$ Hz), 8.08 (1H, d, $J=8.8$ Hz), 4.08 (3H, s, $-OCH_3$) |
| **2d** | 15 | 204 | $C_{18}H_{12}O_3$ | 78.25<br>(78.29 | 4.38<br>4.60) | 10.02 (1H, d, $J=9.3$ Hz), 8.43 (1H, d, $J=7.6$ Hz), 8.05 (1H, d, $J=9.3$ Hz), 3.96 (3H, s, $-OCH_3$) |
| **2e** | 7 | 189 | $C_{19}H_{14}O_4$ | 74.45<br>(74.97 | 4.60<br>4.39) | 9.73 (1H, s), 8.43 (1H, d, $J=7.8$ Hz), 8.02 (1H, d, $J=9.0$ Hz), 4.18 (3H, s, $-OCH_3$), 4.04 (3H, s, $-OCH_3$) |
| **2f** | 11 | 157 | $C_{18}H_{12}O_2$ | 83.06<br>(83.24 | 4.65<br>5.02) | 10.11 (1H, d, $J=8.3$ Hz), 8.23 (1H, s), 8.13 (1H, d, $J=9.3$ Hz), 2.51 (3H, s, $-CH_3$) |
| **2g** | 13 | 194—196 | $C_{19}H_{14}O_2$ | 83.20<br>(83.45 | 5.15<br>5.46) | 9.94 (1H, s), 8.21 (1H, s), 8.08 (1H, d, $J=9.3$ Hz), 7.80 (1H, d, $J=8.3$ Hz), 2.65 (3H, s, $-CH_3$) |
| **2h** | 2 | 194—195 | $C_{19}H_{14}O_3$ | 78.60<br>(78.36 | 4.85<br>4.79) | 9.69 (1H, s), 8.22 (1H, s), 8.06 (1H, d, $J=8.8$ Hz), 7.81 (1H, d, $J=9.0$ Hz), 4.08 (3H, s), $-OCH_3$), 2.51 (3H, s, $-CH_3$) |
| **2i** | 31 | 186—187 | $C_{17}H_9BrO_2$ | 62.77<br>(62.71 | 3.38<br>3.03) | 10.18 (1H, d, $J=8.8$ Hz), 8.67 (1H, d, $J=10.3$ Hz), 8.45 (1H, d, $J=7.8$ Hz) |
| **4** | 11 | 174—175 | $C_{21}H_{12}O_2$ | 85.12<br>(85.14 | 4.08<br>4.12) | 8.55—8.37 (2H, m), 8.09 (1H, d, $J=8.8$ Hz) |

obtained in 22% yield. In the mass spectrum (MS), **2a** showed the molecular ion at *m/e* 246 ($M^+ = C_{17}H_{10}O_2$) and fragment peaks at 218 ($M^+ - CO$), 189 ($218 - HCO$), 163, 123 and 109. The infrared (IR) spectrum of **2a** showed the carbonyl absorption band at 1640 $cm^{-1}$. The ultraviolet spectrum (UV) of **2a** showed absorption maxima at 236, 260 and 320 nm. The PMR spectrum of **2a** has doublet peaks at $\delta$ 10.10 ppm ($J = 8.5$ Hz) due to the C-1 proton. This significant downfield shift of the C-1 proton may be caused by the deshielding effect of the carbonyl group at C-12.[4] The signals at $\delta$ 8.44 (1H, d, $J = 7.8$ Hz) and 8.13 (1H, d, $J = 9.0$ Hz) were assigned to the protons at C-11 and C-5, respectively. From these spectral data and elemental analysis, **2a** was determined to be 12H-benzo[*a*]xanthen-12-one.[5] Irradiation of **1b**—**i** was carried out under the same conditions to yield the corresponding cyclized products (**2b**—**i**). The results of photocyclization are summarized in Table II.



**3**

**4**

styrylnaphthalene

benzo[*c*]phenanthrene

Fig. 2

In the case of **1d** and **1e**, there are two possible directions of cyclization, *ortho* or *para* to the methoxy group on the benzene ring. However, the photocyclized products (**2d** and **2e**) each showed a single spot on TLC. In the PMR spectra of **2d** and **2e**, the C-1 protons appeared at $\delta$ 10.02 (1H, d, $J = 9.3$ Hz) and 9.73 (1H, s), respectively. On the basis of these data, the cyclization occurred *para* to the methoxy group. This result is consistent with the data reported by Kanaoka[6] and Jungmann.[7]

As carbon-halogen bonds are known to be cleaved by photolysis[8] and the elimination of *ortho* groups on stilbenes was observed by some workers,[9] **1i** was irradiated under the same conditions, and **2i**, mp 186—187°C, PMR $\delta$ 10.18 (1H, d, $J = 8.8$ Hz, C-1 proton), was obtained A trace of **2a**, which might be formed by the elimination of HBr, was detected in the reaction mixture by gas chromatography (GC)–MS. This means that the *ortho* elimination process was minor in this photoreaction.

Irradiation of **3**, synthesized from 2-naphthyl aldehyde and 2-methyl-4H-chromen-4-one, gave compound **4**, mp 174—175°C, pale yellow crystals. In the PMR spectrum of **4**, no signals at around $\delta$ 10 ppm could be observed and the C-1 proton appeared at $\delta$ 8.55—8.37 ppm (2H, m) overlapped with C-13 proton. In comparison with the chemical shift of the C-1 proton of **2**, this highfield shift in the case of **4** may be ascribed to the location of the C-1 proton, which lies in the plane of the carbon-oxygen double bond at C-14.[4] From these data, the cyclization was concluded to have occurred at the $\alpha$-position of the naphthalene ring. This cyclization pattern is consistent with that of styryl-naphthalene to benzo[*c*]phenanthrene as shown in Fig. 2.[10]

From Table II, it is clear this photocyclization occurs generally in styryl-chromones and also provides a synthetic route to polycyclic xanthene derivatives.

## Experimental

All melting points were taken on a Yanagimoto MP-S3 micromelting point determination apparatus and are uncorrected. UV and IR spectra were obtained with Nihonbunko UVIDEC-1 and IRA-1 spectrometers. MS were recorded with a JEOL JMS-01SG machine and GC-MS on a Shimadzu LKB-9000 spectrometer. PMR spectra were recorded on a JEOL PS-100 spectrometer with TMS as an internal standard and CDCl$_3$ as the solvent. Chemical shifts are given on the $\delta$ scale (ppm) and coupling constants ($J$ values) are expressed in Hz (s, singlet; d, doublet; t, triplet; m, multiplet).

Photolyses were carried out in a quartz immersion apparatus equipped with a high pressure mercury lamp (Toshiba 400 P) which was cooled internally with running water. Irradiation was conducted through a Pyrex filter under air with stirring.

**General Procedure for the Synthesis of 2-Styryl-4H-chromen-4-ones (1a—i)**——To a solution of Na (0.46 g, 0.02 mol) in 10 ml of EtOH was added 1.6 g of 2-methylchromone (0.01 mol) and 0.012 mol of aromatic aldehyde. The solution was left to stand at room temperature for 12 h then poured into ice-water, and filtered to obtain the precipitate, which was washed with water and recrystallized from methanol to give 2-styrylchromones (**1a**—**i** and **3**). The yields and physical data are summarized in Table I.

**1a**: mp 141—143°C11) IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1620 (C=O). MS *m/e*: 248 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 241 (4.32), 330 (4.64).

**1b**: mp 164°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1620 (C=O). MS *m/e*: 262 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 244 (4.21), 330 (4.29).

**1c**: mp 139—140°C.11) IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 278 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 246 (4.13), 361 (4.51).

**1d**: mp 144—145°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 278 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 256 (4.13), 334 (4.51).

**1e**: mp 163—164°C.11) IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1620 (C=O). MS *m/e*: 308 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 250 (4.11), 367 (4.26).

**1f**: mp 137°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 262 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 272 (3.93), 331 (4.49).

**1g**: mp 140°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 276 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 244 (3.95), 339 (4.32).

**1h**: mp 162—163°C.12) IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1650 (C=O). MS *m/e*: 292 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 250 (4.27), 358 (4.41).

**1i**: mp 212—214°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1650 (C=O). MS *m/e*: 325 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 248 (4.17), 320 (4.38).

**3**: mp 191—192°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1650 (C=O). MS *m/e*: 298 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ (log $\varepsilon$): 292 (4.23), 351 (4.53).

**Irradiation of 2-Styryl-chromones (1a—i and 3) leading to Benzo[*a*]xanthones (2a—i and 4)**——A solution of 500 mg of **1** in 500 ml of benzene was irradiated until the starting material had disappeared (15—20 h). The solvent was evaporated off under reduced pressure and the residue was purified by chromatography on silica gel with benzene. The yields and physical data of **2** and **4** are listed in Table II.

**2a**: mp 144—145°C.5) IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 246 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$) 236 (4.57), 260 (4.52), 320 (3.25).

**2b**: mp 151°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 260 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 238 (4.62), 262 (4.54), 331 (4.28).

**2c**: mp 154°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1650 (C=O). MS *m/e*: 276 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 238 (4.57), 261 (4.51), 354 (4.23).

**2d**: mp 204°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 276 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 238 (4.56), 262 (4.59), 321 (4.20).

**2e**: mp 189°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 306 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 242 (4.72), 262 (4.60), 350 (4.20).

**2f**: mp 157°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 260 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 237 (4.31), 262 (4.29), 324 (3.93).

**2g**: mp 194—196°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 274 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 238 (4.36), 262 (4.33), 333 (3.42).

**2h**: mp 194—195°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1640 (C=O). MS *m/e*: 290 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 238 (4.14), 262 (4.16), 357 (3.72).

**2i**: mp 186—187°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1650 (C=O). MS *m/e*: 324 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 239 (4.56), 262 (4.30), 325 (4.15).

**4**: mp 174—175°C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm$^{-1}$: 1650 (C=O). MS *m/e*: 296 (M$^+$). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log $\varepsilon$): 229 (4.70), 292 (4.54), 336 (3.86).

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