Synthesis and Spectral Characteristics of 4*H*-1-Benzothiopyran-4-ones

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The physical properties of 4*H*-1-benzothiopyran-4-ones (thiochromones) and related compounds were characterized by means of mass, NMR, and UV spectra in order to distinguish thiochromones from 2*H*-1-benzothiopyran-2-ones (thiocoumarins). In the mass spectra, the fragmentation due to the retro-Diels-Alder reaction directly from the molecular ion is the most useful for differentiation. In the NMR spectra, thiochromones show the characteristic deshielding effect of benzenoid proton in 5-position and in the UV spectra a very strong absorption band in the region 250—270 nm. It was found that in the reaction of *S*-phenyl 3-oxobutanethioates with PPA, most of these compounds afford thiochromones through rearrangement giving an intermediate (IVa). The effect of the substituent of the *S*-phenyl 3-oxobutanethioate on the formation of the thiocoumarin was also discussed.

4*H*-1-Benzothiopyran-4-ones (thiochromones) and 2*H*-1-benzothiopyran-2-ones (thiocoumarins) are well known as a structural isomer. The thermal conversion of the thiochromone into the thiocoumarin is also known.[1] A new synthesis of thiocoumarin derivatives was reported by Konishi *et al.*,[2] but some structural formulas of these compounds are doubtful. We therefore carried out an extensive study of the chemical structure of the related compounds by means of mass and NMR spectra. We found that some thiocoumarins are in line with the structural formulas of thiochromone derivatives. In this paper, we wish to report on a) the characteristic physical properties of thiochromone derivatives in order to distinguish them from thiocoumarins by means of their mass, NMR, IR, and UV spectra, and b) the effect of the substituent of the *S*-phenyl 3-oxobutanethioate on the formation of the thiocoumarin by the reaction with polyphosphoric acid (PPA).

Results and Discussion

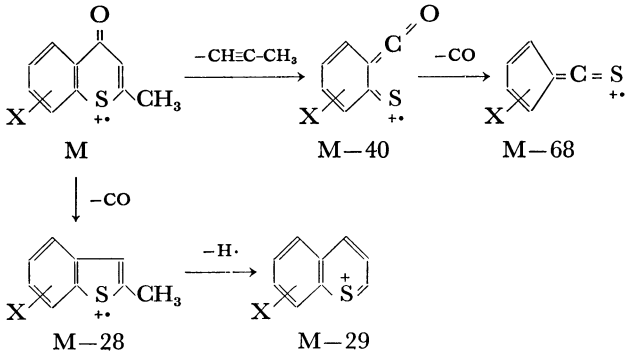
Most of the thiochromones and thiocoumarins were prepared from *S*-phenyl 3-oxobutanethioate derivatives obtained by the reaction of substituted thiophenols with diketene. The IR, NMR, UV, and mass spectra of these compounds are summarized in Tables 1 and 2.

Identification of Thiochromone and Thiocoumarin Derivatives. It is very difficult to distinguish thiochromones from thiocoumarins. Lozac'h and Pfister-Guillouzo[3] reported a comparative method to distinguish them by means of their IR spectra. However, sufficient and systematic data necessary for identification are still lacking. In the case of compound **2**, the mass spectra showed the fragmentation of retro-Diels-Alder reaction characteristic of chromone derivatives[4] and we deduced the compound to be 2-methyl(thiochromone). This is also supported by the following experimental results: When compound **2** was hydrolyzed with NaOH, isolated products were bis(*o*-acetylphenyl) disulfide and bis(*o*-carboxyphenyl) disulfide. Compound **2** was also obtained by the authentic method.[5]

Thus, 4-methyl(thiocoumarin) reported[2] should be 2-methyl(thiochromone). 2-Methyl-7-methoxy(thiochromone) (**3**), the isomer of thiocoumarin **12**, was prepared by the well known method[6] for thiochromone derivatives. Compounds **4**—**9** were also identified as thiochromone derivatives by means of their mass and NMR spectra. The structure of compound **11** was determined to be thiochromone derivative by the following preparative method and chemical reactivity. The same product was obtained by the reaction of 2,5-dimethoxybenzenethiol with ethyl acetoacetate in PPA. A bluish thianaphthalenium salt (λ_{max} 590 nm (in acetone)) was obtained by the *O*-alkylation of compound **11** with dimethyl sulfate and 60% $HClO_4$. A similar alkylation afforded a yellow thianaphthalenium salt[7] (λ_{max} 386 nm) in the case of compound **12** and a bluish thianaphthalenium salt (λ_{max} 590 and 596 nm) in the case of compounds **2** and **3**, respectively.

Spectral Characteristics. *1) NMR Spectra*: Methyl(thiochromone) derivatives showed the characteristic deshielding effect of benzenoid proton in 5-position by contribution of the carbonyl group in peri-position as indicated in the case of some thiochromones.[8,9] The proton showed the chemical shift in the range 8.30—8.50 ppm. The values are unusually greater than those of the aromatic protons (*ca.* 1 ppm). The abnormally strong deshielding effect might be due to the even closer proximity of the proton on the annelated benzene in compound **8**, which was observed at 10.10 ppm. In the case of thiocoumarin derivatives, no such unusual deshielding effect was observed because of the lack of carbonyl group affecting the benzenoid proton. This difference may be utilized to distinguish them.

2) Mass Spectra: Thiochromone derivatives were characterized by an abundant molecular ion as the base peak. The major fragmentation pathway for these compounds was the elimination of $CH{\equiv}C{-}CH_3$ by the retro-Diels-Alder reaction, followed by the loss of



Scheme 1.

TABLE 1. SPECTRAL DATA OF THIOCHROMONE AND THIOCOUMARIN DERIVATIVES

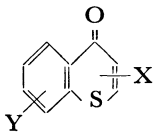
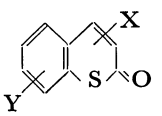
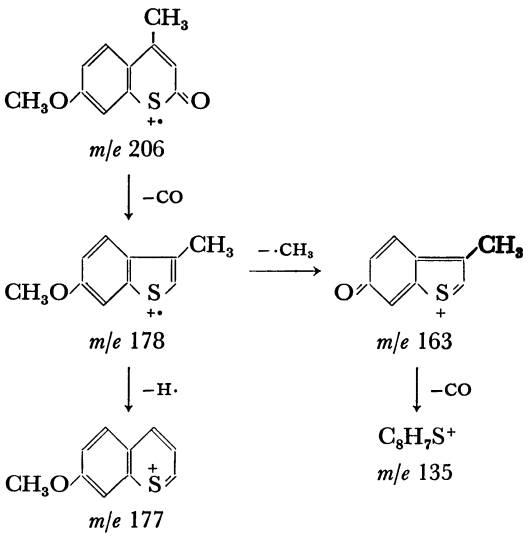
No.	Compound		IR in KBr ν_{CO} (cm^{-1})	NMR in $CDCl_3$ δ (ppm)	UV in EtOH λ_{max} (nm)	UV in EtOH ε ($\times 10^{-4}$)
2		X=2-CH_3 Y=H	1620	2.40 (3H)s 6.75 (1H)s 7.37—7.50 (3H)m 8.40 (1H)m	224 247 335	1.8 2.4 1.1
3		X=2-CH_3 Y=7-OCH_3	1630	2.40 (3H)s 3.89 (3H)s 6.71 (1H)s 6.80—7.10 (2H)m 8.34 (1H)d	235 261 268 328	1.6 3.0 2.6 1.1
4		X=2-CH_3 Y=6-OCH_3	1625	2.45 (3H)s 3.90 (3H)s 6.80 (1H)s 7.15 (1H)d 7.45 (1H)d 7.90 (1H)d	224 254 260 357	1.6 2.4 2.4 0.88
5		X=2-CH_3 Y=7-CH_3	1610	2.41 (3H)s 2.43 (3H)s 6.75 (1H)s 7.15—7.30 (2H)m 8.30 (1H)d	228 254 337	1.6 2.4 1.1
6		X=2-CH_3 Y=6-CH_3	1620	2.40 (3H)s 2.45 (3H)s 6.80 (1H)s 7.40 (2H)m 8.30 (1H)s	225 249 345	1.4 2.7 1.1
7		X=2-CH_3 Y=7-Cl	1635	2.40 (3H)s 6.75 (1H)s 7.30—7.45 (2H)m 8.35 (1H)d	229 255 261 338	1.7 3.0 2.7 1.1
8		X=2-CH_3 Y=5,6-Benzo	1620	2.44 (3H)s 6.97 (1H)s 7.37—8.00 (5H)m 10.10 (1H)m	216 278 326 340 356	5.3 2.2 0.89 0.84 0.53
9		X=2-CH_3 Y=7,8-Benzo	1605	2.48 (3H)s 6.90 (1H)s 7.48—7.95 (4H)m 8.15 (1H)m 8.42 (1H)d	217 277 314 342 360	3.8 2.8 0.81 0.73 0.75
10		X=3-CH_3 Y=H	1610	2.20 (3H)s 7.35—7.65 (4H)m 8.50 (1H)m	223 250 341	1.2 1.9 1.1
11		X=2-CH_3 Y=5,8-Dimethoxy	1620	2.35 (3H)s 3.88 (3H)s 3.90 (3H)s 6.70 (1H)s 6.90 (1H)s 6.93 (1H)s	241 293 363	2.2 1.2 0.71
12		X=4-CH_3 Y=7-OCH_3	1645	2.50 (3H)s 3.92 (3H)s 6.48 (1H)s 6.95—7.15 (2H)m 7.80 (1H)d	224 273 343	4.2 0.64 1.0
13		X=4-OH Y=H	1620	6.24 (1H)s 7.50—7.84 (3H)m 8.28 (1H)m	232 320	4.0 1.4

Table 2. Mass spectra of thiochromone and thiocoumarin derivatives

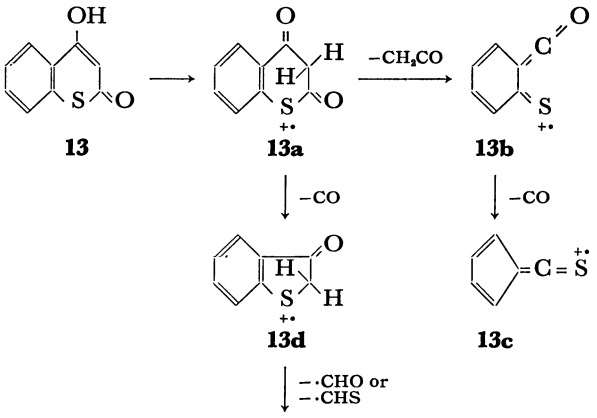
Compound No.	Major fragment ion (*m/e*) [relative abundance (%)]
2	176[M, 100], 148[M−28,64], 147[M−29,62], 136[M−40,58], 115[10], 108[M−68,44]
3	206[M,100], 178[M−28,57], 177[M−29,7], 166[M−40,52], 163[64], 138[M−68,7], 136[8], 135[17], 134[9], 123[22]
4	206[M,100], 205[65], 191[M−15,10], 177[M−29,26], 176[41], 166[M−40,7], 163[15], 147[10], 138[M−68,7], 135[29], 134[9], 123[25]
5	190[M,100], 162[M−28,76], 161[M−29,57], 150[M−40,57], 147[27], 121[46]
6	190[M,100], 162[M−28,65], 161[M−29,51], 150[M−40,62], 147[22], 121[42]
7	212[38], 210[M,100], 184[29], 183[28], 182[M−28,82], 181[M−29,56], 172[24], 170[M−40,63], 147[30], 144[13], 142[M−68,32]
8	226[M,100], 225[43], 198[M−28,47], 197[M−29,41], 186[M−40,17], 165[12], 158[M−68,27]
9	226[M,100], 198[M−28,39], 197[M−29,37], 186[M−40,15], 165[9], 158[M−68,24]
10	176[M,100], 148[M−28,15], 147[M−29,34], 143[40], 136[M−40,63], 115[19], 108[M−68,36]
11	236[M,96], 221[100], 207[26], 203[36], 193[61], 192[37], 191[17], 178[12], 165[34], 164[15], 163[13], 150[13]
12	206[M,43], 178[M−28,100], 177[M−29,9], 163[82], 147[6], 135[51], 134[19], 102[10]
13	178[M,37], 150[M−28,100], 136[M−42,82], 121[56], 108[80], 105[16]

carbon monoxide (M→[M−40]→[M−68]). The other important 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 (M→[M−28]→[M−29]) (Scheme 1). The results are given together with relative abundance in Table 2. In the case of compounds **3** and **4**, the subsequent fragmentation of M-28 is modified by the methoxy substituent, *viz.*, the loss of methyl radical from M−28 giving an intensive fragment ion peak at *m/e* 163. However, in the case of 5,8-dimethoxy derivative **11**, fragmentation due to the retro-Diels-Alder reaction was not observed as in the case of some methoxyfuranochromones.[10]



Scheme 2.

On the other hand, the base peak of thiocoumarin derivatives was due to M−28. The main fragmentation of thiocoumarin **12** involved the ejection of carbon monoxide followed by the loss of methyl radical and carbon monoxide. The sequence may be rationalized as in Scheme 2.



Scheme 3.

The mass spectra of 4-hydroxy(thiocoumarin) **13** showed the fragmentation of the retro-Diels-Alder reaction in spite of thiocoumarin derivatives. If the molecular ion exists in the tautomeric form **13a**, the spectra can be easily rationalized. There are two fragmentation pathways. One which differs a great deal from that of other thiocoumarins is the loss of a neutral ketene by the retro-Diels-Alder reaction, followed by the loss of carbon monoxide (**13a**→**13b**→**13c**). The other is the loss of carbon monoxide from the molecular ion, which gives **13d** as the base peak of the spectrum (**13a**→**13d**→*m/e* 121 and 105).

The fragmentations were formulated by analogy of coumarin derivatives[4] and by following the fragmention containing a chlorine atom in the fragmentation of compound **7**. The retro-Diels-Alder reaction of the molecular ion of thiochromones might be the most useful for mass spectrometric differentiation between isomeric thiocoumarin and thiochromone, except for hydroxy(thiocoumarin) and dimethoxy(thiochromone) derivatives.

3) UV Spectra: Monosubstituted methyl(thiochromone) derivatives showed three complicated strong absorption bands due to the substituent in the benzene ring. On the other hand, the spectra of thiocoumarins showed two strong absorption bands, very weak in the region 250—270 nm.

4) IR Spectra: The carbonyl bands of methyl(thiochromone) derivatives were found in the region 1605—1630 cm^{-1}, which is considerably lower than that of a general ketone. Legrand and Lozac'h[1] reported that carbonyl bands of thiochromone are lower by 10—20 cm^{-1} than those of thiocoumarins. However, the difference can not be used reliably to distinguish them, since the region of thiocoumarins overlapped considera-

TABLE 3. THE NMR AND IR SPECTRA OF *S*-PHENYL 3-OXOBUTANETHIOATE DERIVATIVES

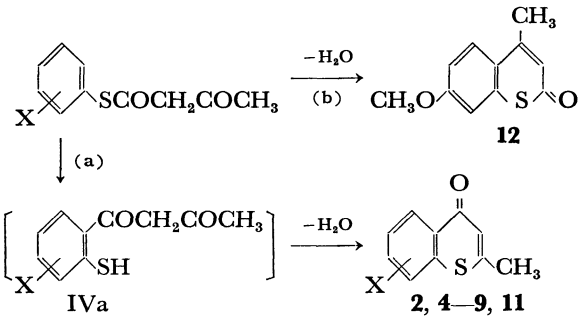
Compound No.	X	IR in KBr ν_{CO} (cm^{-1})	NMR in $CDCl_3$ δ (ppm)			
1a	H	1670	2.38 (3H)s	5.20 (1H)s	7.51 (5H)s	8.28 (1H)b
1b	*m*-OCH_3	1675	1.90 (3H)s	3.80 (3H)s	5.90 (1H)s	7.00—7.30 (4H)m[a]
1c	*p*-OCH_3	1665	2.38 (3H)s 7.38 (2H)d	3.80 (3H)s 9.25 (1H)b	5.15 (1H)s	6.90 (2H)d
1d	*m*-CH_3	1670	2.30 (3H)s	2.35 (3H)s	5.15 (1H)s	7.35 (4H)m[b]
1e	*p*-CH_3	1665	2.30 (3H)s	2.35 (3H)s	5.10 (1H)s	7.35 (4H)m[b]
1f	*m*-Cl	1670 (s 1680)	2.43 (3H)s	5.25 (1H)s	7.38—7.48 (4H)m	9.0 (1H)b
1g	2,3-Benzo	1670	2.40 (3H)s	4.85 (1H)s	7.60—8.20 (7H)m[b]	
1h	3,4-Benzo	1670	2.40 (3H)s	5.15 (1H)s	7.55—8.20 (7H)m[b]	
1i	2,5-Dimethoxy	1675	1.90 (3H)s 6.90—7.10 (3H)m[a]	3.78 (3H)s	3.83 (3H)s	5.90 (1H)s

a) No enol proton was observed. b) The NMR spectra were measured in DMSO-d_6, no enol proton being observed.

bly with that of thiochromones as shown in compound **13** and 3-methyl(thiocoumarin) (1620 cm^{-1}).

Synthesis of Thiochromone Derivatives from S-*Phenyl 3-Oxobutanethioates.* It was shown by spectral data that all *S*-phenyl 3-oxobutanethioates retain the enol form; ν_{OH} was observed at 2500—3000 cm^{-1} in IR and a vinyl proton was observed at 5.15—5.90 ppm as shown in Table 3. When these *S*-phenyl 3-oxobutanethioates were cyclodehydrated with PPA, only *m*-methoxy derivative (compound **1b**) gave a thiocoumarin **12**. However, the other *S*-phenyl 3-oxobutanethioates with substituents such as chlorine and methyl group in the meta-position gave thiochromones (compounds **5** and **7**) as the isomeric product of thiocoumarins. Two annelated derivatives **1g** and **1h** gave the corresponding thiochromones.

Thus, the meta-position of methoxyl group on *S*-phenyl 3-oxobutanethioate seems to be important for the preparation of thiocoumarin derivatives. In the case of compounds **1c** and **1i** where one or two methoxyl group(s) are introduced in the other position, thiochromone derivatives **4** and **11**, respectively, were obtained as isomeric products.



Scheme 4.

Cyclodehydration of *S*-phenyl 3-oxobutanethioate with 100% H_2SO_4 instead of PPA also afforded 2-methyl(thiochromone). The reaction with 100% H_2SO_4 in ether solution or concd H_2SO_4 gave diphenyl disulfide in a high yield (81%). The rearrangement of *S*-phenyl 3-oxobutanethioates giving an intermediate [IVa] (path a) predominantly occurs rather than the direct dehydration (path b) as shown in Scheme 4.

The synthesis of thiocoumarins by the Pechmann reaction[11] is very difficult even from *S*-phenyl 3-oxobutanethioate.

Experimental

All the melting points are uncorrected. Infrared spectra were recorded on a Hitachi ESI-S2 spectrophotometer using KBr pellets. Ultraviolet spectra were recorded on a Hitachi EPS-3T spectrophotometer. H-NMR spectra were taken on a Hitachi Perkin-Elmer Model R-20 spectrometer, unless otherwise stated in $CDCl_3$ solution with tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi RMU-6E mass spectrometer operating at 80 eV. Elemental analyses were recorded on a Yanaco CHN corder MT-2.

S-*Phenyl 3-Oxobutanethioate (**1a**).* Compound **1a** was obtained by the reaction of thiophenol with diketene.[2]

S-*(m-Methoxyphenyl) 3-Oxobutanethioate (**1b**).* Compound **1b** was prepared by the method reported[2] and isolated from the isomer mixture by repeated recrystallization from EtOH. The mixture contained an unidentified compound with the following data. NMR: δ 2.40 (3H) s, 3.80 (3H) s, 5.25 (1H) s, 6.90—7.30 (4H) m, 8.35 (1H) b; Found, C, 59.29; H, 5.52%. From the results, the compound was assigned as the structural isomer of compound **1b**.

S-*(p-Methoxyphenyl) 3-Oxobutanethioate (**1c**).* Concd H_2SO_4 (9.2 g) was added dropwise at 30 °C to a stirred Et_2O (50 ml) solution of *p*-methoxybenzenethiol (6.3 g, 0.045 mol).[12] Diketene (4.5 g, 0.054 mol) was then added to this reaction mixture at 25 °C. After 2.5 h, the ether was removed by rotary evaporation *in vacuo* at 20 °C and the residue was poured into an ice-water solution. White solid separated from the solution was collected by filtration and was recrystallized from EtOH to give 0.5 g of **1c**. Compounds **1d**, **1e**, **1g**, and **1h** were prepared by a similar method.

Recrystallization of compound **1g** from EtOH was repeated until the melting point became constant (mp 161—163 °C[2]).

S-*(m-Chlorophenyl) 3-Oxobutanethioate (**1f**).* *m*-Chlorobenzenethiol was obtained as a pale yellow oily material from *m*-chloroaniline by the Leukart reaction[12] in 60% yield; bp 76—78 °C (7 Torr), NMR (CCl_4); δ 2.30 (1H) s, 7.05 (3H) m, 7.20 (1H) m. Compound **1f** was prepared by the same method as for **1c** from *m*-chlorobenzenethiol.

S-*(2,5-Dimethoxyphenyl) 3-Oxobutanethioate (**1i**).* 2,5-Dimethoxybenzenethiol was obtained from 2,5-dimethoxyaniline by the Leukart reaction[12] in 64% yield; bp 104—106 °C (4 Torr), NMR (CCl_4); δ 3.70 (3H) s, 3.80 (3H) s, 3.75

Table 4. Physical properties of *S*-phenyl 3-oxobutanethioate derivatives

Compd	Mp (°C)	Yield (%)	Formula (MW)	Analysis (%) Calcd (Found) C	H
1b	170—171	trace	$C_{11}H_{12}O_3S$ (224)	58.93 (58.79	5.36 5.47)
1c	172—175	5	$C_{11}H_{12}O_3S$ (224)	58.93 (58.23	5.36 5.39)
1d	165—166	65[75][a]	$C_{11}H_{12}O_2S$ (208)	63.46 (62.91	5.77 5.81)
1e	204—207	60[65][a]	$C_{11}H_{12}O_2S$ (208)	63.46 (63.56	5.77 5.89)
1f	154—155	29[44][a]	$C_{10}H_9O_2SCl$ (228.5)	52.52 (53.04	3.94 4.14)
1g	194—196	10	$C_{14}H_{12}O_2S$ (244)	68.85 (67.92	4.92 4.89)
1i	169—171	22	$C_{12}H_{14}O_4S$ (254)	56.69 (57.07	5.51 5.66)

a) Yield (%) of the crude product.

(1H) b, 6.55—6.70 (3H) m. Concd H_2SO_4 (6.1 g, 0.060 mol) was added dropwise to a stirred solution of 2,5-dimethoxybenzenethiol (5 g, 0.029 mol) in ether (30 ml) at 5 °C. Diketene (3 g, 0.036 mol) was then added to this reaction mixture at the same temperature. After 5 h at 5—10 °C, a white solid was separated from the solution by filtration. Recrystallization from EtOH afforded 1.4 g (22%) of **1i**.

The results of elemental analysis, yield and mp are given in Table 4.

2-Methyl-4H-1-benzothiopyran-4-one (2). Method A). Compound **2** was obtained from condensation of thiophenol (10 ml, 0.1 mol) and ethyl acetoacetate (11 ml, 0.1 mol) in polyphosphoric acid (PPA).[5] Method B). *S*-Phenyl 3-oxobutanethioate **1a** (3 g, 0.015 mol) was added to 60 g of PPA at 60 °C. The solution was heated for 1 h at the same temperature. After cooling, the reaction mixture was poured into an ice-water solution and neutralized with NaOH. Crude product (2.3 g) was collected by filtration and washed with water. Recrystallization from a methanol-water mixture (3: 1) afforded 1.8 g (66%) of **2**.

7-Methoxy-2-methyl-4H-1-benzothiopyran-4-one (3). A solution of 14 g (0.1 mol) of *m*-methoxybenzenethiol and 28 g (0.2 mol) of ethyl acetoacetate was added to 300 g of PPA at 80 °C. The reaction mixture was heated at 90 °C for 2 h. After cooling, it was poured into an ice-water solution and collected by filtration and washed with water. Recrystallization from EtOH–water afforded 4 g (20%) of compound **3** as a pale yellow material; mp 118—119.5 °C, Found: C, 63.76; H, 4.85%; Calcd for $C_{11}H_{10}O_2S$: C, 64.08; H, 4.85%; mol wt 206.

Compounds **4—9** were prepared by a method silimar to method B for compound **2**. Reaction time in the case of compounds **8** and **9** was 2 h and 3 h, respectively. The yield, mp and elemental analysis are given in Table 5.

3-Methyl-4H-1-benzothiopyran-4-one (10). Compound **10** was prepared by the method of Martin *et al.*,[8] mp 103—104.5 °C (lit, 105 °C), Found: C, 67.42; H, 4.54%; Calcd for $C_{10}H_8OS$: C, 68.18; H, 4.54%; mol wt 176.

5,8-Dimethoxy-2-methyl-4H-1-benzothiopyran-4-one (11). Compound **11** was prepared by method B for compound **2** (36% yield) or by the method for compound **3** (31%).

7-Methoxy-4-methyl-2H-1-benzothiopyran-2-one (12) and 4-Hydroxy-2H-1-benzothiopyran-2-one (13). Compounds **12** **13** were prepared by method B for compound **2** (reaction time 2 h) and by the method of Ruwet *et al.*[13] (mp 212—213.5; lit, 215 °C), repsectively.

Table 5. reaction of *S*-phenyl 3-oxobutanethioate derivatives with PPA

Compd	Yield (%)	Mp (°C)	Formula (MW)	Analysis (%) Calcd (Found) C	H
2	66[85][a]	103—104	$C_{10}H_8OS$ (176)	68.18 (68.20	4.54 4.78)
12	27	158—160	$C_{11}H_{10}O_2S$ (206)	64.08 (64.28	4.85 5.08)
4	87[90][a]	102—103	$C_{11}H_{10}O_2S$ (206)	64.08 (64.24	4.85 4.93)
5	38[44][a]	98—100	$C_{11}H_{10}OS$ (190)	69.47 (68.78	5.26 5.20)
6[b]	59	121 (lit,[5] 122)	$C_{11}H_{10}OS$ (190)	69.47 (69.74	5.26 5.37)
7	59[74][a]	163—165	$C_{10}H_7OSCl$ (210.5)	57.01 (57.26	3.33 3.45)
8	60[65][a]	126—128	$C_{14}H_{10}OS$ (226)	74.34 (74.28	4.42 4.42)
9[c]	44	192—194	$C_{14}H_{10}OS$ (226)	74.34 (75.88	4.42 4.45)
11	36[59][a]	146—148	$C_{12}H_{12}O_3S$ (236)	61.02 (61.58	5.08 5.23)

a) Yield (%) of the crude product. b) (**1e**) recovered (18% Yield). c) (**1g**) recovered (24% yield).

Hydrolysis of Compound 2. Compound **2** (5 g) was added to a solution of MeOH (100 ml) and NaOH (40 g). The reaction mixture was heated under reflux for 4.5 h. After cooling, the solution was neutralized to pH 5—6 with HCl and filtered. The residue was washed with water and extracted with ether. The extract was evaporated and the residue recrystallized from EtOH to give 0.6 g (7% yield) of bis(*o*-acetylphenyl) disulfide; mp 162—164 °C (lit,[14] 167 °C), γ_{CO} 1650 cm^{-1}, NMR; δ 2.65 (6H) s, 7.20—7.80 (8H) m. The first filtrate was, after concentration by evaporation, was extracted with MeOH. The extract was recrystallized from MeOH to give 0.5 g (6% yield) of bis(*o*-carboxyphenyl) disulfide; mp 287—288 °C (lit,[15] 288.5); γ_{CO} 1680 cm^{-1}, γ_{OH} 2500—3000 cm^{-1}.

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