### SYNTHESIS OF SULPHUR HETEROCYCLICS—I DISPROPORTIONATION OF THIACHROMENES TO THIACHROMANS AND THIANAPHTHALENIUM SALTS INVOLVING HYDRIDE TRANSFER

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Abstract—Interaction of 4-methyl- $\Delta^{4}$ -thiachromene with polyphosphoric acid (PPA) yields 4-methylthiachroman and a blue thiacyanine dye. The latter is formed from 4-methylthianaph-thalenium salt as a precursor.

 $\beta$ -Arylmercaptoethyl methyl ketones and 4-methylthaichroman-4-ols on treatment with PPA similarly yield thiachromans and thianaphthalenium salts or thiacyanine dyes. These reactions involve acid catalysed intermolecular hydride shift from  $\Delta^*$ -thiachromenes.

The structural and stereochemical factors which govern the hydride transfer have been studied.

THE present work was undertaken as an extension of the synthesis of polycyclic thiophenes and thiapyrans in progress in this laboratory.<sup>1</sup> The synthesis of thia-chromans by the following general route has been studied:



The keto sulphides (I) were prepared in good yield (72-99%) by base catalysed addition of arylmercaptans to methyl vinyl ketone (MVK) or by interaction of arylmercaptans with Mannich bases derived from ketones.

Cyclodehydration of the keto sulphides (I) by interaction with PPA was expected to yield thiachromenes (II). However instead of the latter, thiachromans (III) (yield > 35%) and thianaphthalenium salts (which subsequently change in suitable cases to thiacyanine dyes) were obtained. Preliminary reports on this work have been published earlier<sup>2,3</sup> and in the present paper details of this and additional work is now reported.

The thiachromans, also obtained by alternative routes are exemplified by the synthesis of 4-methylthiachroman (IV), in Chart 1.

In view of the above reactions, the following mechanism is suggested for the cyclodehydration of VIII with PPA or perchloric acid (Chart 2).

An essential step in the above sequence of reactions is the intermolecular hydride shift from the 2-carbon atom of one molecule of the thiachromene (VII) to the 4carbonium ion position (in VIIa) of another molecule (VII) which has been protonated. In the case of phenyl 2-(2-methyl-4-oxo)pentyl sulphide (VIIIA), PPA

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- <sup>1</sup> B. D. Tilak, Tetrahedron 9, 76 (1960).
- \* B. D. Tilak and V. M. Vaidya, Tetrahedron Letters 487 (1963).
- <sup>8</sup> B. D. Tilak, C. V. Deshpande, S. K. Jain, G. T. Panse and V. M. Vaidya, 2nd International Color Symposium Schloss Elmau, W. Germany, April (1964).













H<sup>-</sup> shift

<u>-н</u>\* +н\*







treatment gave 2,2,4-trimethyl- $\Delta^3$ -thiachromene (VIIA), which does not suffer disproportionation due to absence of hydrogen in the 2-position. In the case of the above ketosulphide (VIII), 4-methylthianaphthalenium salt (IX) formed together with (IV), undergoes further change to the bis-thianaphthalenium salt (X) through the dihydro derivative (IXa) by loss of hydride as shown above. Compound (X) is then converted to the blue thiacyanine dye (XI) on deprotonation by interaction with a Lewis base (water, ethanol, ether etc.) during work up of the acidic reaction mixture containing (X). In the alternative, (IXa) may be converted to the dye (XI) by loss of hydrogen and the latter is then protonated to give the di-cation (X) under the conditions of the experiment.

The formation of (X) has been proved by protonation of the cyanine dye (XI) by dissolution in perchloric acid. The solution thus obtained showed a spectrum which was identical with the cyclodehydration mixture obtained from (VIII) after removal of 4-methylthiachroman (IV). Further, the molar extinction of the protonated thiacyanine dye (X,  $X^- = ClO_4$ ; solution in perchloric acid) was nearly double that of 2,4-dimethylthianaphthalenium perchlorate (XXX) (described later) (Fig. 1).



If cyclodehydration of (VIII) is carried out with perchloric acid in presence of a hydride abstractor such as trityl chloride, then the protonated cyanine dye (XI) is obtained in better yield (77%).

Condensation of different aryl mercaptans and MVK and cyclization of the resulting  $\beta$ -arylmercaptoethyl methyl ketones gave the thiachromans listed below together with the relevant thiacyanine dyes (Chart 3). The latter were separately prepared and characterized in the cases cited below by cyclization of the relevant ketosulphides by interaction with perchloric acid in presence of trityl chloride.

Cyclization of XXI with perchloric acid in presence of trityl chloride led to the



thianaphthalenium perchlorate (XXIIa), whereas treatment of XXI with PPA gave 4-methyl-5,6-benzothiachroman (XXII).

Cyclization of XXIII gave the bis-thiapyran (XXIV) which on desulphurization gave 2,6-diisobutylnaphthalene (XXIVa). The UV absorption spectrum of the latter was nearly identical with the known 2,6-dimethylnaphthalene and different from 1,5- and 1,3-dimethylnaphthalenes (Fig. 2). The cyclization of the side chains in XXIII thus occurs in the  $\beta$ , $\beta'$ -positions.



In the case of cyclodehydration of XVI by treatment with perchloric acid, trityl chloride and acetic acid, the intermediate thianaphthalenium perchlorate (XVIb), m.p. 205° could be isolated and identified. The latter gave the expected thiacyanine dye (XVIc). The stability of XVIb is associated with the presence of the 7-methoxy-group. The reaction mechanism outlined in Chart 2 is thus further established by isolation of XVIb as shown above.

When the ketosulphide (XVIII) was cyclized with perchloric acid in the presence of trityl chloride, a dye of complex structure was obtained which has been assigned the structure XVIIIb. Sodium borohydride reduction of the dye gave a neutral pale yellow monohydro derivative (XVIIIc). Although the latter decomposed in the mass spectrometric determination of mol. w., peaks (384-6, 464-7) corresponding to masses between the dimeric structure (mass 380) and the trimeric structure (mass 568) were observed. The dye therefore is a trimeric thiacyanine such as XVIIIb. A cyclic monocationoid protonated structure (XVIIId) was also considered for the dye, but was ruled out in favour of XVIIIb, since the NMR spectrum of the hydro derivative (XVIIIc) revealed the presence of three methoxyl groups to one C-methyl group. The hydro derivative of a cyclic compound such as XVIIId will not contain a C-methyl group.



Sodium borohydride reduction of model thianaphthalenium perchlorates (XXV and XXVII) has been found to lead to  $\Delta^{3}$ -thiachromenes (XXVI and XXVIII) respectively.



The above thiacyanine dyes show characteristic high extinction coefficients (Fig. 3). They are, however, insoluble in water (as perchlorates). Cyclization of the ketosulphide (VIII) by interaction with a solution of anhydrous ferric chloride in conc. hydrochloric acid gave the water-soluble thiacyanine (XI,  $X^- = \text{FeCl}_4^-$ ) which dyed an attractive blue shade on synthetic polyester fibres. The above dyes are therefore of potential interest in dyeing of this fibre and also of other regenerated and synthetic fibres.

The cyclodehydration of other aryl 3-oxoalkyl sulphides has also been studied. In this connection we wish to correct our earlier observation<sup>2</sup> that  $\Delta^3$ -thiachromene (XXVIII) on treatment with perchloric acid, yields only thianaphthalenium perchlorate (XXVII) without concomitant formation of thiachroman (XXIX) which might be expected to be formed in the disproportionation of the thiachromene. We have now isolated thiachroman (XXIX) also and perchloric acid appears to be only acting as a hydride transfer medium and not as a hydride abstractor as reported earlier.<sup>2</sup> The above intermolecular hydride shifts may be expected to be subject to stereoregulation by structural features in the molecule. Thus hydride shift can only occur if C-2 hydrogen in  $\Delta^3$ -thiachromene (XXVIII) can come within C-H bond forming distance of the C<sub>4</sub>-carbonium ion formed by the protonation of another molecule of  $\Delta^3$ -thiachromene. If this is sterically precluded, then hydride shift should not occur. It also follows from the mechanism suggested above (Chart 2) that further conversion of thianaphthalenium salts, to thiacyanine dyes will depend on the availability of a



2- or 4-methyl group in the relevant thianaphthalenium perchlorate with a free 4- or 2-position respectively. These expectations have been realised as a result of suitably designed experiments illustrated in Chart 4.



Our earlier suggestion<sup>2</sup> that the thiacyanine dye (XI) is formed through the intermediate thianaphthalenium salt (IX), has been further proved by analogous synthesis of other thianaphthalenium salts such as XXX, XXV and XLIV as indicated in Chart 4. In these disproportionations, further conversions of the above thianaphthalenium salts to thiacyanine dyes is either precluded or rendered difficult by structural and stereochemical factors.

The above points were studied by synthesis of relevant compounds shown in Chart 4.



Compound XXXVII, which is isomeric with the dye XI, could not be obtained in the pure state. It absorbs at a longer wavelength (740 m $\mu$ ) as compared to XI (728 m $\mu$ ), although at lower wavelengths the two dyes give similar absorption maxima. The dye XL also could not be obtained in an analytically pure state. Its spectrum was radically different from other thiacyanine dyes. It may be noted that disproportionation of the thiachromenes (XXXII, XLII and XXVI) gave the expected thiachromans and thianaphthalenium salts. In these cases no thiacyanine dyes were obtained as would be expected from the structures of the relevant thiachromenes. However, 3,4-dimethylthianaphthalenium perchlorate (XXV) on boiling with ethanolacetic acid gave a red coloured dye which is under investigation.

The structure of the above compounds is supported by satisfactory analysis, UV and visible spectra and NMR studies. The spectral characteristics of the compounds described in the paper are given in Tables 8, 9 and 10 in the Experimental.

The absorption spectra of the thiachromans are recorded in Table 8. The thiachromans gave a characteristic peak at 255-257 m $\mu$  (log  $\epsilon$  about 4.1) and a shoulder or a peak between 280-295 m $\mu$  (log  $\epsilon$  about 3.1).

The absorption spectra of the  $\Delta^3$ -thiachromenes are recorded in Table 9. The thiachromenes gave characteristic absorption maxima at 242-247 m $\mu$  (log  $\epsilon$  4·1-4·3) and 320-325 m $\mu$  (log  $\epsilon$  about 3·1) and a shoulder around 272-283 m $\mu$ . Compound VIIa showed a characteristically distinct sharp absorption band at 298 m $\mu$  (log  $\epsilon$ , 3·05).

The absorption spectra of thianaphthalenium perchlorates and the thiacyanine dyes (as perchlorates) are recorded in Table 10. The thianaphthalenium perchlorates (XXVII, XLIV, XXX, XXV and XLVIII) gave characteristic absorption bands at 385–388 m $\mu$  (369 m $\mu$  in the case of XXX) (log  $\epsilon$  nearly 3.7), 332–338 m $\mu$  (log  $\epsilon$  nearly 3.8) and 257–260 m $\mu$  (log  $\epsilon$  nearly 4.6).

All the thiacyanine dyes with the exception of the dye XL showed a characteristic strong absorption maximum in the region 610-622 m $\mu$ . The dye XVIIIb gave a somewhat different spectrum in that it showed additional absorption bands at 760 (shoulder), 450 m $\mu$  and the absorption band at 257-266 was shifted to 290 m $\mu$ . The dye XL showed overall weaker and broad absorption bands and this dye appears to be distinct from the other thiacyanine dyes. The inter-relation between structure and absorption characteristics of the thiacyanine dyes is being further examined and will be reported later together with an examination of several other thiacyanine dyes which are being synthesized.

The above work has also been extended to the synthesis of other thianaphthalenium salts. Several cyanine, hemicyanine and carbocyanine dyes have also been prepared from these thianaphthalenium salts. This work will form the subject of following communications.

### EXPERIMENTAL

The temp recorded in the paper are uncorrected and b.ps refer to bath temp except those marked by an asterisk.

### General methods for the synthesis of aryl 3-oxo-alkyl sulphides

(a) Interaction of aryl mercaptans with methyl vinyl ketone (MVK). Methyl vinyl ketone (MVK) (1.21 moles to 2.53 moles, the latter in the case of older samples; 3.43 moles in the case of naphthalene-1,5-dithiol) was added to a solution of the aryl mercaptan (1 mole) in dry benzene with a few drops of piperidine, when the reaction mixture became warm. The mixture was heated under reflux for 5 hr on a water bath. After the mixture attaining room temp, the benzene solution was washed with NaOHaq to remove any unreacted mercaptan and then washed free of alkali. After drying (Na<sub>3</sub>SO<sub>4</sub>), benzene was removed by distillation. The keto sulphide thus obtained was purified by distillation *in vacuo* or by crystallization or by both. In the case of the preparation of VIIIa mesityl oxide was used in place of MVK.

(b) Interaction of aryl mercaptans with Mannich bases. A mixture of an aryl mercaptan (1 mole) and a Mannich base (1.1 to 1.2 moles) was heated in an oil bath for 30 min, using  $N_a$  to remove the liberated base. Mannich bases used for the preparation of XVI, XVII and XVIII were prepared from the relevant ketones by interaction with paraformaldehyde and dimethylamine as the base. In these cases the Mannich bases were reacted with the relevant thiols at 130° whereupon dimethylamine was evolved. The Mannich base used for the preparation of XXVIb was prepared from the relevant ketone, paraformaldehyde and morpholine as the base. In this case the condensation with thiol was carried out at 160–170° whereupon morpholine was liberated.

The above reaction mixture was extracted with ether, the ether extract washed with aqueous alkali to remove unreacted thiol and with HClaq to remove basic products. The keto sulphide was then purified by distillation *in vacuo*.

Compounds prepared by above general methods are described in Table 1. The yield figures

Compound	% Viald	A				Ana	lysis		
No.	from	Appearance	or	F	ound			Requi	red
	diioi		0.p.	С	н	S	С	н	S
VIII	88	Colourless liquid	100–105° 1 mm	66.6	6.3	17-2	66.7	6.7	17.8
XII	95	Colourless liquid	115–119° 1 mm	67.6	7·4	16·0	68·0	7.2	16.5
XIII	82	Pale yellow liquid	178–183° 7 mm	62·5	7∙0	15·2	62·8	6.7	15-2
XIV	72	White flakes	m.p. 52° (pet. ether 60–80°)	56.5	5-3	14.5	56-1	5-1	15.0
XV	99	Colourl <b>ess</b> liquid	128–131° 3–4 mm	67·5	7.6	16-2	68·0	7.2	16.5
XVI	80 (82)	Almost colourless liquid	146–150° 2 mm	63·1	<b>6</b> ∙0	15.6	62·8	6.7	15-2
XVII	74 (80)	Colourless liquid	115–120° 1 mm	67·9	7.1	16.4	<b>68</b> ∙0	7.2	16.5
XVIII	78 (82)	Pale yellow liquid	145–150° 2 mm	62.6	6∙8	—	62·8	<del>6</del> ·7	
XIX	83	Pale yellow liquid	85–90° 3 mm	A	Analyti	ically p not ob	ure sam tained.	ple wa	IS
XXI	91	White flakes	m.p. 70–72°	72.6	5.7	13.7	73·0	6.0	14.0
ХХШ	78	Colourless elongated flakes	m.p. 97°	64.9	5.9	19-1	65·1	6.0	19-3
XXVIb	(80–85)	Colourless liquid	150–155° 9 mm	68-0	7·2		<b>68</b> ∙0	7.3	
VIIIA	83	Colourless liquid	145–150° 9 mm	<b>69</b> ∙0	7.3	15.0	69·2	7.7	15.7

TABLE 1. SYNTHESIS OF ARYL 3-OXO-ALKYL SULPHIDES AF

					Ana	lysis		
Compound	Appearance	m.p.		Found	l	R	equire	d
No.			C	н	N	С	Н	N
VIII	Yellow needles	142°	53·4	4.3	15-2	53.3	4.4	15.6
XII	Orange needles	105–107°	54.3	4·9	15.0	54.5	4.9	14.9
XIII	Orange-red crystals	105-106°	52.4	4.7	14-2	52-3	4.7	14.4
XIV	Orange needles	134-136°	<b>49</b> ∙1	4∙0	14·2	<b>48</b> ·7	3.8	14-2
xv	Yellow needles	128°	54.5	4∙5	14.9	54-5	4.9	14-9
XVI	Orange crystals	131°	52-1	4∙6	14-4	52.3	4.7	14•4
XVII	Orange crystals	150–151°	54-6	4.6	14-7	54.5	4.9	14.9
XVIII	Orange needles	145-146°	52-2	4.6	13.8	52.3	4.7	14.4
XIX	Orange needles	<b>19</b> 1°	58-8	4∙6	13.5	58.5	4.4	13-7
XXI	Lustrous orange needles	142°			13-3			13-7
XXVIb	Yellow	120°	54.7	4∙8	14.7	54·5	4.8	14-9
VIIIA	Orange needles	122°	55-4	4.7	14.1	55.7	5-2	14•4

TABLE 2. 2,4-DINITROPHENYLHYDRAZONES FROM ARYL 3-OXO-ALKYL SULPHIDES

given in parenthesis in this Table refer to compounds which have been prepared by Method (b) above, the others are prepared by Method (a).

Table 2 describes the 2,4-dinitrophenylhydrazone derivatives obtained from aryl 3-oxo-alkyl sulphides. The hydrazones were crystallized generally from EtOH or mixtures of benzene-EtOH or acetone-EtOH.

3,4-Dimethylthiachroman-4-ol XXVIa. 3-Methylthiachroman-4-one<sup>4</sup> (3.4 g) was slowly added to a cold ethereal solution of MeMgI (prepared from 0.96 g Mg and 5.6 g MeI). The mixture was allowed to attain room temp slowly and was heated under reflux for 1 hr. The mixture was cooled, cold NH<sub>4</sub>Claq (10%) added and stirred for  $\frac{1}{2}$  hr. The mixture was extracted with ether, the ether extract washed with NaClaq, dried (Na<sub>1</sub>SO<sub>4</sub>) and the ether distilled off. The residue (3.5 g, yield, 91%) did not show the characteristic IR absorption due to carbonyl function. Attempts to crystallize this compound failed and it was used as such for further reaction.

2,4-Dimethylthiachroman-4-ol XXXI. To a cold ether solution (80 ml) of MeMgI (prepared from 2.1 g Mg and 10.1 ml MeI) was added 2-methylthiachroman-4-one<sup>4</sup> (7.64 g in 25 ml ether) during 30 min. The mixture was further stirred for 30 min in the cold and for 1 hr at room temp. The mixture was then worked up as above. The residue (8.23 g) on crystallization from pet. ether (b.p. 50-60°) gave colourless flakes (6.85 g; yield, 82%), m.p. 73-75°. (Found: C, 67.5; H, 7.0; S, 16.4.  $C_{11}H_{14}OS$  requires: C, 68.0; H, 7.3; S, 16.5%.)

2-Methylthiachroman-4-ol XXXIV. 2-Methylthiachroman-4-one (5·12 g) in ether (25 ml) was added to a suspension of LAH (0·39 g) in ether (40 ml) during 50 min. The mixture was heated under reflux for 2 hr. Ethyl acetate (5 ml) was added, followed by ether and water. HCl (1:1) was added to dissolve the white precipitate. The aqueous solution was extracted with ether, the combined ether extracts washed with water, dried (Na<sub>1</sub>SO<sub>4</sub>) and the ether removed by distillation. The residue

<sup>4</sup> J. C. Petropoulos, M. A. McCall and D. S. Tarbell, J. Amer. Chem. Soc. 75, 1130 (1953).

(4.5 g) crystallized from pet. ether (b.p. 60-80°) in silky white needles (3.9 g; yield, 75%), m.p. 74°. (Found: C, 66.8; H, 6.5; S, 17.2.  $C_{10}H_{13}OS$  requires: C, 66.7; H, 6.7; S, 17.7%.)

4-Ethylthiachroman-4-ol (XXXVIII). Thiachroman-4-one (2.9 g) in ether (25 ml) was slowly added to a cold ethereal solution of EtMgBr (prepared from 0.9 g Mg and 4.0 g EtBr). The mixture was stirred at room temp for 3 hr and worked up as above. The residue (3.86 g) crystallized from a mixture of pentane and pet. ether (b.p. 60-80°) in colourless needles (3.5 g; yield, 90%), m.p. 44°. (Found: C, 68.1; H, 7.4; S, 16.2.  $C_{11}H_{14}OS$  requires: C, 68.0; H, 7.2; S, 16.4%.)

3-Methylthiachroman-4-ol (XLI). 3-Methylthiachroman-4-one (2.45 g) was added to a suspension of LAH (0.25 g) in ether (30 ml). The mixture was heated under reflux for 30 min and stirred for

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chromanols	chromenes	% Yield	b.p.	·	Found	1	R	equire	xd
			•	С	Н	S	С	н	S
VI	VII	75	110–115° 3 mm	74-4	6.3	-	74.1	6.2	
XXVIa	XXVI	70	105–110° 3 mm	7 <b>5</b> ·1	7.1	18.1	74.9	6.8	18-1
XXXI	XXXII	75	110–115° 3 mm	74·9	7∙0		75-0	6.8	
XXXIV	XXXV	79	90–95° 4–5 mm	73.7	6.7	19.6	74.0	6.2	19·8
XLI	XLII	75	110–115° 5 mm	74.0	6.2	20•4	<b>74</b> ∙0	6.2	19.8

Table 3. Dehydration of thiachroman-4-ols to  $\Delta^{a}$ -thiachromenes

1 hr more and worked up as above. The product obtained was chromatographed on alumina and then crystallized from pet. ether (b.p. 40-60°), white needles (2.0 g; yield, 80%), m.p. 78-80°. (Found: C, 66.8; H, 6.8; S, 18.0.  $C_{16}H_{18}OS$  requires: C, 66.6; H, 6.6; S, 17.7%.)

#### General method for the dehydration of thiachroman-4-ols to $\Delta^*$ -thiachromenes

A mixture of powdered thiachroman-4-ol and KHSO<sub>4</sub> (approximately half the weight of thiachromanol) was heated *in vacuo* in an oil bath maintained at a temp above the m.p. of thiachromanol for  $\frac{1}{2}$  hr. The temp of the oil-bath was then raised to 140–160° and the mixture heated until all the thiachromene distilled over. The distillate was dissolved in ether, the ether extract washed with NaHCO<sub>3</sub>aq, water, dried (Na<sub>3</sub>SO<sub>4</sub>) and the ether removed by distillation. The residue was purified by distillation *in vacuo*. Compounds (VI), XXXI, XXXIV, XXVIa and XLI on dehydration in this manner yielded VII, XXXII, XXXV, XXVI and XLII respectively as colourless liquids (Table 3).

### **Disproportionation Reactions**

## General procedure for the treatment of keto sulphides, 4-methyl- $\Delta^{s}$ -thiachromene (VII) and 4-methyl-thiachroman-4-ol (VI) with PPA

The keto sulphide or thiachromene or thiachromanol was added in one lot to polyphosphoric acid [PPA prepared by heating 4 g of  $P_3O_5$  and 2.5 ml of ortho-phosphoric acid (d. 1.75, purity Ca. 89%) at 150° for 1 hr—for 1 g of the starting material] at room temp. The reaction mixture was stirred mechanically and heated on water bath or an oil bath at temp varying from 70° to 130° for a period of 1.5 to 4 hr. The mixture which acquired red-brown colour was then cooled and poured into ice water. The solution was extracted with ether. The ether extract was washed with NaHCO<sub>5</sub>aq, water and dried (Na<sub>5</sub>SO<sub>4</sub>).

After removal of the ether the thiachromans obtained were purified by distillation *in vacuo*, except in the case of XXIV which was purified by crystallization from benzene (Table 4).

# General method for disproportionation of keto sulphides, $\Delta^3$ -thiachromenes and 4-ethylthiachroman-4-ol (XXXVIII) by treatment with 60% aqueous perchloric acid

The keto sulphides,  $\Delta^3$ -thiachromenes, and XXXVIII were treated with perchloric acid (4 ml to 10 ml per 1 g of the starting material) at temp varying from 30° to 90° for 2.5 to 9 hr. After cooling,

							Analysis							
Starting compound	Temp of reaction	Time of reaction	Thiachromans	% Yield	m.p./b.p.	5./6.p. Appearance –		Found		F	Require	d		
		ши					С	н	S	С	н	S		
VI	90°	4	IV	36	123–131° 8 mm	Colourless liquid	73·5	7-3	19.6	73-2	7.3	19-5		
VII	95°	2	IV	61ª	95–100° 4 mm	Colourless liquid	72.6	7.7	19-1	73-2	7.3	19-5		
VIII	70°	2	IV	30	85–90° 2 mm	Colourless liquid	73.6	7.4	19-4	73·2	7.3	19.5		
ХП	80°	2	XIIa	27	100–105° 1 mm	Colourless liquid	74·2	8∙3	17.5	74.1	7·9	17·9		
XIII	80°	2	XIIIa	19	95–100° 0∙02 mm	Pale yellow liquid	<b>68</b> ∙4	7.1	15-9	68·0	7·2	16.5		
XIV	100°	2	XIVa	26	85–90° 0-02 mm	Pale yellow liquid	61·0	5.7	15.7	60.5	5.5	16-1		
XV	70°	3	XVa	21	90–95°	Colourless	74·4	7·9	17.5	74.1	7·9	17·9		
XVI	60°	2	XVIa	30	95–100° 0-04 mm	Pale yellow	68·3	7.3	16.0	<b>68</b> ∙0	7·2	16.5		
XVII	70°	1.5	XVIIa	31	95–100° 2 mm	Colourless	73 <b>·9</b>	7·9	17·9	74.1	7 <b>·9</b>	17·9		
XVIII	1 <b>00°</b>	2.5	XVIIIa	18	95–100° 0:02 mm	Pale yellow	<b>68</b> ∙0	7· <b>3</b>	16.3	<u>68</u> ∙0	7·2	16.9		
XIX	<b>90°</b>	3	XX	10	125–130° 0:008 mm	Pale yellow viscous liquid	78·9	6.5	15-3	78-5	6.5	15-0		
XXI	110°	3	XXII	35	115–120° 0.02 mm	Pale yellow viscous liquid	78.6	6-1	15.3	78·5	6.2	15.0		
XXIII	120°	2.5	XXIV	6	m.p. 220°	White flakes	71.6	6.2	21.1	72·0	6.7	21.3		
VIIIA	100°	3	VIIA	28	100–105° 1·5 mm	Pale yellow liquid	75-4	7·4	15.9	75.8	7·4	16-8		

TABLE 4. SYNTHESIS OF 4-METHYLTHIACHROMANS FROM KETO SULPHIDES, THIACHROMANOL (VI) AND THIACHROMENE (VII) BY TREATMENT WITH PPA

<sup>a</sup> Starting material contained IV as an impurity.

\* 2,2,4-trimethyl- $\Delta$ \*-thiachromene.

				- <u> </u>		T	hiachro	mans				
Starting	a	b	c	Compound	%	m.p./b.p.			A	nalysis	Aut.	·····
material					yield			Found	1	F	Require	ed .
							c	н	s	С	н	S
VIII	4	30°	9	IV <sup>d</sup>	25							
XXVI	10	30°	3	LXV	37	110–115° 3 mm	74.6	7.5		74.1	7∙8	
XXVIb	6	30°	4	LXV	35	120–125° 4 mm	7 <b>3</b> ·6	7 <b>·9</b>		74.1	7·8	
XXVIII	10	30°	5	XXIX⁴	23	100–110° 4 mm						
XXXII	10	90°	2.5	XXXIII	29	120-125° 10 mm	74-1	7.5	18-5	74-1	7 <b>·9</b>	18-0
XXXV	7	30°	2.5	XXXVI	37	114–117° 16 mm	73-1	7.5		73·2	7.3	-
XXXVIII	6	30°	3	XXXIX	32	120–125° 3 mm	74•2	8∙0	17.7	74·1	7.9	17-9
XLII	10	30°	3	XLIII	28	110–115° 2 mm	72•4	7•4	20-1	73·2	7.3	19-6

 TABLE 5. DISPROPORTIONATION OF KETO SULPHIDES, THIACHROMENES AND 4-ETHYLTHIACHROMAN 

 4-OL BY TREATMENT WITH PERCHLORIC ACID

Volume of 60% perchloric acid per g of starting material in ml.

<sup>b</sup> Temp at which the reaction was carried out.

• Time of reaction in hr.

<sup>d</sup> UV absorption spectrum identical with that reported in the literature.<sup>4</sup>

the reaction mixture was extracted with pet ether (b.p.  $60-80^{\circ}$ ). The pet ether extract was washed free of acid, dried (Na<sub>3</sub>SO<sub>4</sub>) and the solvent removed by distillation. The residue, on distillation *in vacuo*, gave the respective thiachromans as colourless liquids.

The perchloric acid solution left after removal of the pet. ether extract, was cooled in an ice bath and excess ether added. The mixture, on standing for a few hr at  $0-5^{\circ}$  gave the perchlorates or the thiacyanine dyes as a crystalline precipitate. The product was filtered, washed with ether and dried (in the case of VIII and XXXVIII, the perchloric acid solution was diluted with EtOH, whereas in the case of XXXV it was diluted with water).

The above experiments are summarized in Tables 5 and 6. The experimental conditions for the disproportionation studies and data regarding thiachromans are recorded in Table 5, whereas the data regarding the thianaphthalenium salts which are formed concommitantly is recorded in Table 6.

In the case of disproportionation of VIII, XXXV and XXXVIII instead of thianaphthalenium salts the thiacyanine dyes XI (yield, 19%), XXXVII (yield, 27%) and XL (yield, 9%) were obtained.

Synthesis of 4-methylthiachroman IV by catalytic hydrogenation of 4-methyl- $\Delta^3$ -thiachromene VII. A mixture of VII (0.42 g) ethyl acetate (30 ml) and 5% PdC (0.3 g) was treated with H<sub>2</sub> under stirring. After the required amount of H<sub>2</sub> was absorbed, the mixture was filtered. Removal of the solvent and distillation of the residue (0.4 g), gave IV as a colourless liquid (0.28 g), b.p. 90–95°/1 mm. (Found: C, 73.5; H, 7.2; S, 19.5. C<sub>10</sub>H<sub>18</sub>S requires: C, 73.2, H, 7.3; S, 19.5%.)

Desulphurization of XXIV. A solution of XXIV, (0.19 g) in absolute EtOH (250 ml) and  $W_{1}$ Raney Ni (10 ml) was heated under reflux under stirring for 5 hr. After removal of Raney Ni, the filtrate was evaporated by distillation. The brown oily residue (0.14 g) on distillation gave XXIVa as a pale yellow oil (0.11 g; yield, 72%) b.p. 142-144°/0.3 mm. On redistillation, the latter gave a colourless liquid, b.p. 148-150°/0.5 mm. (Found: C, 90.1; H, 9.9.  $C_{18}H_{14}$  requires: C, 90.0; H, 10.0%.)

Synthesis of XXIIa from XXI. A mixture of XXI (1.01 g), trityl chloride (1.38 g) and perchloric acid (60%; 10 ml) was heated intermittently on a boiling water bath for 10 hr. After cooling the mixture was saturated with excess ether. Compound XXIIa separated out as brownish yellow tiny needles. The latter were filtered off, washed with ether and dried (0.954 g, yield, 70%), m.p. 208°. (Found: Cl, 11.3; S, 10.7.  $C_{14}H_{11}ClO_4S$  requires: Cl, 11.4; S, 10.3%.)

			Thiar	naphthalenium	perchlo	orates				
Starting	Compound	%	m.p.	Appearance			An	alysis		
material	Number	Yield	•	••		Found	1	F	equire	d
					С	н	S	$\overline{\mathbf{c}}$	Н	S
XXVI	XXV	35	160°	Yellow needles	<b>48</b> ∙0	<b>4</b> ∙0	13.0	48·1	<b>4</b> ·0	12.7
XXVIb	XXV	36	160°	Yellow needles	<b>48</b> ∙1	4∙0	-	<b>48</b> ∙1	4∙0	—
XXVIII	XXVIIª	31	218–219°	Greenish yellow needles						
XXXII	XXX	21	125–126°	Greenish yellow needles	<b>48</b> ∙6	4.3		<b>48</b> ∙1	<b>4</b> ∙0	—
XLII	XLIV	25	137–138°	Yellow needles	<b>45</b> ∙8	3.2	-	<b>46</b> ∙0	3∙5	

TABLE	6.	DISPROPORTIONATION	OF	KETO SULPHIDES	, THIACHROMENES	AND	4-ETHYLTHIACHROMAN-4-
		OL	BY	TREATMENT WIT	H PERCHLORIC AC	D	

<sup>a</sup> Product identical with thianaphthalenium perchlorate.<sup>3</sup>

TABLE 7.

						Aı	nalysis			
Starting	Compound	%		Fo	und			Req	uired	
material	Number	Yield	С	н	s	Cl	C	Н	S	Cl
VIII	$\begin{array}{c} XI\\ X^- = ClO_{4}^{-}\end{array}$	77	57.8	3.6	15.6	_	57.3	3.6	15-3	
XV	XVb	68	_		13.5	7.9			14.3	8.0
XVI	XVIb	87	<b>45</b> ·8	3-5	11-3		45-4	3.8	11-0	_
XVIII	XVIIIb	88	58·9	4∙8	13.7	5.1	59·4	4-1	14.4	5.3

TABLE 8. ABSORPTION SPECTRA OF THIACHROMANS

Compound No.	$\lambda_{\max}$ in m $\mu$ and log $\epsilon$ in parenthesis*
XXXVI	256 (4·10), S 286 (3·07)
XLIII	257 (4·07), S 296 (2·93)
IV	256 (4-08), S 290 (3-00)
XXXIX	255 (3·89), S 283 (3·84)
XXXIII	257 (4·09), S 288 (2·99)
XLV	255 (3·95), S 283 (3·90)
XIIa	257 (4·12), 294 (3·07)
XVa	257 (4.06), 288 (3.08)
XVIIa	253 (4·05), S 281 (3·10)
XIVa	262 (4·25), S 295 (3·10)
XVIa	256 (3.99), 291 (3.49), 299 (3.42)
XVIIIa	257 (3·99), 288 (3·30)
XX	244 (4·34), 308 (3·85), S 318 (3·80)
XXII	254 (4.75), 278 (3.84), 288 (3.94), 299 (3.84)
	332 (3.18), 347 (3.07)
XXIV	252 (4.79), 320 (4.05), 330 (4.05), 345 (4.01)

\* Solvent: EtOH, except XXIV where cyclohexane was used.

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Compound (XI,  $X^- = \text{FeCl}_4^-$ ). Phenyl 3-oxobutyl sulphide (VIII; 1.0 g) was heated with a solution of anhydrous FeCl<sub>3</sub> (3.0 g) in conc. HCl (5 ml) on a boiling water bath for 1.5 hr. The mixture was cooled and large excess of ether (150 ml) added. The blue thiacyanine dye (XI,  $X^- = \text{FeCl}_4^-$ ) which separated out, was filtered off and washed with a small amount of water and dried, yield, 52%.

Table 9. Absorption spectra of  $\Delta^{s}$ -thiachromenes in ethanol

Compound No.	$\lambda_{\max}$ in m $\mu$ and log $\epsilon$ in parenthesis
XXVIII	242 (4.36), 275 (3.41), 325 (3.09)
XXXV	242 (4·35), S 280 (3·35), 324 (3·13)
XLII	246 (4·06), S 283 (3·76), 320 (3·14)
VII	244 (4·33), S 272 (3·78), 323 (3·12)
XXXII	244 (4·29), S 275 (3·70), 322 (3·05)
XXVI	247, 280, 315
VIIA	240 (426), 298 (3.05), 322 (3.00)

### General method for preparation of thiacyanine dyes

Aryl 3-oxo-butyl sulphides (1.0 g, 1 mole) were heated with trityl chloride (2 moles) and excess perchloric acid (70%, 5 ml) on a boiling water bath for 2 hr. The mixture was cooled and saturated with ether, when the blue thiacyanine dyes separated out. The dyes were filtered washed with ether and dried. Data regarding the synthesis of the dyes and XVIb are tabulated in Table 7.

### General method for reduction of thianaphthalenium salts and thiacyanine dyes by treatment with sodium borohydride

A solution of the thianaphthalenium salt or the dye (0.1 g, 1 mole) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was stirred with a solution of excess of NaBH<sub>4</sub> (1 mole) in EtOH (5 ml) for 30 min at room temp (ca. 27°). The mixture was acidified with dil. acetic acid and the CH<sub>2</sub>Cl<sub>2</sub> layer separated, washed with dil. NaHCO<sub>2</sub>aq, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and CH<sub>2</sub>Cl<sub>2</sub> removed by distillation. The residue was purified by chromatography on alumina in the case of solids and by vacuum distillation in the case of liquids. These experiments are briefly described below.

Compound No.	$\lambda_{\max}$ in m $\mu$ and log $\epsilon$ in parenthesis
XXVII	385 (3.58), 335 (3.71), 260 (4.60)
XLIV	388 (3.64), 338 (3.70), 260 (4.58)
XXX	369 (3.77), 336 (3.93), 258 (4.66)
XXV	384 (4.10), 334 (3.73), 257 (4.23).
XVIb	413 (3.82), 339 (3.70), 271 (4.53)
XXIIa	423 (3·91), 305 (4·16), S 288 (4·14)
XXXVII	740, 611, 570, 390, 345, S 314, 243.
XI	728 (3·27), 610 (4·95), S 570 (4·50), 395 (4·05),
	315 (3·94), 257 (4·41), 247 (4·43).
XL	664, S 380, 330, 250
XVb	\$ 720 (3·17), 613 (4·71), \$ 575 (4·32), 402 (3·75),
	337 (3.86), 319 (3.93), 262 (4.49)
XVIc	622 (4·57), S 572 (3·37), 420 (3·57), 342 (3·62),
	320 (3·70), S 273 (3·50), 266 (4·25).
XVIIb	S 760 (3·20), S 720 (3·28), 618 (4·79), S 580 (4·38),
	450 (3.76), 373 (3.62), 330 (3.76), 290 (4.41).

TABLE 10. ABSORPTION SPECTRA OF THIANAPHTHALENIUM PERCHLORATES AND THIACYANINE DYES

Note: Methylene chloride was used for XI, XVb, XVIc, XVIIIb, XXXVII, XL. For the rest acetic acid was used.

Compound XXVII gave on reduction, XXVIII in 80% yield (crude). The UV absorption spectrum  $[\lambda_{max}^{B10H} 325, 275, 242 \text{ m}\mu; \log \epsilon (3.09, 3.41, 4.36)]$  of the reduction product was identical with that reported in the literature.<sup>6</sup>

Compound XXV gave XXVI on reduction (yield, 81%). The UV absorption spectrum of XXVI was identical with the compound prepared by the alternative method, of dehydration of XXVIa reported earlier in this paper.

Reduction of the dye (XVIIIb) gave a pale yellow solid (yield, 94%). On chromatography on alumina using benzene, the latter gave XVIIIc as an orange coloured solid, m.p. 66-67°. (Found: C, 70·3, H, 6·4. C<sub>33</sub>H<sub>35</sub>S<sub>3</sub>O<sub>3</sub> requires: C, 69·7; H, 4·9%.) The reduction product decomposed in the mass spectrometric determination of mol. wt. However peaks (384-386, 464-467), corresponding to masses between the dimeric structure (mass 380) and trimeric structure (mass 568) were observed.

The absorption spectra of the compounds described in this paper are given in Tables 8, 9 and 10.

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<sup>8</sup> W. E. Parham and R. Koncos, J. Amer. Chem. Soc. 83, 4034 (1961).