Synthesis and Absorption Spectra of 2-Substituted 5,8-Dimethoxy-4*H*-1-benzothiopyran-4-one 1,1-Dioxides

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2,3-Dibromo-5,8-dimethoxy-4*H*-1-benzothiopyran-4-one (thiochromone) 1,1-dioxide which was a starting material to prepare sulfone analogues of 1,4-naphthoquinone dyes was easily prepared from 5,8-dimethoxythiochroman-4-one by oxidation and bromination. The reactions of 2,3-dibromo-5,8-dimethoxythiochromone 1,1-dioxide **4** with aliphatic and aromatic amines in ethanol below 20° gave 2-substituted derivatives **12a-e** and at higher reaction temperature the amination gave 2-arylamino derivatives **13c-e** debrominated at C-3. The visible absorption spectra of these derivatives were investigated by the PPP MO method.

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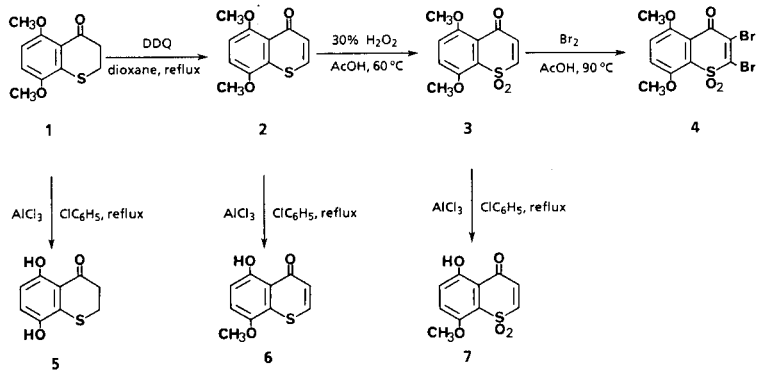
We have systematically studied the relationship between structure and light absorption properties of 4*H*-1-benzothiopyran-4-one (thiochromone) 1,1-dioxides [1,2]. The 2-arylamino and 2-aryl derivatives give the absorption band at shorter wavelength than the corresponding 1,4-naphthoquinones because of less contribution of the sulfonyl group to the color development. Thiochromone 1,1-dioxides are chromophores remarkably different from 1,4-naphthoquinones though the former can be regarded as the sulfone analogous of the latter. 5,8-Disubstituted 1,4-naphthoquinones are useful as a potential deep colored dyes in optical recording media and guest-host liquid crystal display. From these view points, 2,3-dihalogenated 5,8-dimethoxythiochromone 1,1-dioxides **4** and **10** appeared to be attractive starting materials to prepare 5,8-disubstituted thiochromone 1,1-dioxides chromophores as sulfone analogues of 1,4-naphthoquinones.

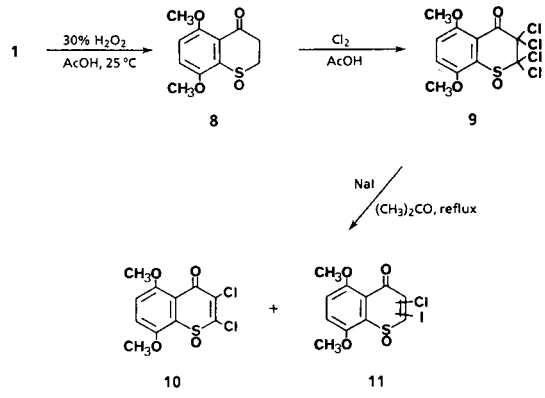
The present paper describes synthesis of 2,3-dibromo-5,8-dimethoxythiochromone 1,1-dioxide **4**, the reactions of **4** with some amines, and their absorption spectra investigated by PPP MO method.

2,3-Dibromo-5,8-dimethoxythiochromone 1,1-dioxide **4** was prepared as shown in Scheme I. 5,8-Dimethoxythiochroman-4-one **1**, which was prepared from 2,5-dimethoxybenzenthiol by the usual method [3], was oxidized with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to give 5,8-dimethoxythiochromone **2** in 65% yield. The oxidation of **2** with 30% hydrogen peroxide in acetic acid at 60° gave 5,8-dimethoxythiochromone 1,1-dioxide **3** in 68% yield. The sulfone compound **3** reacted with bromine in acetic acid at 90° to give 2,3-dibromo-5,8-dimethoxythiochromone 1,1-dioxide **4** in 84% yield. The reaction of **1** with anhydrous aluminum chloride in reflux of chlorobenzene gave 5,8-dihydroxythiochroman-4-one **5** in 85% yield, whereas under the same conditions the thiochromones **2** and **3** gave only monohydroxy derivatives in 58% and 18% yields, respectively. Monohydroxy derivatives are assigned to the 5-hydroxy derivatives **6** and **7**, as the hydroxy proton at 12.2 or 13.3 ppm which was assigned to the proton formed a hydrogen bond to adjacent the carbonyl group. A similar observation was made in the ^{1}H nmr spectrum of **5**.

Scheme I

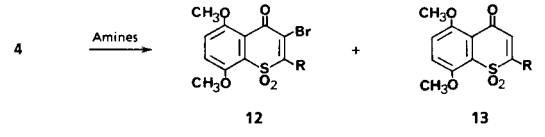


Scheme II



Dehalogenation of 2,2,3,3-tetrachlorothiochroman-4-one 1-oxide, prepared by reaction of **8** with chlorine, the general route to 2,3-dichlorothiochromone 1-oxide (Scheme II) [4], gave a mixture of **10** and **11**. The mixture was inseparable by normal column chromatography on silica gel.

Scheme III



a, R = NHMe
b, R = NMe_2
c, R = NHPh
d, R = 4-$MeOC_6H_4NH$
e, R = 4-MeC_6H_4NH
f, R = 4-$Me_2NC_6H_4$

Table I

Reactions of 2,3-dibromo-5,8-dimethoxythiochromone 1,1-dioxide 4 with amines in ethanol [a]

Amine	Temp. (°C)	Time (hours)	Products (%) [b]	
			12	13
$MeNH_2$	−20	24	24	
Me_2NH	−20	24	40	
$PhNH_2$	20	2	46	
$PhNH_2$	40	2		1.2
p-$MeOC_6H_4NH_2$	0	24	66	
p-$MeOC_6H_4NH_2$	20	2		5.3
p-$MeC_6H_4NH_2$	20	2	33	
p-$MeC_6H_4NH_2$	40	2		4.6
$PhNMe_2$	reflux	9		6.2

[a] Ratio of 5 to amines is 1 : 2, except for N,N-dimethylaniline (1 : 4). [b] Isolated yields.

2,3-Dibromo-5,8-dimethoxythiochromone 1,1-dioxide **4**, as well as 2,3-dibromothiochromone 1,1-dioxide [1], reacted with aliphatic amines in ethanol at −20° to give 2-alkylamino derivatives **12a** and **12b** in 24% and 40% yields, respectively. The reaction of **4** with aniline and *p*-toluidine in ethanol at 20° also gave 2-arylamino derivatives **12c** and **12e** in 46% and 33% yields, respectively. The reaction of **4** with *p*-anisidine readily proceeded at 0° to give the 2-anisidino derivative **12d** in 66% yield. At a higher reaction temperature, however, the reactions of **4** with aromatic amines gave 2-arylamino derivatives **13c-e** debrominated at C-3 (Table 1). A trace amount of 2,3-dianisidino-5,8-dimethoxythiochromone 1,1-dioxide detectable by mass spectroscopy (m/e, 496) was also isolated, but the chemical structures of the other products were undetermined. The reaction of **4** with *N,N*-dimethylaniline in reflux of ethanol gave 2-aryl derivative **13f** debrominated at C-3 in low yield.

Table II

Experimental and PPP MO calculated absorption spectra of 4, 12, and 13

Compound	λ_{max}(Exp.) [a] (nm)	λ_{max}(Exp.) [b] (nm)	ε [a] ($dm^3 mol^{-1} cm^{-1}$)
4	403	402	4710
12a	379	384	10300
12b	402	402	10200
12c	390	396	11500
12d	388	398	10900
12e	390	394	11200
13c	398	398	12000
13d	400	400	11300
13e	382	385	13000

[a] Solvent: chloroform. [b] Solvent: ethanol.

The visible absorption spectra of these derivatives are summarized in Table II. The 2-substitutions of **4** causes a small hypsochromic shift of the longest wavelength band and the marked increase in absorption intensity compared with compound **4**. The 2-substituted derivatives **12** and **13** show a π-π^* band in the visible region, whereas the corresponding 1,4-naphthoquinones have two absorption bands which are assigned as the benzenoid and quinonoid bands, respectively [5]. The absorption bands of 2-substituted derivatives are little affected by solvent.

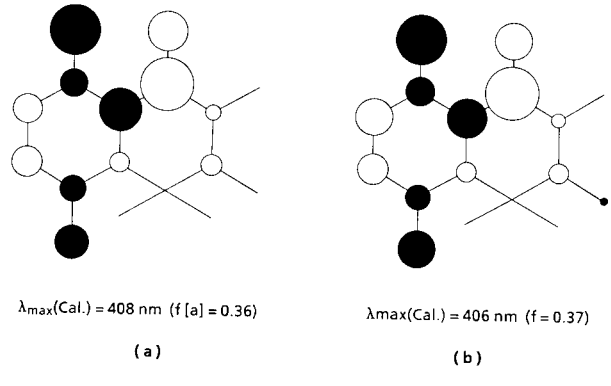


Figure 1. π-Electron density changes for the first transition of (a) **4** and (b) **12a**. The open (shaded) circles signifies that increase (decrease) in π-electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change. [a] Oscillator strength.

The absorption spectra of **12** and **13** were investigated in detail by the PPP MO method using parameters described previously [2]. The CI calculations indicate that the first transitions of these derivatives are approximated

by HOMO→LUMO transition. The π-electron density changes for the first electron transition of **4** and **12a** are shown in Figure 1. It shows that the nature of the first transition of **4** is little affected by the 2-substitution of the donor groups. The calculated wavelength for **12b** and **12c** was the same as **12a**. Though the electron density clearly decreases on the methoxy and alkylamino groups, the acceptor components are very complex. It is quite different from the corresponded 1,4-naphthoquinones which can be regarded as the donor-acceptor chromophore.

Table III

Analytical and i.r. data of thiochromone 1,1-dioxides **12** and **13**

Compound	Mp (°C) [a]	IR (cm^{-1})	Formula	Analysis (%) Calcd. / Found C	H	N
12a	207–208	3300 (NH)	$C_{12}H_{12}BrNO_5S$	39.79	3.34	3.87
		1630 (C=O)		39.70	3.30	3.81
12b	171–172	1640 (C=O)	$C_{13}H_{14}BrNO_5S$	41.50	3.75	3.72
				41.39	3.67	3.65
12c	193–194	3260 (NH)	$C_{17}H_{14}BrNO_5S$	48.13	3.33	3.30
		1655 (C=O)		48.14	3.27	3.32
12d	186–187	3350 (NH)	$C_{18}H_{16}BrNO_6S$	47.59	3.55	3.08
		1645 (C=O)		47.36	3.38	3.04
12e	195–196	3340 (NH)	$C_{18}H_{16}BrNO_5S$	49.33	3.68	3.20
		1645 (C=O)		49.25	3.76	3.13
13c	179–180	3380 (NH)	$C_{17}H_{15}NO_5S$	59.12	4.38	4.06
		1610 (C=O)		59.10	4.14	3.96
13d	207–208	3250 (NH)	$C_{18}H_{17}NO_6S$	57.59	4.56	3.73
		1620 (C=O)		57.61	4.36	3.64
13e	213–215	3250 (NH)	$C_{18}H_{17}NO_5S$	60.16	4.77	3.90
		1620 (C=O)		60.10	4.72	3.83
13f	245–246	1640 (C=O)	$C_{19}H_{19}NO_5S$	61.11	5.13	3.75
				61.10	5.10	3.70

[a] Crystallization from ethanol.

Table IV

^1H N.m.r and mass spectral data of thiochromone 1,1-dioxides **12** and **13** [a]

Compound	^1H NMR δ (J, Hz) [b]	MS m/e (rel. int., %)
12a	3.43 (d, 3 H, J = 6), 3.88 (s, 3 H), 3.99 (s, 3 H),6.75–6.88 (br, 1 H), 7.51 (d, 1 H,J = 9),7.58 (d, 1 H,J = 9)	363 (M^+ + 2, 1.4), 361 (M^+, 1.4), 297 (69), 282 (30), 218 (100)
12b	3.27 (s, 6 H), 3.91 (s, 3 H), 4.00 (s, 3 H), 7.22 (d, 1H, J = 9), 7.26 (d, 1 H, J = 9)	377 (M^+ + 2, 29), 375 (M^+, 28), 311 (5), 296 (47), 232 (100)
12c	3.92 (s, 3 H), 3.98 (s, 3 H), 7.11–7.19 (m, 3 H), 7.36 (dt, 2 H, J = 1, 7),7.56 (d, 1 H, J = 9), 7.62 (d, 1 H, J = 9), 8.51 (br s, 1 H)	425 (M^+ + 2, 0.9), 423 (M^+, 0.9), 359 (40), 280 (100)
12d	3.82 (s, 3 H), 3.90 (s, 3H), 3.96 (s, 3 H), 6.93 (d,2 H, J = 9), 7.19 (d, 2 H, J = 9), 7.53 (d, 1 H, J = 9), 7.58 (d, 1 H, J = 9), 8.41 (br s, 1 H)	455 (M^+ + 2, 13), 453 (M^+, 13), 389 (52), 310 (100)
12e	2.32 (s, 3 H), 3.91 (s, 3H), 3.97 (s, 3 H), 7.10 (d, 2 H, J = 9), 7.17 (d, 2 H, J = 9), 7.54 (d, 1 H, J = 9), 7.60 (d, 1 H, J = 9), 8.43 (br s, 1 H)	439 (M^+ + 2, 1.3), 437 (M^+, 1.3), 373 (40), 294 (100)
13c	3.86 (s, 3 H), 4.00 (s, 3 H), 5.90 (d,1 H, J = 3),7.29 (t, 1 H, J = 7), 7.43–7.50 (m, 4 H), 7.50 (d, 1H, J = 9), 7.57 (d, 1H, J = 9), 8.66 (br s, 1H)	345 (M^+, 10), 329 (10), 281 (100)
13d	3.84 (s, 3 H), 3.85 (s, 3H), 3.99 (s, 3 H), 5.67 (d, 1H, J = 3), 7.05 (d, 2 H, J = 9), 7.33 (d, 2 H, J = 9), 7.47 (d, 1 H, J = 9), 7.55 (d, 1 H, J = 9), 8.53 (br s, 1 H)	375 (M^+, 1.7), 360 (2), 332 (12), 311 (100), 296 (84), 283 (18)
13e	2.36 (s, 3 H), 3.86 (s, 3H), 3.99 (s, 3 H), 5.80 (1H, d, J = 3), 7.30 (s,4H), 7.49 (d, 1 H, J = 9), 7.55 (d, 1 H, J = 9),8.57 (br s,1 H)	359 (M^+, 2), 343 (5), 295 (100), 280 (92)
13f	3.06 (s, 6 H), 3.95 (s, 3H), 4.03 (s, 3H), 6.67 (s, 1H), 6.73 (d, 2 H, J = 9), 7.24 (d, 1 H, J = 10), 7.34 (d, 1 H, J = 10),7.84 (d, 2 H, J 9)	373 (M^+, 100), 359 (41), 309 (24), 294 (71)

[a] Mass spectra of 2,3-dianisidino-5,8-dimethoxythiochromone 1,1-dioxide: 496 (M^+,60), 432 (72), 417 (58), 349 (100). [b] Deuterioacetone solution, except for **12b** : deuteriochloroform solution.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Yamato MD-21 apparatus and are uncorrected. The ^1H nmr spectra were recorded with a JEOL JMN-GX270 spectrometer at 270 MHz. All spectra employed tetramethylsilane as the internal standard. The mass spectra were obtained with a Shimadzu LKB-9000 spectrometer operating at 70 eV. The ir spectra were recorded with a Shimadzu IR-420 spectrometer using potassium bromide discs. Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrometer using solutions of compounds in chloroform and ethanol (*ca.* 1 x 10^{-4} mol dm^{-3}). Elemental analysis were recorded with a Yanaco CHN CORDER MT-3.

5,8-Dimethoxythiochroman-4-one (**1**).

A solution of 2,5-dimethoxybenzenthiol (9.6 g, 56 mmoles) in 7.4% aqueous sodium hydroxide (46 ml) was added dropwise to a solution of 3-chloropropionic acid (6.4 g, 59 mmoles) in 7.4% aqueous sodium hydroxide (46 ml) at 10°. The mixture was stirred at 40° for 3 hours, cooled, and then acidified with concentrated hydrogen chloride. After standing overnight, the precipitate was filtered off and recrystallized from ligroin to give 3-(2,5-dimethoxyphenylthio)propionic acid as colorless crystals 7.5 g (55%), mp 90-92°; ir (potassium bromide): ν max 2900 (OH), 1710 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.68 (t, 2H, J = 7 Hz), 3.14 (t, 2H, J = 7 Hz), 3.77 (s, 3H), 3.85 (s, 3H), 6.74 (dd, 1H, J = 3, 9 Hz), 6.80 (d, 1H, J = 9 Hz), 6.91 (d, 1H, J = 3 Hz), no hydroxy proton was observed.

Anal. Calcd. for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 54.49; H, 5.79.

A mixture of the propionic acid (7.5 g, 31 mmoles) prepared above and polyphosphoric acid (100 g) was stirred at 80° for 3 hours. The reaction mixture was poured into ice-water and extracted with ether. The extract was washed with 5% aqueous sodium carbonate, dried over magnesium sulfate, and evaporated under reduced pressure. The residue was recrystallized from benzene-hexane (1:5, v/v) to give 5,8-dimethoxythiochroman-4-one (**1**) as yellow crystals 3.7 g (53%), mp 130-132°; ir (potassium bromide): ν max 1680 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.95 (t, 2H, J = 7 Hz), 3.18 (t, 2H, J = 7 Hz), 3.85 (s, 3H), 3.87 (s, 3H), 6.67 (d, 1H, J = 9 Hz), 6.92 (d, 1H, J = 9 Hz); ms: 224 (M^+, 100), 209 (30), 196 (56), 181 (11).

Anal. Calcd. for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.90; H, 5.35.

5,8-Dimethoxythiochromone (**2**).

A mixture of 5,8-dimethoxythiochroman-4-one (**1**) (1.0 g, 4.5 mmoles), DDQ (1.4 g, 6.2 mmoles), and dry 1,4-dioxane (40 ml) was refluxed for 1 hour, cooled, and poured into water. The precipitate was filtered off and the filtrate was extracted with ether. The extract was dried over calcium chloride and evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene-acetone (3:1, v/v) and recrystallized from ethanol to give 5,8-dimethoxythiochromone (**2**) as colorless crystals 0.64 g (65%), mp 103-103.5°; ir (potassium bromide): λ max 1620 (C=O) cm^{-1}; uv (chloroform): λ max 358 nm (ε 6,770); ^1H nmr (deuteriochloroform): δ 3.93 (s, 3H), 3.96 (s, 3H), 6.89 (d, 1H, J = 10 Hz), 6.94 (d, 1H, J = 9 Hz), 7.05 (d, 1H, J = 9 Hz), 7.64 (d, 1H, J = 10 Hz); ms: 222 (M^+, 100), 207 (70).

Anal. Calcd. for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.53. Found: C, 59.54; H, 4.58.

5,8-Dimethoxythiochromone 1,1-Dioxide (**3**).

To a solution of 5,8-dimethoxythiochromone (**2**) (0.5 g, 2.2 mmoles) in acetic acid (1.5 ml), 30% hydrogen peroxide (1.5 ml)

was added at room temperature. The mixture was stirred at 60° for 2 hours, cooled, and poured into water. The precipitate was filtered off and recrystallized from ethanol to give 5,8-dimethoxythiochromone 1,1-dioxide (**3**) as yellow crystals 0.39 g (68%), mp 203-203.5°; ir (potassium bromide): ν max 1660 (C=O) cm^{-1}; uv (chloroform): λ max 391 nm (ϵ 3,300); ^1H nmr (deuteriochloroform): δ 3.94 (s, 3H), 4.02 (s, 3H), 6.57 (d, 1H, J = 11 Hz), 7.11 (d, 1H, J = 11 Hz), 7.26 (d, 1H, J = 10 Hz), 7.37 (d, 1H, J = 10 Hz); ms: 254 (M^+, 100), 163 (30).

Anal. Calcd. for $C_{11}H_{10}O_5S$: C, 51.96; H, 3.96. Found: C, 51.89; H, 3.90.

2,3-Dibromothiochromone 1,1-Dioxide (**4**).

A mixture of 5,8-dimethoxythiochromone 1,1-dioxide (**3**) (0.15 g, 0.6 mmole), bromine (0.1 ml, 1.9 mmoles), and acetic acid (5 ml) was stirred at 90° for 2 hours, poured into water and then sodium hydrogen sulfite was added to the mixture. The precipitate was filtered off and recrystallized from ethanol to give 2,3-dibromothiochromone 1,1-dioxide (**4**) as yellow crystals 0.205 g (84%), mp 181-181.5°; ir (potassium bromide): ν max 1665 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.96 (s, 3H), 4.02 (s, 3H), 7.30 (d, 1H, J = 10 Hz), 7.39 (d, 1H, J = 10 Hz); ms: 414 (M^+ +4, 60), 412 (M^+ +2, 100), 410 (M^+, 51), 332 (55), 267 (29), 163 (93).

Anal. Calcd. for $C_{11}H_8Br_2O_5S$: C, 32.06; H, 1.96. Found: C, 32.11; H, 2.00.

5,8-Dihydroxythiochroman-4-one (**5**).

A mixture of 5,8-dimethoxythiochroman-4-one (**1**) (2.8 g, 12 mmoles), anhydrous aluminum chloride (6 g, 45 mmoles), and chlorobenzene (5 ml) was refluxed for 24 hours, cooled, and acidified with dilute hydrogen chloride. The mixture was steam distilled and the precipitate was filtered off. Recrystallization from benzene gave 5,8-dihydroxythiochroman-4-one (**5**) as yellow crystals 2.1 g (86%), mp 183-184°; ir (potassium bromide): ν max 3150 (OH), 1610 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.05 (t, 2H, J = 6 Hz), 3.23 (t, 2H, J = 6 Hz), 4.78 (s, 1H), 6.67 (d, 1H, J = 9 Hz), 7.03 (d, 1H, J = 9 Hz), 12.3 (s, 1H); ms: 196 (M^+, 100), 178 (92), 149 (29).

Anal. Calcd. for $C_9H_8O_3S$: C, 55.09; H, 4.11. Found: C, 55.34; H, 4.00.

5-Hydroxy-8-methoxythiochromone (**6**).

This compound (58%) was prepared from 5,8-dimethoxythiochromone (**2**) by the same manner with (**5**), mp 144.1° (from ethanol); ir (potassium bromide): ν max 3050 (OH), 1635 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.95 (s, 3H), 6.93 (d, 1H, J = 10 Hz), 6.94 (d, 1H, J = 9 Hz), 7.13 (d, 1H, J = 9 Hz), 7.92 (d, 1H, J = 10 Hz), 13.3 (s, 1H); ms: 208 (M^+, 41), 193 (100), 165 (8).

Anal. Calcd. for $C_{10}H_8O_3S$: C, 57.68; H, 3.87. Found: C, 57.65; H, 3.70.

5-Hydroxy-8-methoxythiochromone 1,1-Dioxide (**7**).

This compound (18%) was prepared from 5,8-dimethoxythiochromone 1,1-dioxide (**3**) in the same manner as **5**, mp 169.0° (from ethanol); ir (potassium bromide): ν max 3080 (OH), 1665 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.02 (s, 3H), 6.64 (d, 1H, J = 12 Hz), 7.23 (d, 1H, J = 12 Hz), 7.27 (d, 1H, J = 9 Hz), 7.42 (d, 1H, J = 9 Hz), 12.2 (s, 1H); ms: 240 (M^+, 100), 176 (19).

Anal. Calcd. for $C_{10}H_8O_5S$: C, 50.00; H, 3.36. Found: C, 50.15; H, 3.34.

5,8-Dimethoxythiochroman-4-one 1-Oxide (**8**).

To a solution of 5,8-dimethoxythiochroman-4-one (**1**) (0.3 g, 1.3 mmoles) in acetic acid (3 ml), 30% hydrogen peroxide (1 ml) was added dropwise at room temperature. After 1 hour, the mixture was poured into ice-water. The precipitate was filtered off and recrystallized from ethanol to give 5,8-dimethoxythiochroman-4-one 1-oxide (**8**) as yellow crystals (0.218 g, 68%), mp 171-173°; ir (potassium bromide): ν max 1685 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.95 (t, 2H, J = 7 Hz), 3.18 (t, 2H, J = 7 Hz), 3.85 (s, 3H), 3.87 (s, 3H), 6.67 (d, 1H, J = 9 Hz), 6.92 (d, 1H, J = 9 Hz); ms: 240 (M^+, 52), 224 (110), 212 (50).

Anal. Calcd. for $C_{11}H_{12}O_4S$: C, 54.99; H, 5.03. Found: C, 54.91; H, 4.58.

5,8-Dimethoxy-2,2,3,3-tetrachlorothiochroman-4-one 1-Oxide (**9**).

Excess chlorine (7.4 g, 104 mmoles) was bubbled into a solution of 5,8-dimethoxythiochroman-4-one 1-oxide (**8**) (1.5 g, 6.2 mmoles) in acetic acid (85 ml). After keeping the above solution for 5 days in a closed vessel, the mixture was poured into ice-water. The precipitate was filtered off and recrystallized from ligroin to give 5,8-dimethoxy-2,2,3,3-tetrachlorothiochroman-4-one 1-oxide (**9**) as yellow crystals 1.0 g (42%), mp 176-178°; ir (potassium bromide): ν max 1720 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.86 (s, 3H), 3.92 (s, 3H), 7.16 (d, 1H, J = 9 Hz), 7.28 (d, 1H, J = 9 Hz); ms: 382 (M^+ +6, 1.8), 380 (M^+ +4, 5), 378 (M^+ +2, 9), 376 (M^+, 7), 341 (17), 306 (6), 290 (100), 275 (85).

Anal. Calcd. for $C_{11}H_8Cl_4O_4S$: C, 34.95; H, 2.13. Found: C, 35.27; H, 2.49.

2,3-Dichloro-5,8-dimethoxythiochromone 1-Oxide (**10**).

A mixture of 5,8-dimethoxy-2,2,3,3-tetrachlorothiochroman-4-one 1-oxide (**9**) (0.395 g, 1.0 mmole), sodium iodide (0.313 g, 2.1 mmoles), and acetone (10 ml) was refluxed for 3 hours and then evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene-acetone (5:1, v/v) and recrystallized from ethanol to give a mixture of **10** and **11** 0.182 g, mp 182-187.5°; ir (potassium bromide): ν max 1670 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.95 (s, 3H), 4.01 (s, 3H), 7.26 (d, 1H, J = 9 Hz), 7.32 (d, 1H, J = 9 Hz); ms: 310 (M^+ +4, 1.8), 308 (M^+ +2, 9), 3.06 (M^+, 12), 291 (100), 276 (91) for **10** and 400 (M^+ +2, 1.0), 398 (M^+, 2.5), 383 (100), 368 (59) for **11**.

The mixture was inseparable by the chromatography on silica gel.

General Procedure for the Reactions of 2,3-Dibromo-5,8-dimethoxythiochromone 1,1-Dioxide **4** with Amines.

A mixture of 2,3-dibromo-5,8-dimethoxythiochromone (**4**), amines, and ethanol was treated under the conditions shown in Table I and then poured into water. The precipitate was filtered off and purified by column chromatography on silica gel with benzene-acetone (5:1, v/v) (Tables III and IV).

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