

Syntheses of 2*H*-1-Benzothiopyran-2-ones (Thiocoumarins) and Related Compounds from Benzenethiols and Diketene

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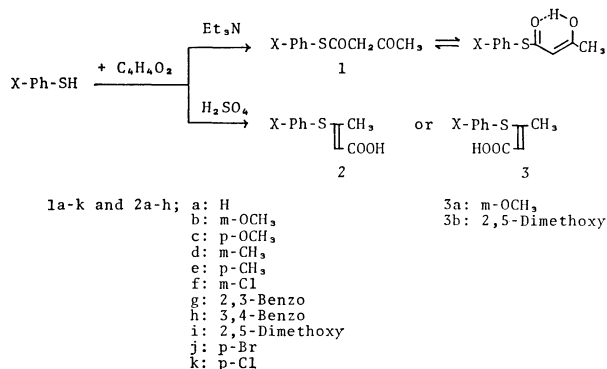
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The products formed by the reaction of benzenethiols with diketene in the presence of H_2SO_4 are (*E*)- β -(arylthio)crotonic acids (**2**) and/or isomeric (*Z*)- β -(arylthio)crotonic acids and not, as has been reported, *S*-phenyl 3-oxobutanethioates (**1**). Compounds **1a–k**, as the precursor of thiocoumarins, were prepared from benzenethiols and diketene in the presence of triethylamine. The reaction of **1** with various condensing agents has been examined to prepare 2*H*-1-benzothiopyran-2-ones (thiocoumarins). It is found that 4-methyl(thiocoumarins) were conveniently prepared by the reaction of **1** with anhydrous aluminium chloride in yields of 16–48%. When **1** was treated with PPA, isomeric 2-methyl(thiochromones) were preferentially obtained in yields of 5–66%, and compound **2** was isolated as an intermediate. The spectral characteristics of 4-methyl(thiocoumarins) have also been described.

It is well known that 2*H*-1-benzothiopyran-2-ones (thiocoumarins) can not be obtained by the Pechmann reaction of benzenethiols.¹⁾ Thiocoumarins are generally prepared from the unstable 2-mercaptobenzaldehydes which require multistage processes from benzenethiols.²⁾ Although Konishi *et al.* reported the convenient method to prepare thiocoumarins by the cyclization of *S*-phenyl 3-oxobutanethioates with PPA,³⁾ the products are mostly not thiocoumarins, but isomeric thiochromones (4*H*-1-benzothiopyran-4-ones).⁴⁾ Furthermore, recently we found that the *S*-phenyl 3-oxobutanethioates, described in our previous paper,⁴⁾ were really isomeric (*E*)- β -(arylthio)crotonic acids (**2**) and/or (*Z*)- β -(arylthio)crotonic acids (**3**).

We have now prepared a number of *S*-(substituted phenyl) 3-oxobutanethioates (**1**) from benzenethiols and diketene, and studied the cyclization of **1** with various condensing agents to prepare thiocoumarin derivatives. These works were reported in a preliminary form,⁵⁾ but in this paper we wish to report further details of these reactions. We also wish to report the spectral characteristics of 4-methyl(thiocoumarins), compared with those of isomeric 2-methyl(thiochromones).

of authentic (*E*)- β -(arylthio)crotonic acids (**2**) were prepared from sodium (*E*)- β -chlorocrotonate and sodium benzenethiolates by a similar method to that for **2a**.⁷⁾ The IR spectra and mp's of previously reported products, obtained by the reaction of benzenethiols with diketene in the presence of H_2SO_4 , were in agreement with those of authentic samples (**2**), except for *m*-methoxy (**3a**) and 2,5-dimethoxy (**3b**) derivatives. No depression in melting point was observed in admixture of any pair of those samples. However, the melting points and IR spectra of *m*-methoxy and 2,5-dimethoxy derivatives are quite different from those of authentic samples. These compounds were assigned to (*Z*)- β -(arylthio)crotonic acid derivatives (**3**), as isomers of **2**, on the basis of NMR spectra of (*Z*)- and (*E*)- β -thio-substituted crotonates.⁸⁾ That is, the chemical shifts for the vinylic methyl group and vinylic proton for **3a** and **3b** showed upfield chemical shift of *ca.* 0.5 ppm for vinylic methyl group and downfield chemical shift of *ca.* 0.65 ppm for vinylic proton, compared to the corresponding values for authentic samples. From the results, the products obtained from the reaction of benzenethiols with diketene in the presence of H_2SO_4 are not **1**, described in previous paper, but the isomeric **2** and/



Scheme 1.

Results and Discussion

Preparation of *S*-Phenyl 3-Oxobutanethioates.

Recently Yaggi and Douglas reported that the product obtained from the reaction between benzenethiols and diketene in the presence of sulfuric acid was (*E*)- β -(arylthio)crotonic acid **2** (X=H or *p*-Cl).⁶⁾ A number

TABLE 1. THE NMR SPECTRA OF *S*-PHENYL 3-OXOBUTANETHIOATES (**1**)

Compound No.	X	NMR in CCl ₄ (ppm)
1f	<i>m</i> -Cl	1.95 and 2.25 (total 3H, each s), 3.65 and 5.50 (total <i>ca.</i> 1.2H, each s), 7.20–7.60 (4H, m), 12.20 (broad)
1g	2,3-Benzo	1.90 and 2.15 (total 3H, each s), 3.68 and 5.45 (total <i>ca.</i> 1.4H, each s), 7.20–8.20 (7H, m)
1i	2,5-Dimethoxy	1.90 and 2.18 (total 3H, each s), 3.73 (3H, s), 3.75 (3H, s), 3.52 and 5.36 (total <i>ca.</i> 1.2H, each s), 6.50–7.00 (3H, m)
1j	<i>p</i> -Br	1.92 and 2.20 (total 3H, each s), 3.58 and 5.32 (total <i>ca.</i> 1.3H, each s), 7.00–7.55 (4H, m), 12.50 (broad)

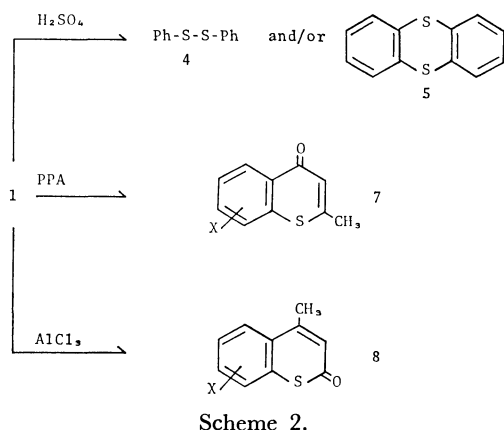
See Ref. 5 for **1a–e** and **1h**.

TABLE 2. SPECTRAL DATA OF 4-METHYL(THIOCOUMARINS) (**8**)

Compound X	NMR (ppm) in CDCl ₃	ν_{CO} (cm ⁻¹)	UV λ_{max} ($\epsilon \times 10^{-4}$) (nm) in EtOH	m/e (rel. intensity)
8a H	$\left\{ \begin{array}{l} 2.58 \text{ (3H, s)} \\ 6.62 \text{ (1H, s)} \\ 7.45\text{--}7.56 \text{ (3H, m)} \\ 7.95 \text{ (1H, m)} \end{array} \right.$	1635	$\left\{ \begin{array}{l} 235 \text{ (2.5), } 241 \text{ (2.5)} \\ 289 \text{ (0.7), } 298 \text{ (0.7)} \\ 342 \text{ (0.29)} \end{array} \right.$	176 (M, 46), 148 (M-28, 76) 147 (M-29, 100)
8d 7-CH ₃	$\left\{ \begin{array}{l} 2.44 \text{ (3H, s)} \\ 2.52 \text{ (3H, s)} \\ 6.53 \text{ (1H, s)} \\ 7.20\text{--}7.30 \text{ (2H, m)} \\ 7.78 \text{ (1H, d, } J=10 \text{ Hz)} \end{array} \right.$	1645	$\left\{ \begin{array}{l} 230 \text{ (2.4), } 239 \text{ (2.4)} \\ 295 \text{ (0.8), } 303 \text{ (0.9)} \\ 343 \text{ (0.4)} \end{array} \right.$	190 (M, 45), 162 (M-28, 100) 161 (M-29, 100)
8e 6-CH ₃	$\left\{ \begin{array}{l} 2.50 \text{ (3H, s)} \\ 2.54 \text{ (3H, s)} \\ 6.62 \text{ (1H, s)} \\ 7.44 \text{ (2H, s)} \\ 7.78 \text{ (1H, s)} \end{array} \right.$	1635	$\left\{ \begin{array}{l} 237 \text{ (2.8), } 243 \text{ (3.0)} \\ 290 \text{ (0.8), } 298 \text{ (0.8)} \\ 350 \text{ (0.3)} \end{array} \right.$	190 (M, 48), 162 (M-28, 95) 161 (M-29, 100)
8f 7-Cl	$\left\{ \begin{array}{l} 2.54 \text{ (3H, s)} \\ 6.57 \text{ (1H, s)} \\ 7.20\text{--}7.50 \text{ (2H, m)} \\ 7.80 \text{ (1H, d, } J=10 \text{ Hz)} \end{array} \right.$	1645	$\left\{ \begin{array}{l} 233 \text{ (2.8), } 241 \text{ (2.9)} \\ 266 \text{ (1.1), } 290 \text{ (1.2)} \\ 301 \text{ (1.0), } 337 \text{ (0.3)} \end{array} \right.$	212 (M+2, 9), 210 (M, 24) 184 (40), 183 (47) 182 (M-28, 100), 181 (M-29, 90)
8g 7,8-Benzo	$\left\{ \begin{array}{l} 2.65 \text{ (3H, s)} \\ 6.68 \text{ (1H, s)} \\ 7.48\text{--}8.37 \text{ (6H, m)} \end{array} \right.$	1650 1630	$\left\{ \begin{array}{l} 275 \text{ (2.6), } 286 \text{ (2.5)} \\ 319 \text{ (0.6), } 333 \text{ (0.6)} \\ 373 \text{ (0.24), } 390 \text{ s (0.19)} \end{array} \right.$	226 (M, 43), 198 (M-28, 100) 197 (M-29, 79)
8h 5,6-Benzo	$\left\{ \begin{array}{l} 2.60 \text{ (3H, s)} \\ 6.48 \text{ (1H, s)} \\ 7.25\text{--}8.30 \text{ (6H, m)} \end{array} \right.$	1650 s 1630	$\left\{ \begin{array}{l} 246 \text{ (5.4), } 281 \text{ (2.2)} \\ 295 \text{ (2.3), } 333 \text{ (1.2)} \\ 380 \text{ b (0.2)} \end{array} \right.$	226 (M, 64), 198 (M-28, 100) 197 (M-29, 57)
8j 6-Br	$\left\{ \begin{array}{l} 2.50 \text{ (3H, s)} \\ 6.50 \text{ (1H, s)} \\ 7.30\text{--}7.65 \text{ (2H, m)} \\ 7.88 \text{ (1H, d, } J=2 \text{ Hz)} \end{array} \right.$	1625	$\left\{ \begin{array}{l} 248 \text{ (4.5), } 287 \text{ (0.65)} \\ 298 \text{ (0.60), } 351 \text{ (0.28)} \end{array} \right.$	256 (M+2, 71), 254 (M, 68), 228 (100), 227 (83), 226 (M-28, 98), 225 (M-29, 72)
8k 6-Cl	$\left\{ \begin{array}{l} 2.50 \text{ (3H, s)} \\ 6.50 \text{ (1H, s)} \\ 7.35 \text{ (2H, s)} \\ 7.74 \text{ (1H, s)} \end{array} \right.$	1625	$\left\{ \begin{array}{l} 246 \text{ (4.5), } 287 \text{ (0.65),} \\ 298 \text{ (0.60), } 350 \text{ (0.29)} \end{array} \right.$	212 (M+2, 28), 210 (M, 73) 184 (38), 183 (45), 182 (M-28, 100), 181 (M-29, 96)

or **3**.

S-Phenyl 3-oxobutanethioates (**1**), precursor of thiocoumarins, were quantitatively prepared by the reaction of benzenethiols with diketene in the presence of triethylamine for 5–20 h at room temperature, and existed in a mixture of the keto-enol tautomeric forms, NMR spectra of which were shown in Table 1.



The Reaction of S-Phenyl 3-Oxobutanethioates (1) with Various Condensing Agents. The reaction of **1a** with sulfuric acid gave diphenyl disulfide (**4**) which was formed by decomposition of **1a**, and/or thianthrene derivatives (**5** and thianthrene 5,10-bis(dioxide) **6**) as

oxidized products of **4**.

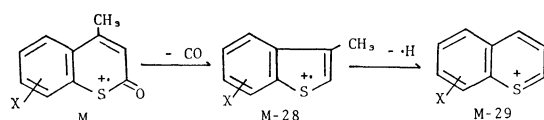
2-Methyl(thiochromone) derivatives (**7**), as the isomeric product of thiocoumarin, were preferentially obtained by treating **1** with polyphosphoric acid (PPA) at 70 °C. In the case of *m*-methoxy derivative (**1b**), only thiocoumarin **8b** was obtained. Compound **8b** also could be obtained from **2b** (X=*m*-OCH₃) and PPA. However, the other *S*-phenyl 3-oxobutanethioates, even with substituents such as methoxyl group(s) (**1c** and **1i**) gave the thiochromone **7** in yields of 10–79%. At lower temperatures of 5–10 °C, the same reaction of **1** afforded (*E*)- β -(arylthio)crotonic acid **2** (X=H, *m*-CH₃, or *p*-CH₃) in a low yield (4–10%). It is also known that the reaction of **1a** or **1d** with concd H₂SO₄ (1 equivalent) in Et₂O gave **2** (X=H or *m*-CH₃) in a yield of 21%.⁹ It is concluded that compound **2** will be an intermediate to give **7**.

In the case of the use of anhydrous aluminium chloride as a condensing agent, some of 4-methyl-(thiocoumarins) (**8**) were conveniently obtained in yields of 10–48% and no 2-methyl(thiochromones) (**7**) were obtained. However, the reaction of all methoxy derivatives of **1** with AlCl₃ gave only an oily undetermined material, and none of thiocoumarins was isolated. As the direct reaction of **1** with AlCl₃, without solvent, was favorable as regards to yield,⁵ some of **8** were prepared by this method. In the cases of reaction of **1a**, **1j**, and **1k** with the suspension

of AlCl_3 , carbon disulfide or benzene was used as the solvent.

When ZnCl_2 was used as a condensing agents for **1a**, **4** was obtained in 11% yield. In the cases of other condensing agents such as PCl_5 , P_2O_5 , and Ac_2O , oily undetermined materials were obtained.

Spectral Characteristics. The NMR, IR, UV, and mass spectra of **8** are summarized in Table 2. In the mass spectra, the major fragmentation was initial loss of carbon monoxide from the molecular ion, followed by the loss of a hydrogen atom leading to the formation of the ring-expanded thianaphthalenium ion as shown in Scheme 3. There was not the M-40 fragment ion, which was found characteristically in the mass spectra of 2-methyl(thiochromones) (**7**).⁴⁾ The base peak of **8** was the M-28 or M-29 fragment ion (Table 2).



Scheme 3.

In the NMR spectra, the benzenoid proton at the 5-position of **8** showed the chemical shift in the range of 7.78–8.00 ppm. The difference between the proton at the 5-position and other aromatic protons was 0.34–0.53 ppm, whereas that of **7** was *ca.* 1.00 ppm.

In the IR spectra, the carbonyl bands of **8** were found in the range 1635–1650 cm^{-1} and higher by 10–35 cm^{-1} than those of the corresponding thiochromones, except for **8j** and **8k**.

The fluorescent spectra of **8** and **7** were generally very weak, compared to those of the corresponding coumarins.

Experimental

All the melting points are uncorrected. IR spectra were recorded on a Hitachi ESI-S2 spectrophotometer using KBr pellets. ^1H -NMR spectra were taken on a Hitachi R-24A spectrometer with tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi RMU-6E mass spectrometer operating at 80 eV. The fluorescent spectra were recorded on a Hitachi MPF-2A fluorescent spectrophotometer. Elemental analyses were recorded on a Yanaco CHN recorder MT-2.

(E)- β -(Arylthio)crotonic Acid Derivatives (2). **Method A:** Conc'd H_2SO_4 (9.0 g) was added dropwise to Et_2O (50 ml) solution of benzenethiol (5.0 g) at 30 °C. Diketene (5.0 g) was then added to this mixture. After 2 h, ether was removed *in vacuo* at 20 °C, and the residue was poured into an ice-water solution. White solid was separated, collected by filtration and recrystallized from EtOH to give **2a** (5.3 g). Other compounds **2** were prepared by a similar method. **2a**: 60%, mp 174.5–175.5 °C; **2c**: 5%, mp 172–175 °C; **2d**: 65%, mp 165–166 °C; **2e**: 60%, mp 204–205 °C; **2f**: 29%, mp 154–155 °C; **2g**: 10%, mp 198–202 °C; **2h**: 65%, mp 191–195 °C.

The NMR and IR spectra of these compounds corresponded to data of Table 3 described in previous paper.⁴⁾

Method B: NaOH (1.2 g) was added to a solution of (E)- β -chlorocrotonic acid (2.0 g) in EtOH (10 ml). To the

TABLE 3. ELEMENTAL ANALYSES OF 4-METHYL-(THIOCOUMARINS) (**8**)

Compound	Formula (MW)	Analysis (%)	
		Calcd (Found)	
		C	H
8f	$\text{C}_{10}\text{H}_7\text{OSCl}$ (210.5)	57.01 (56.76)	3.33 (3.28)
8g	$\text{C}_{14}\text{H}_{10}\text{OS}$ (226)	74.34 (74.96)	4.42 (4.51)
8h	$\text{C}_{14}\text{H}_{10}\text{OS}$ (226)	74.34 (74.30)	4.42 (4.49)
8j	$\text{C}_{10}\text{H}_7\text{OSBr}$ (254.9)	47.08 (47.07)	2.75 (2.69)
8k	$\text{C}_{10}\text{H}_7\text{OSCl}$ (210.5)	57.01 (57.25)	3.33 (3.40)

mixture, a solution of sodium *m*-methoxybenzenethiolate (*m*-methoxybenzenethiol (2.0 g) + NaOH (1.6 g)) in EtOH (5 ml) was added dropwise at 50 °C and stirred for 2 h. After cooling, dilute HCl was added to this solution until the pH was 1. The resulting solid was separated, and recrystallized from EtOH to give **2b** ($\text{X}=\text{m-OCH}_3$), yield 62%, mp 119–121 °C; NMR (CDCl_3): $\delta=2.40$ (3H, s), 3.80 (3H, s), 5.28 (1H, s), 6.90–7.30 (4H, m), and 10.2 (1H, b); ν_{CO} : 1680 cm^{-1} . Found: C, 58.76; H, 5.48%. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}$: C, 58.93; H, 5.36%. **2i** ($\text{X}=2,5$ -Dimethoxy): yield 50%, mp 126–128 °C; NMR (CDCl_3): $\delta=2.40$ (3H, s), 3.80 (3H, s), 3.83 (3H, s), 5.23 (1H, s), 6.95–7.10 (3H, m), and 10.80 (1H, b); ν_{CO} : 1680 cm^{-1} . Found: C, 56.53; H, 5.59%. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{S}$: C, 56.69; H, 5.51%. Other compounds **2a** and **2c–h** were also prepared by a similar method in yields of 10–51%.

(Z)- β -(Arylthio)crotonic Acid Derivatives (3). Compound **3b** ($\text{X}=2,5$ -dimethoxy) was prepared by the method A for **2a**: yield 22%, mp 169–171 °C; NMR (CDCl_3): $\delta=1.90$ (3H, s), 3.78 (3H, s), 3.83 (3H, s), 5.90 (1H, s), and 6.90–7.10 (3H, m); ν_{CO} : 1675 cm^{-1} . Compound **3a** ($\text{X}=\text{m-OCH}_3$) was prepared by a similar method and isolated from the isomer mixture (**2b** and **3a**) by repeated recrystallization from EtOH. **3a**: mp 170–171 °C; NMR (CDCl_3): $\delta=1.90$ (3H, s), 3.80 (3H, s), 5.90 (1H, s), and 7.00–7.30 (4H, m).

S-Phenyl 3-Oxobutanethioates (1). Compound **1a** was quantitatively obtained from benzenethiol and diketene in the presence of Et_3N in dichloromethane at room temperature for 20 h.⁶⁾ Other compounds **1b–k** were prepared similarly. All of compounds **1a–i** were colorless liquid, and **1j** and **1k** were recrystallized from Et_2O ; **1j**: mp 51–53 °C; **1k**: mp 45 °C (lit.⁶⁾ 45–46 °C). Liquid **1** was used without purification for the cyclization with condensing agents.

The Reaction of 1 with Conc'd H_2SO_4 . **Method I:** The mixed acid of 30% fuming H_2SO_4 (1.0 g) and conc'd H_2SO_4 (10 g) was added dropwise to **1a** (5.5 g) under stirring at 0 °C. The mixture was stirred at room temperature for 5 h, and was poured into an ice-water solution. The resulting solid was separated and recrystallized from EtOH to give diphenyl disulfide **4** (1.9 g): yield 61%, mp 58–59 °C.

Method II: Compound **1a** (5.0 g) was added dropwise to conc'd H_2SO_4 (20 ml) at 15 °C. The mixture was stirred for 5 h at 15 °C and was poured into an ice-water solution. The resulting solid was separated, washed with EtOH and acetone, and purified by acid-pasting to give thianthrene

5,10-bis(dioxide) **6** in 56% yield (mp > 320 °C, lit.¹⁰) > 360 °C). Found: C, 51.67; H, 2.97%. From the first filtrate in EtOH, thianthrene **5** was isolated in 4% yield; mp 152—154 °C (lit.¹¹) 157—159 °C).

The Reaction of 1 with PPA. Compound **1a** (3.0 g) was added to PPA (60 g) at 70 °C and stirred for 1—2 h. After cooling, the mixture was poured into an ice-water solution. The resulting solid was separated and recrystallized from EtOH-water mixture to give **7a** (1.8 g, 66%). Other **7** were similarly prepared. **7c**: X=6-OCH₃, 10%, mp 102—103 °C; **7d**: X=7-CH₃, 23%, mp 98—100 °C; **7e**: X=6-CH₃, 53%, mp 120 °C; **7f**: X=7-Cl, 25%, mp 165—166 °C; **7g**: X=7,8-benzo, 25%, mp 194—195 °C; **7h**: X=5,6-benzo, 15%, mp 126—128 °C; **7i**: X=5,8-dimethoxy, 79%, mp 146—148 °C; **7j**: X=6-Br, 23%, mp 181—182 °C (lit.¹²) 176 °C); NMR (CDCl₃): δ=2.43 (3H, s), 6.79 (1H, s), 7.23—7.70 (2H, m), and 8.55 (1H, d, *J*=2 Hz); ν_{co}: 1623 cm⁻¹. Found: C, 46.87; H, 2.81%. λ_{max} (EtOH): 224 (ε 1.8 × 10⁴), 252 (2.5 × 10⁴), 281 (0.3 × 10⁴), 292 (0.3 × 10⁴), and 342b nm (0.8 × 10⁴); **7k**: X=6-Cl, 34%, mp 164—166 °C (lit.¹²) 170 °C); NMR (CDCl₃): δ=2.46 (3H, s), 6.81 (1H, s), 7.48 (2H, s), and 8.43 (1H, s); ν_{co}: 1628 cm⁻¹. Found: C, 57.13; H, 3.46%. λ_{max} (EtOH): 223 (ε 1.7 × 10⁴), 250 (2.4 × 10⁴), 280 (0.5 × 10⁴), 291 (0.4 × 10⁴), and 342b nm (0.9 × 10⁴).

From the same reaction of **1a**, **1d**, and **1e** at 5—10 °C, **2a** (yield, 4%), **2d** (4%), and **2e** (10%) were isolated, respectively. Under the same conditions at 70 °C, **8b** (X=7-OCH₃) was obtained in 54% yield from **1b**.

The Reaction of 1 with Aluminium Chloride. *Method (i):* Compound **1a** (3.0 g, 15 mmol) was added to a suspension of AlCl₃ (20 g) in CS₂ (20 ml). After reflux for 5 h, the mixture was poured into cold water. The resulting solid was separated and recrystallized from EtOH to give **8a** (1.0 g) in 38% yield, mp 126—127 °C (lit.²) 124 °C). When benzene was used in the place of CS₂, **8j** and **8k** were obtained; **8j**: 27%, mp 184—185 °C; **8k**: 23%, mp 177—179 °C.

Method (ii): Compound **1a** (3.0 g, 15 mmol) was added to AlCl₃ (20 g), and stirred at 80—90 °C for 2 h. After cooling, the mixture was poured into cold water. The resulting solid was separated and recrystallized from EtOH to give **8a** in 48% yield. The others of **8** were similarly obtained by the method (ii); **8d**: 42%, mp 108—109 °C (lit.²)

110 °C); **8e**: 31%, mp 114—115 °C (lit.²) 120 °C); **8f**: 22%, mp 157—158 °C; **8g**: 16%, mp 169—171 °C; **8h**: trace, mp 133—134 °C.

The elemental analyses of those compounds were shown in Table 3.

The Fluorescent Spectra. **8b**: F_{max} (EtOH): 402 nm (rel. intensity based on **8b** as a standard); **8g**: F_{max}: 467 nm (1.5); **8h**: F_{max}: 405 (0.74) and 435 nm (0.66); **7b**⁴) (X=7-OCH₃): F_{max}: 382 nm (2.0); **7g**: F_{max}: 398 nm (0.73); **7h**: F_{max}: 402 nm (0.6); **7i**: F_{max}: 494 nm (2.9 × 10); 7-MeO-4-methylcoumarin: F_{max}: 410 nm (2.7 × 10²); 7,8-benzo-4-methylcoumarin:³) F_{max}: 418 nm (9.1 × 10); 5,6-benzo-4-methylcoumarin:³) F_{max}: 403 nm (9.6 × 10²). The other thiocoumarins and thiochromones which were prepared herein showed no detectable fluorescence.

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