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Synthesis of Bis(silyloxy) Cross-Conjugated Polyenes and Their Sequential Ring Formations via Electrocyclization

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Presented are the synthesis of several bis(silyloxy) cross-conjugated polyenes and some synthetic utilization of these new types of conjugation systems via thermal or photochemical electrocyclization.

Diene-transmissive Diels-Alder reactions of bis(silyloxy)-substituted cross-conjugated trienes **A**, as well as equivalent reactions, have found wide synthetic applications as a new strategy to construct carbocycles and heterocycles which consist of two six-membered rings.¹⁾ It is especially important that this sequential ring-forming reaction offers a highly regio- and stereoselective synthetic route to fused ring systems with many functional groups.²⁾

Our long-standing interest in developing the synthetic utilization of bis(silyloxy) cross-conjugated polyenes let us deal in the synthetic work of new types of cross-conjugated polyenes and further investigate a new synthetic method consisting of their sequential cycloaddition or cyclization reactions.

Our new method for sequential cycloaddition reaction of bis(silyloxy) cross-conjugated polyenes **B** involves i) a moiety of linearly conjugated triene of polyenes **B** undergoes the initial intramolecular 6π -electrocyclization forming **C** and ii) the second Diels-Alder cycloaddition reaction across the newly formed bis(silyloxy) diene leading to fused 6/6-ring compounds **D** as outlined in Scheme 1. Transformation of the cyclization products **C** into the dehydrogenated compound **E**, and further into the corresponding chromone derivatives, has been also carried out.

Results and Discussion

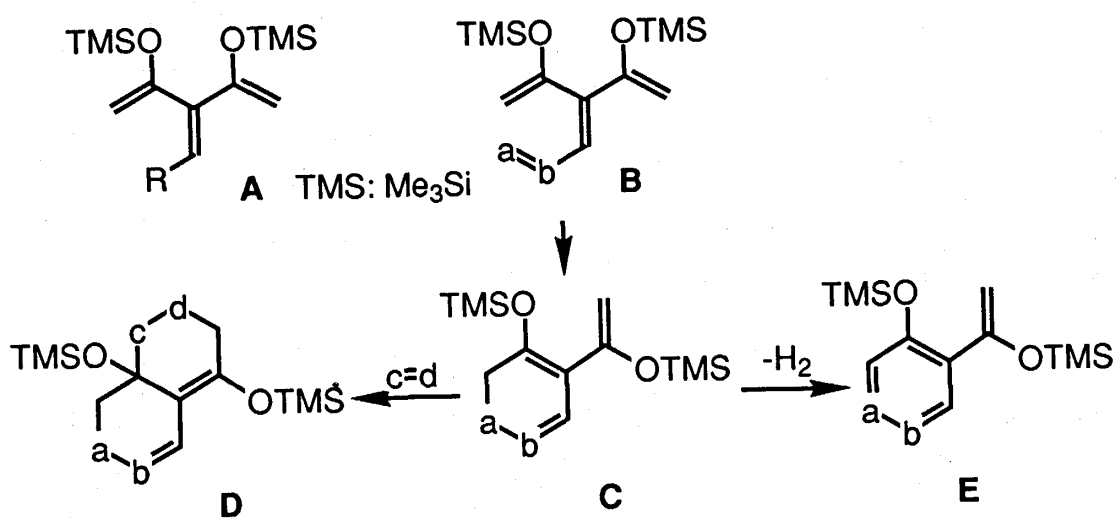
Synthesis of Bis(silyloxy) Cross-Conjugated Polyenes. 2,4-Pentanedione underwent ready condensations with aldehydes such as (E)-cinnamaldehyde,³⁾ 2-furanecarbaldehyde,⁴⁾ and 2-thiophenecarbaldehyde⁴⁾ to produce the corresponding 3-alkylidene-2,4-pentanediones **1a-c** (Scheme 2). These diketones **1a-c** were then silylated with chlorotrimethylsilane in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dichloromethane⁵⁾ to give 3-cinnamylidene-(**2a**, 76%), 3-(2-furylmethylene)-(**2b**, 94%), and 3-(2-thienylmethylene)-2,4-bis(trimethylsilyloxy)-1,4-pen-

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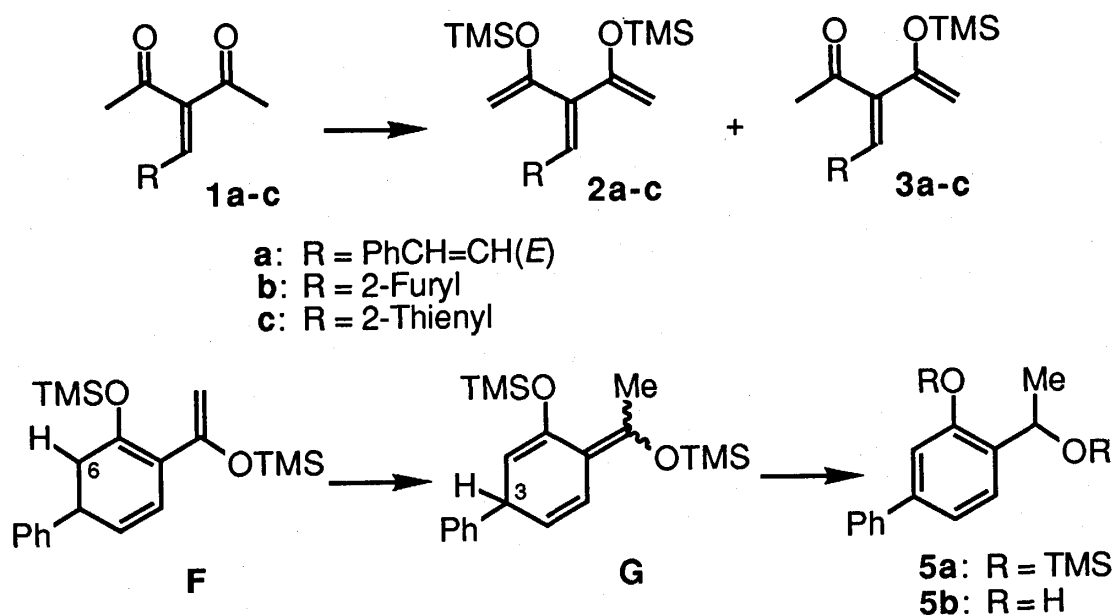
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tadiene (**2c**, 97%).

The purity of the polyenes **2a-c** thus obtained was about 80%. Although they could be purified by silica gel column chromatography, a significant decomposition of **2** into diketones **1** and dienyl ketones **3** took place on silica gel to result in some critical weight loss of **2**. Thus, yields of pure samples of **2** were finally 34% for **2a**, 31% for **2b**, and 35% for **2c**. Attempted separation of pure **2** by vacuum distillation was not successful either, mixtures of **2b** and **3b** (4:1, 72%) or **2c** and **3c** (4:1, 68%) being only obtained. Therefore, the polyenes **2a-c** obtained pure by silica gel column chromatography were used for the following reactions.



Scheme 1.



Scheme 2.

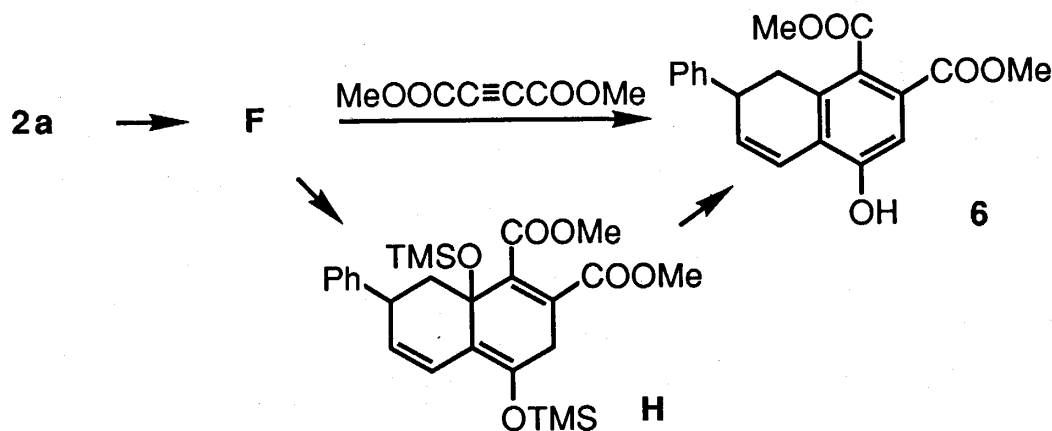
On the other hand, when diketone **1a** was silylated with chlorotrimethylsilane by use of triethylamine under reflux in dry *N,N*-dimethylformamide (DMF),⁶⁾ a cyclized product **5a** was obtained in 30% yield. This unusual reaction probably took place through the steps shown in Scheme 2: i) the initial thermal electrocyclic reaction of polyene **2a** forming six-membered ring **F** with a cross-conjugated triene moiety, ii) a 1,5-proton migration forming another cross-conjugated triene **G**, and iii) the further 1,5-proton migration leading to aromatic compound **5a**. Compound **5a** was easily hydrolyzed to **5b** in quantitative yield on treatment with MeOH.

This result indicates a possible formation of cross-conjugated trienes, e.g. **F**, through 6π -electrocyclic reaction of cross-conjugated polyenes **2** by a proper choice of reaction conditions. Therefore, an effective utilization of the resulting cross-conjugated trienes in Diels-Alder cycloaddition is expected.

Synthetic Utilization of Bis(silyloxy) Cross-Conjugated Polyenes 2a-c. First of all, a sequence of an electrocyclic reaction and Diels-Alder cycloaddition was investigated by employing polyene **2a**. Heating **2a** under reflux in dry xylene for 24 h, followed by treating the resulting reaction mixture with an equivalent of dimethyl acetylenedicarboxylate (DMAD) at 90°C for 36 h, afforded a dihydronaphthalene derivative **6** in 25% yield, after work up with methanol (Scheme 3). The structure was confirmed on the basis of the spectral data as well as the elemental analysis.

This reaction probably proceeded through the steps shown in Scheme 3. The initial 6π -electrocyclization of **2a** forms **F** that carries a peripheral diene moiety activated by the two trimethylsilyloxy substituents. The intermolecular second cycloaddition with DMAD leads to another intermediate **H**. A 1,4-elimination of trimethylsilanol from **H** is followed by hydrolysis into the isolated product **6**.

Disappointingly, intermolecular Diels-Alder cycloadditions of the peripheral diene **F** with olefinic dienophiles were not clean reactions, mixture of complex products being formed. As a



Scheme 3.

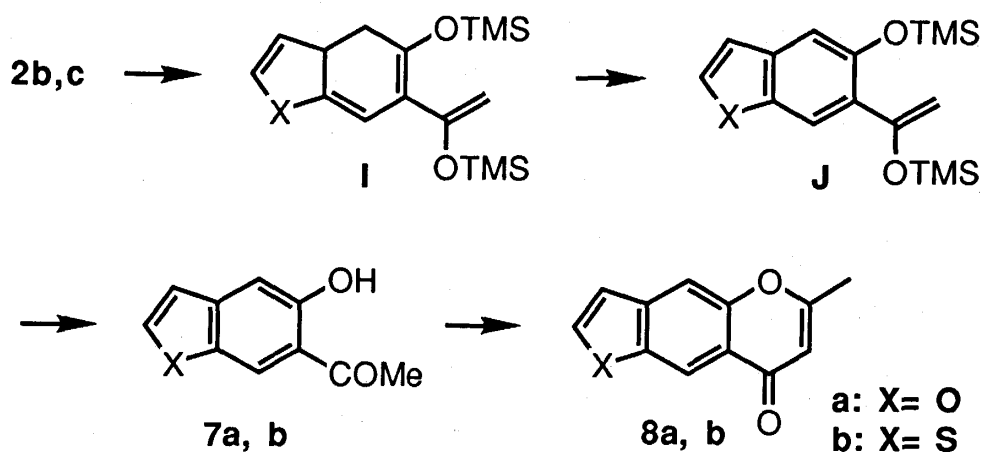
result, dienophiles which can be effectively utilized in the reaction with **F** would be limited to acetylenic ones such as DMAD.

Since heating **2b** under reflux in toluene for 24 h was not sufficient enough to cause a thermal 6π -electrocyclization and **2b** was quantitatively recovered, its photochemical cyclization was investigated. Irradiation of the diluted solution of **2b** in benzene by using a 400-W mercury lamp for 6 h gave, after the work up with methanol, a benzofuran derivative **7a** in 70% yield (Scheme 4). A similar irradiation procedure of **2c** gave a benzothiophene derivative **7b** only in 12% yield, which was accompanied by a lot of products insoluble in benzene.

Both **7a** and **7b** correspond to the products which are derived by a spontaneous dehydrogenation of the photocyclized products **I** followed by hydrolytic desilylation. This unexpectedly ready dehydrogenation of **I** forced us to give up their utilization in the further Diels-Alder cycloaddition reaction.⁷⁾

As these transformations are a new process to construct the heterocycle-fused benzene ring bearing both a hydroxy and an adjacent acetyl functional groups, they can be promising synthetic intermediates for the synthesis of heterocycle-fused chromone derivatives.⁸⁾

In this view, the condensation of **7a** and **7b** with ethyl acetate was carried out to give furochromone **8a** (70%) and thienochromone **8b** (52%), respectively. Their structures were based upon spectral data. To the best of our knowledge, any process leading to chromones via a photocyclization is unknown. This sequence offers a convenient and short synthesis of heterocycle-fused chromones by starting from readily available 3-(heteroarylmethylene)-2,4-pentadienes (Scheme 4).⁹⁾



Scheme 4.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO A-720 spectrometer. ¹H NMR spectra

were recorded on a Hitachi R-40 (90 MHz) or a JEOL FX-100 (100 MHz) instrument, and ^{13}C NMR on a JEOL FX-100 (25.05 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra as well as high-resolution mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. Elemental analyses were performed on a Hitachi 026 CHN analyzer. For preparative column chromatography Silica gel 60 (Merck) was employed. Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50°C unless otherwise stated.

Material. 3-Alkylidene-2,4-pentanediones **1a-c** were prepared according to the procedure reported in the literatures.^{3) 4)}

General Procedure for the Synthesis of Cross-conjugated Polyenes 2. To a mixture of a 2-alkylidene-2,4-pentanedione derivative **1** and DBU (2 equivalents) in dichloromethane (6–7 ml per 10 mmol of **1**) was added chlorotrimethylsilane (2 equivalents) at room temperature. The mixture was heated at 40°C for 24 h under nitrogen and then all the volatile materials were removed in vacuo. The residue was triturated with hexane (20 ml per 10 mmol of **1**), the hexane separated from the insoluble DBU · HCl was concentrated in vacuo, and the crude product **2** was purified by column chromatography.

3-Cinnamylidene-2,4-bis(trimethylsilyloxy)-1,4-pentadiene (2a): The reaction between 3-cinnamylidene-2,4-pentanedione (**1a**, 6.42 g, 30 mmol) and chlorotrimethylsilane (8.5 ml, 67 mmol) in the presence of DBU (9.12 g, 60 mmol) and the followed column chromatography of the crude product (8.2 g, 76%) with hexane-benzene (9:1 v/v) gave **2a** (4.0 g, 36%) as a pale yellow oil: IR (neat) 1625, 1595, 1250, and 850 cm^{-1} ; ^1H -NMR (CDCl_3) δ = 0.20, 0.24 (each 9H, s, TMS), 4.30, 4.40, 4.60, 4.76 (each 1H, s, 1- and 5- CH_2), 6.63 (1H, d, J = 10.0 Hz, $\text{PhCH}=\text{CH}-$), 6.63 (1H, d, J = 16.5 Hz $\text{PhCH}=\text{CH}$), and 7.00–7.50 (6H, m, ArH and $\text{PhCH}=\text{CH}$); MS m/z 358 (M^+ , base peak).

3-(2-Furylmethylene)-2,4-bis(trimethylsilyloxy)-1,4-pentadiene (2b): The reaction between 3-(2-furylmethylene)-2,4-pentanedione (**1b**, 3.32 g, 19 mmol) and chlorotrimethylsilane (5.2 ml, 41 mmol) in the presence of DBU (5.67 g, 37 mmol) and the followed column chromatography of the crude product (5.74 g, 94%) with hexane-benzene (1:1 v/v) gave **2b** (1.85 g, 31%). The fraction eluted with benzene gave **3b** (0.36 g, 8%). Further elution with hexane-ethyl acetate (3:1 v/v) gave **1b** (1.71 g, 51%). The attempted purification of the crude **2b** (3.45 g) by vacuum distillation (at 120°C at 0.3 mmHg) afforded a 4:1 mixture of **2b** and **3b** (2.62 g, 72% by ^1H -NMR). **2b**: Pale yellow oil; IR (neat) 1635, 1600, 1250, and 845 cm^{-1} ; ^1H -NMR (CDCl_3) δ = 0.20, 0.28 (each 9H, s, TMS), 4.29, 4.55 (each 1H, d, J = 1.0 Hz, 1- and/or 5- CH_2), 4.45, 4.78 (each 1H, br s, 1- and/or 5- CH_2), 6.38 (1H, m, 4-H of furan ring), 6.68 (1H, m, 3-H of furan ring), 6.70 (1H, s, $\text{CH}=\text{CH}$), and 7.34 (1H, m, 5-H of furan ring); ^{13}C -NMR (CDCl_3) δ = 0.00, 0.20, 95.65, 95.80, 110.98, 111.91, 116.02, 134.32, 142.23, 152.34, 153.32, and 155.22; MS

m/z (rel intensity) 322 (M^+ , base peak), 307 (35), 147 (32), and 73 (over). HRMS Found: m/z 332.1426. Calcd for $C_{16}H_{26}O_3Si_2$: M , 332.1421. **3b**: Only 1H -NMR spectrum of this compound is available. 1H -NMR ($CDCl_3$) δ =0.24 (9H, s, TMS), 2.36 (3H, s, COMe), 4.42, 4.65 (each 1H, d, J =1.5 Hz, $=CH_2$), 6.46 (1H, m, 4-H of furan ring), 6.97 (1H, m, 3-H of furan ring), 7.28 (1H, s, $CH=$), and 7.49 (1H, m, 5-H of furan ring).

3-(2-Thienylmethylene)-2,4-bis(trimethylsilyloxy)-1,4-pentadiene (2c): The reaction between 3-(2-thienylmethylene)-2,4-pentanedione (**1c**, 5.83 g, 30 mmol) and chlorotrimethylsilane (8.4 ml, 66 mmol) in the presence of DBU (9.13 g, 60 mmol) and the followed column chromatography of the crude product (9.77 g, 97%) with hexane-benzene (1:1 v/v) gave **2c** (3.56 g, 35%) and **3c** (1.34 g, 19%). Further elution with hexane-ethyl acetate (3:1 v/v) gave **1c** (2.31 g, 40%). An attempted purification of the crude **2c** (3.13 g) by vacuum distillation (at 140°C at 0.3 mmHg) gave a 4:1 mixture of **2c** and **3c** (2.23 g, 68% by 1H -NMR). **2c**: Pale yellow oil; IR (neat) 1630, 1595, 1250, and 845 cm^{-1} ; 1H -NMR (C_6D_6) δ =0.20, 0.22 (each 9H, s, TMS), 4.57, 4.71 (each 1H, d, J =1.0 Hz, 1- and/or 5- CH_2), 4.55, 5.00 (each 1H, br s, 1- and/or 5- CH_2), 6.67 (1H, dd, J =5.5 and 3.5 Hz, 4-H of thiophene ring), 6.87 (1H, dd, J =5.0 and 1.5 Hz, 3-H of thiophene ring), 7.06 (1H, dd, J =3.5 and 1.5 Hz, 5-H of thiophene ring), and 7.31 (1H, t, J =0.5 Hz, $CH=$); ^{13}C -NMR (C_6D_6) δ =0.00, 0.29, 95.48, 97.71, 121.66, 126.77, 127.60, 130.36, 134.83, 140.18, 153.48, and 155.78; MS m/z (rel intensity) 338 (M^+ , 20) and 73 (base peak). HRMS Found: m/z 338.1186. Calcd for $C_{16}H_{26}O_2SSi_2$: M , 338.1189. **3c**: Only 1H NMR of this compound is available. 1H -NMR (C_6D_6) δ =0.19 (9H, s, TMS), 2.20 (3H, s, COMe), 4.52, 4.63 (each 1H, d, J =1.0 Hz, $=CH_2$), 6.57 (1H, dd, J =5.0 and 3.5 Hz, 4-H of thiophene ring), 6.86 (1H, m, 3-H of thiophene ring), 6.95 (1H, m, 5-H of thiophene ring), and 7.68 (1H, br s, $CH=$).

Trimethylsilylation of 1a in DMF Leading to 5a. To a mixture of **1a** (4.49 g, 20 mmol) and triethylamine (8.90 g, 88 mmol) in dry DMF (30 ml) was added chlorotrimethylsilane (5.57 g, 44 mmol). The mixture was refluxed for 48 h under nitrogen, diluted with hexane (200 ml), and washed with cold aqueous $NaHCO_3$. The organic layer separated was dried over anhydrous $MgSO_4$ and concentrated in vacuo to give a viscous oil. Vacuum distillation of the viscous oil gave **5a** (2.1 g, 30%). Hydrolysis of **5a** was carried out in methanol (30 ml) at room temperature overnight to give **5b** in quantitative yield. **5a**: Viscous oil; bp 150–155°C (1 mmHg); IR (neat) 1250 and 850 cm^{-1} ; 1H -NMR ($CDCl_3$) δ =0.01, 0.03 (each 9H, s, TMS), 1.40 (3H, d, J =6.0 Hz, Me), 5.15 (1H, q, J =6.0 Hz, $-CH-O$), 6.90 (1H, s), and 7.00–7.60 (4H, m); MS m/z 358 (M^+ , base peak). **5b**: Viscous oil; IR (neat) 3300 cm^{-1} ; 1H -NMR ($CDCl_3$) δ =1.50 (3H, d, J =6.0 Hz, Me), 5.00 (1H, q, J =6.0 Hz, $-CH-O$), 6.95 (1H, s), and 7.00–7.70 (4H, m).

Sequential Electrocyclization/Diels-Alder Reaction of 1a Leading to 6. A solution of **1a** (1.5 g, 4 mmol) in dry xylene (15 ml) was refluxed for 24 h under nitrogen and cooled to room temperature. To the resulting solution was added DMAD (0.5 g, 4 mmol) and the mixture was

heated at 90°C for 36 h under nitrogen. The xylene was evaporated in vacuo and the residue was treated with methanol (20 ml) at room temperature overnight. The methanol was evaporated in vacuo. The viscous oil was chromatographed over silica gel with hexane-ethyl acetate (1:2 v/v) as an eluent to give **6** (0.34 g, 25%): Colorless prisms from diethyl ether-hexane; mp 57.5–58.5°C; IR (KBr) 3400 and 1700 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =2.80–3.10 (2H, m, 5- CH_2), 3.50–3.70 (1H, m, 6-H), 3.78, 3.83 (each 3H, s, CO_2Me), 6.10 (1H, dd, J =10.0 and 3.2 Hz, 7-H), 6.90 (1H, dd, J =10.0 and 2.5 Hz, 8-H), 7.23 (6H, br s, PhH and 2-H), and 7.20 (1H, s, OH); $^{13}\text{C-NMR}$ (CDCl_3) δ =33.64, 40.15, 52.48, 52.66, 115.59, 121.11, 125.22, 126.22, 126.69, 126.81, 127.51, 128.63, 133.56, 134.32, 144.07, 151.88, 166.14, and 170.37; MS m/z (rel intensity) 338 (M^+ , 59), 307 (50), 306 (base peak), 305 (22), 291 (22), 278 (22), 229 (24), and 91 (25). Found: C, 70.72; H, 5.38%. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_5$: C, 70.99; H, 5.36%.

Irradiation of 2b Leading to 7a. A solution of **2b** (1.5 g, 4.6 mmol) in dry benzene (360 ml) was irradiated with a 400W mercury lamp for 6h. The solvent was evaporated in vacuo and the residue was treated with methanol overnight. The methanol was evaporated in vacuo and the resulting viscous oil was chromatographed over silica gel with hexane-ethyl acetate (9:1 v/v) as an eluent to give **7a** (0.57 g, 70%): Yellow needles from methanol; mp 88.5–89°C; IR (KBr) 1635 (sh), 1620, and 1590 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =2.64 (3H, s, COMe), 6.66 (1H, m, 3-H), 7.05 (1H, s, 4-H), 7.70 (1H, m, 2-H), 7.80 (1H, s, 7-H), and 12.02 (1H, s, OH); $^{13}\text{C-NMR}$ (CDCl_3) δ =26.65, 106.83, 108.13, 112.54, 116.66, 135.42, 148.13, 150.48, 158.37, and 204.19; MS m/z (rel intensity) 176 (M^+ , 51) and 161 (base peak). Found: C, 68.27; H, 4.61%. Calcd for $\text{C}_{10}\text{H}_8\text{O}_3$: C, 68.18; H, 4.58%.

Irradiation of 2c Leading to 7b. A solution of **2c** (2.136 g, 6.12 mmol) in dry benzene (400 ml) was irradiated with a 400W mercury lamp for 20h. Work up of the reaction mixture was similar to that described above. The resultant viscous oil was column-chromatographed over silica gel by using a mixture of hexane-ethyl acetate (9:1 v/v) as an eluent to give **7b** (0.14 g, 12%): Yellow needles from methanol; mp 119–120°C; IR (KBr) 1630 and 1560 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =2.67 (3H, s, COMe), 7.16 (1H, d, J =5.5 Hz, 3-H), 7.28 (1H, s, 4-H), 7.62 (1H, d, J =5.5 Hz, 2-H), 8.20 (1H, s, 7-H), and 11.91 (1H, s, OH); $^{13}\text{C-NMR}$ (CDCl_3) δ =26.65, 110.83, 118.36, 123.48, 125.66, 130.30, 133.71, 146.13, 158.89, and 204.25; MS m/z (rel intensity) 192 (M^+ , 63), 177 (base peak), 121 (29), and 42 (21). Found: C, 62.34; H, 4.16%. Calcd for $\text{C}_{10}\text{H}_8\text{O}_2\text{S}$: C, 62.48; H, 4.19%.

Transformation of 7a into Furochromone 8a. To a solution of **7a** (1.0 g, 5.7 mmol) in dry ethyl acetate (10 ml) was added sodium hydride (60% in mineral oil, 1.0 g, 25 mmol). The mixture was stirred at room temperature for 24 h under nitrogen and then poured into ice-cold 0.1M hydrochloric acid (6 ml). The resultant precipitates were collected by filtration to give **8a** (0.8 g, 70%): Colorless needless from methanol; mp 173–174°C; IR (KBr) 1650, 1460, 1430, and 855 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =2.39 (3H, s, Me), 6.11 (1H, s, 7-H), 6.81 (1H, d, J =3.3 Hz, 3-H), 7.56 (1H, s, 4-H), 7.75 (1H, d, J =3.3 Hz, 2-H), and 8.43 (1H, s, 9-H); $^{13}\text{C-NMR}$

(CDCl₃) δ =20.66, 29.70, 106.55, 106.85, 108.84, 109.02, 127.78, 149.65, 151.90, 152.60, 166.09, and 178.64; MS m/z (rel intensity) 200 (M⁺, base peak), 172 (28), 160 (48), and 132 (25). Found: C, 72.13; H, 4.35%. Calcd for C₁₂H₈O₃: C, 72.00; H, 4.03%.

Transformation of 7b into Thiochromone 8b. To a solution of 7b (0.077 g, 0.40 mmol) in dry ethyl acetate (2 ml) was added sodium hydride (60% in mineral oil, 0.08 g, 2.0 mmol). The mixture was stirred at room temperature overnight under nitrogen, poured into ice-cold 0.1M hydrochloric acid, and extracted with dichloromethane (30 ml). The extracts were dried over anhydrous magnesium sulfate and evaporated in vacuo. To the residue was added acetic acid (3 ml) and a few drops of conc. hydrochloric acid. The mixture was stirred at room temperature and then concentrated in vacuo. The resultant viscous oil was chromatographed over silica gel by using hexane-ethyl acetate (9:1 v/v) as an eluent to give 7b (0.018 g, 23%). Further elution with hexane-ethyl acetate (3:1 v/v) afforded 8b (0.045 g, 52%): Colorless needles from methanol; mp 144–146°C; IR (KBr) 1640 and 1600 cm⁻¹; ¹H-NMR (CDCl₃) δ =2.40 (3H, s, Me), 6.18 (1H, s, 7-H), 7.35 (1H, d, J =5.5 Hz, 3-H), 7.70 (1H, d, J =5.5 Hz, 2-H), 7.80 (1H, s, 4-H), and 8.67 (1H, s, 9-H); MS m/z (rel intensity) 216 (M⁺, base peak), 176 (39), and 57 (27). Found: C, 66.41; H, 3.91%. Calcd for C₁₂H₈O₂S: C, 66.65; H, 3.73%.

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