

**1186.** *Complex Oxonols and Holopolar Merocyanines.*

By E. B. KNOTT.

Oxonols (I), derived from 3-substituted 2-thio-thiazolid-4-ones and -oxazolid-4-ones, yield reactive holopolar betaines (III) on treatment with methyl sulphate or methyl iodide-sodium ethoxide. The betaines condense with reactive methylene compounds to give complex oxonols (VI) and with nucleophilic methyl groups of cyclic quaternary ammonium salts to give a new type of dye (XIII), a holopolar merocyanine which is a hybrid of an oxonol anion and a cyanine cation. Higher vinylogues of these dyes have been obtained and the reaction has been extended to acid dyes containing only one oxygen atom in the resonance system.

THE formation of complex merocyanines and mixed merocyanine-cyanines by the quaternization of merocyanines containing a cyclic thioamide group,  $-NR\cdot CS-$ , and the reaction of the resulting quaternary ammonium salt with a nucleophilic methylene- or methyl-containing compound, was discovered independently by Fry and Kendall,<sup>1</sup> Riester,<sup>2</sup> and Brooker,<sup>3</sup> and was extended by the present author and Jeffreys.<sup>4</sup>

The present Paper is concerned with the synthesis of related dyes derived from oxonols

<sup>1</sup> D. J. Fry and J. D. Kendall, U.S.P. 2,388,963.

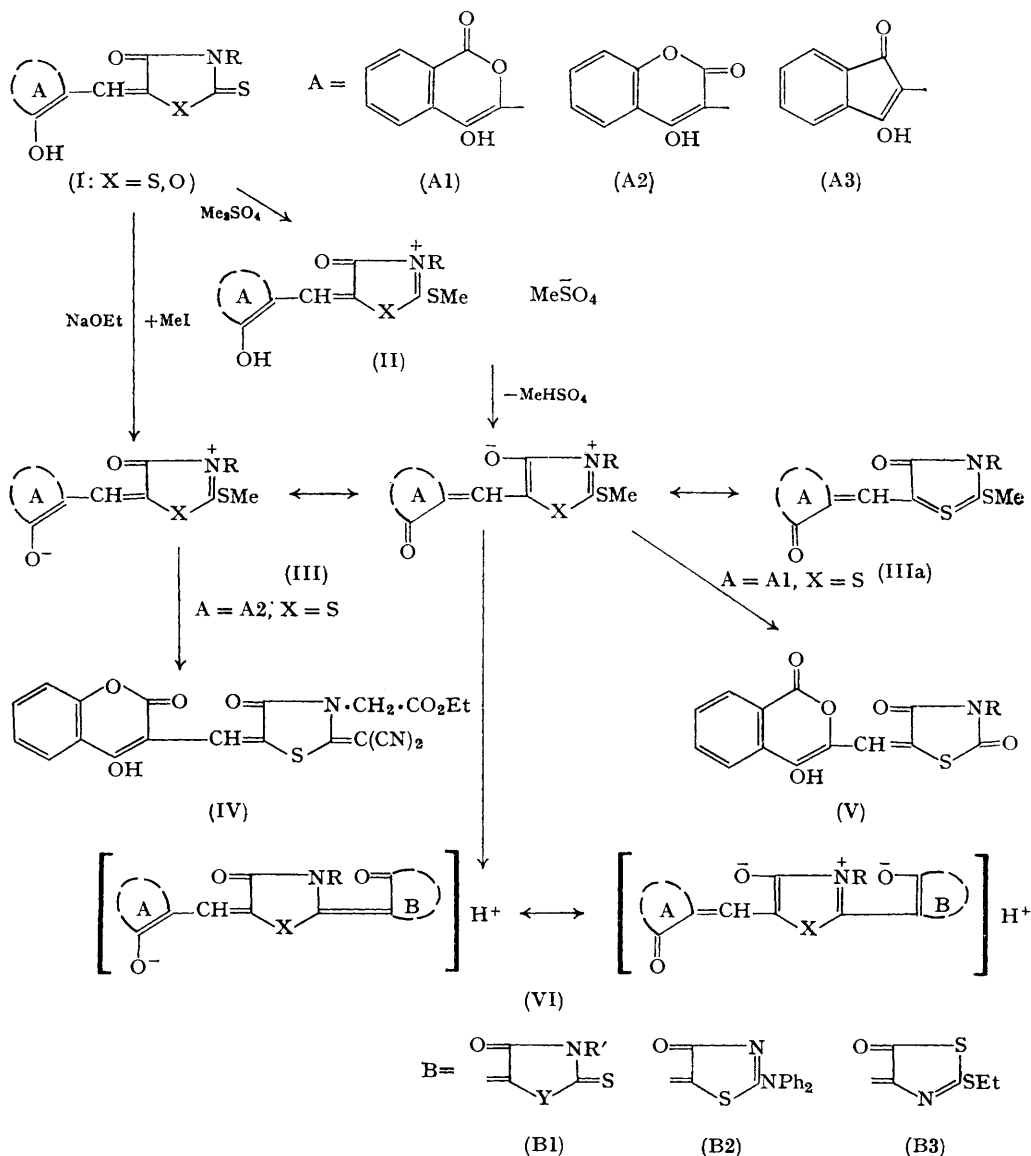
<sup>2</sup> O. Riester, U.S.P. 2,442,710.

<sup>3</sup> L. G. S. Brooker, U.S.P. 2,454,629.

<sup>4</sup> E. B. Knott and R. A. Jeffreys, *J.*, 1952, 4762.

and other acid dyes containing a 3-substituted rhodanine or 2-thio-oxazolid-4-one nucleus, certain of which present rather unusual features.

The simple oxonols (I), where the hydroxylate nucleus A is 4-hydroxy-1-oxoisochromen-3-yl<sup>5</sup> (A1), 4-hydroxy-2-oxochromen-3-yl<sup>5</sup> (A2), and 3-hydroxy-1-oxoindolen-2-yl (A3), were



first examined. Their quaternization with methyl sulphate at 100–170° was rapid and afforded melts possessing the expected reactivities of the quaternary salts (II) and giving complex, trinuclear dyes with suitable intermediates.

Attempts to purify these melts led to the isolation of two types of product. Treatment of the melt derived from the oxonol (I; A = A1, X = S, R =  $\text{CH}_2\cdot\text{CO}_2\text{Et}$ ) with hot ethanol yielded the oxonol (V; R =  $\text{CH}_2\cdot\text{CO}_2\text{Et}$ ) with the loss of methanethiol. The analogous melt

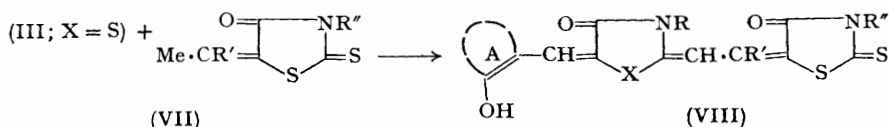
<sup>5</sup> E. B. Knott, *J.*, 1963, 402.

from the oxonol (I; R = Et), on being warmed in dimethylformamide, afforded the coloured, mesomeric, holopolar betaine (III; A = Al, X = S, R = Et) by the loss of methyl hydrogen sulphate. The betaine was hydrolysed to the oxonol (V; R = Et) by hot aqueous ethanol, and readily afforded complex dyes. More stable betaines were obtained from oxonols derived from nuclei A2 and A3.

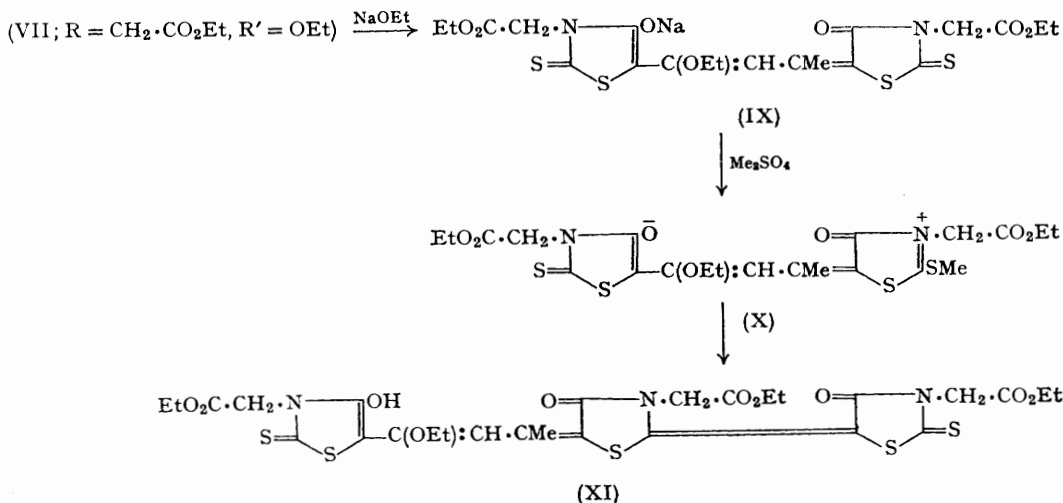
In some cases the betaines (III) were best obtained by forming the sodium salt of the oxonol (I) and treating it with methyl iodide in ethanol. The intensity of the colour of these compounds is a function of their resonance systems, which are analogous to those of the oxonol anions. Contributions to the resonance hybrid of these dyes by structures such as (IIIa) involving the sulphur *d*-orbitals is possible. Their absorption maxima usually lie between those of the oxonol and its anion.

Treatment of the betaines (III) or crude melts (II) with keto-methylenes in ethanol or pyridine in the presence of triethylamine gave complex oxonols (VI). Whereas the free oxonol is pale to deep yellow in solution, the anions are deeply coloured (red, blue) by virtue of the trinuclear resonance system shown. They thus possess outstanding pH-indicator properties.

Other reactive methylene compounds, *e.g.*, malononitrile, also reacted with the betaines to give dyes such as (IV).



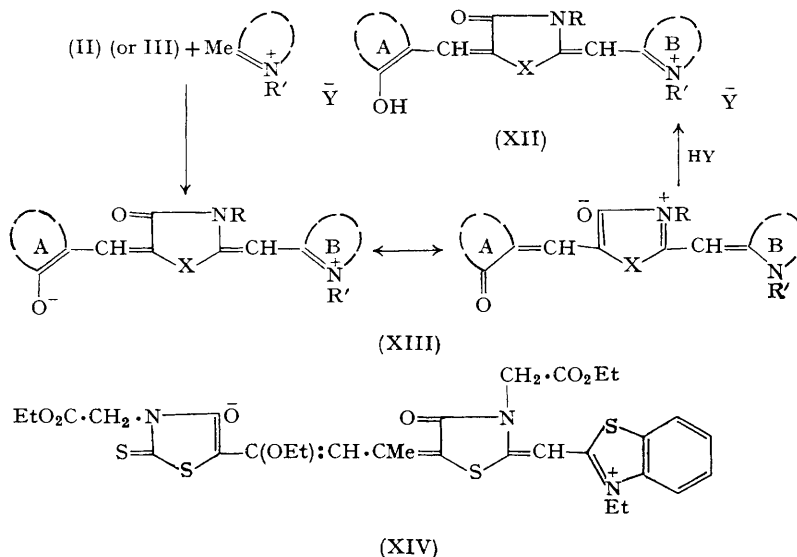
Higher vinylogues of the complex oxonols (VI), *e.g.*, (VIII; R' = H, OEt, SEt), were obtained by treating the betaines with 5-ethylidenerhodanines (VII; R' = H, OEt, SEt),<sup>6</sup> or by commencing with a trimethineoxonol, *e.g.*, (IX), converting it into the betaine (X) and thence into the complex dye (XI). In the latter dye and its betaine precursor the actual positions of the chain methyl and ethoxyl groups may be the reverse of those given.



With nucleophilic methyl derivatives of heterocyclic quaternary salts the crude melt (II) or the betaine (III) yielded the holopolar merocyanines (XIII) and not their salts (XII).

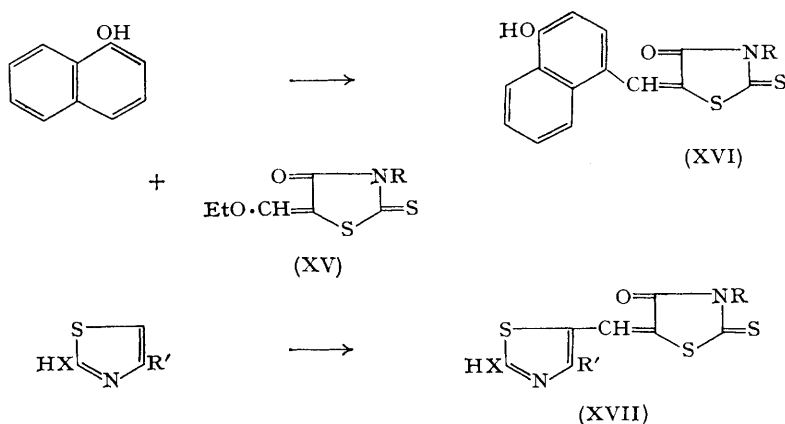
<sup>6</sup> E. B. Knott, *J.*, 1954, 1482.

The latter were obtained from the bases (XIII) by the addition of mineral acid.\* This addition results in a powerful hypsochromic shift, analogous to that shown by proton addition to certain dye bases to give hydroxystyryl derivatives of heterocyclic quaternary ammonium cations.<sup>7</sup>



The dye bases (XIII) are strongly polar, their solutions showing hypsochromic shifts on increasing the solvent polarity (see Experimental section). The shift increases, as would be expected, on increasing the dye polarity by replacing a more weakly basic nucleus B, *e.g.*, 3-ethylbenzothiazoline, by a more strongly basic nucleus, *e.g.*, 1-ethyl-1,4-dihydroquinoline.

The principle of the formation of complex acid or holopolar dyes should be applicable to any derivative of rhodanine containing an acid hydrogen atom attached to an atom conjugated with the 4-carbonyl group. Examples of such compounds are the 5-*o*- or 5-*p*-hydroxyarylmethylidenerhodanines which may be regarded as a type of oxonol. They are usually obtained by the condensation of the rhodanine with the hydroxyarylaldehyde. In

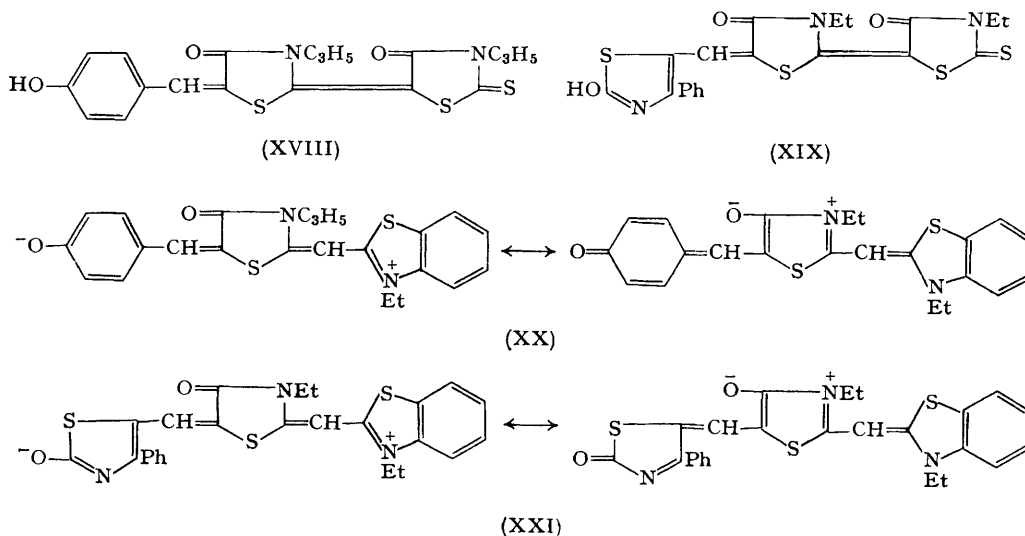


\* Dyes such as (XII, A = 3-substituted rhodanine, X = S, B = thiazolium or benzothiazolium) have been made by T. R. Thompson (U.S.P. 2,518,730; 2,535,994) by the final addition of ring A to the preformed thiazolone cyanine. No mention is made of their conversion into the holopolar, anhydro-form.

<sup>7</sup> E. B. Knott, *J.*, 1951, 3038.

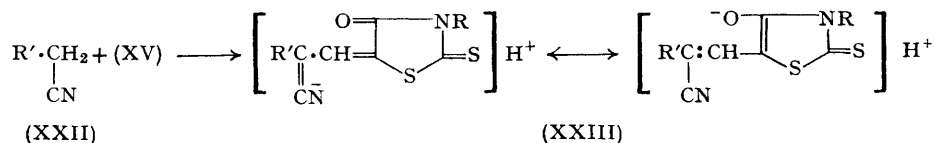
certain cases, particularly in the heterocyclic series, it was found more convenient to obtain them from the hydroxy-aromatic or -heterocycle and a 5-ethoxymethylenerhodanine (XV) in the presence of sodium ethoxide. Thus, *e.g.*, 1-naphthol or a 4-substituted 2-hydroxy- or 2-mercapto-thiazole gave the compounds (XVI) and (XVII), respectively.

Compounds of this type were readily quaternized and converted into complex dyes of the oxonol (XVIII) (XIX) or holopolar merocyanine (XX) (XXI) types.



The  $pK$  value of dye (XVIII) is higher (8.5) than that of dye (XIX) (6.5) which is higher than that of the related oxonols (VI; A = A1) (4.5), (VI; A = A2) (3.7), (VI; A = A3) (0.5). This is consistent with the expected increase in acidity of the left-hand nucleus based on resonance considerations on proceeding through this series. The same effect is observed in the formation of the related holopolar merocyanines from their hydrohalides, a much stronger base being necessary in the case of the dye (XX).

An extension of the reaction leading to the substituted 5-methylenerhodanines (XVI) and (XVII) was found in the condensation of the 5-ethoxymethylenerhodanine (XV) with cyanomethyl derivatives (XXII;  $R' = \text{CN}$ ,  $\text{CO}_2\text{Et}$ ,  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4$ ) which yielded acidic compounds (XXIII) suitable for quaternization and conversion into complex dyes.



Thus malononitrile and ethyl cyanoacetate reacted with the 5-ethoxymethylenerhodanine (XV) in the presence of triethylamine to give the 2-cyanovinylthiazolinols (XXIII;  $R' = \text{CN}$  and  $\text{CO}_2\text{Et}$  respectively).

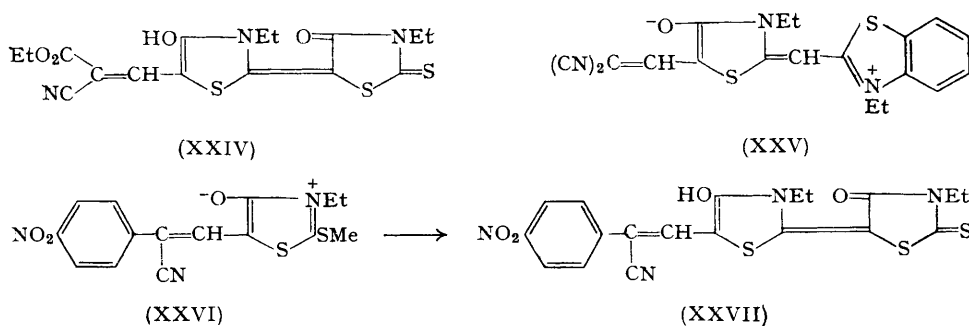
*p*-Nitrophenylacetonitrile condensed with the ether (XV) in ethanolic sodium ethoxide to yield the purple sodium salt of the 5-styrylthiazolinol (XXIII;  $R' = p\text{-NO}_2\cdot\text{C}_6\text{H}_4$ ). All the anions of these acid dyes (XXIII) are highly coloured, as would be expected from the resonance system shown. Dyes (XXIII;  $R' = \text{CN}$  or  $\text{CO}_2\text{Et}$ ) were quaternized as the free acids and afforded complex dyes (XXIV, XXV) as their hydrates.

The dye (XXIII;  $R' = p\text{-NO}_2\cdot\text{C}_6\text{H}_4$ ) was best quaternized by treatment of its sodium

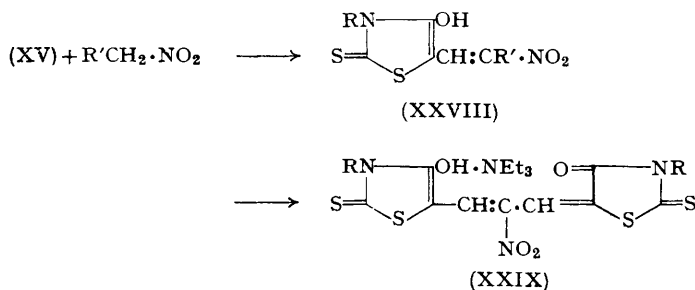
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salt with methyl iodide to give the crystalline betaine (XXVI) and thence the complex oxonol (XXVII).



Suitable acidic intermediates might also be expected from the condensation of a 5-ethoxymethylenerhodanine (XV) with nitroalkanes. In ethanolic triethylamine, the ether (XV) and nitromethane did not yield the expected 2-nitrovinyl derivative (XXVIII; R' = H), the latter presumably reacting further to give the *meso*-nitrotrimethineoxonol (XXIX) in the form of its triethylammonium salt.



This oxonol formation was excluded by the use of nitroethane and 1-nitropropane; these condensed with the 5-ethoxymethylenerhodanine (XV) in the presence of sodium ethoxide to give the stable, highly coloured sodium salt of the 5-2'-nitroalkenylthiazolinols (XXVIII; R' = Me and Et, respectively). The corresponding free acids were isolated but the acid with R' = Me gradually decomposed on storage. It also decomposed in boiling chloroform with loss of nitrous acid to give a red crystalline solid. Quaternization of (XXVIII) gave products which did not yield complex dyes.

#### EXPERIMENTAL

**3-Ethyl-5-(3-hydroxy-1-oxoinden-2-ylmethylene)-2-thiothiazolid-4-one** (I; A = A3, X = S, R = Et).—5-Ethoxymethylene-3-ethylrhodanine (4.38 g., 0.02 mole), indane-1,3-dione (2.92 g., 0.02 mole), ethanol (25 ml.), and triethylamine (3 ml., 0.02 mole) were heated on a steam-bath for 5 min. Concentrated hydrochloric acid (2.5 ml.) was added to the orange solution which solidified. The solid was washed with ethanol, dissolved in hot ethanolic triethylamine and acidified, while hot, with ethanolic hydrochloric acid. The compound (5.0 g., 79%) formed maroon flakes softening from 165° onwards (Found: C, 57.0; H, 3.5; N, 4.2; S, 20.5. C<sub>15</sub>H<sub>11</sub>NO<sub>3</sub>S<sub>2</sub> requires C, 56.75; H, 3.45; N, 4.4; S, 20.2%); λ<sub>max</sub>. 423 mμ in chloroform, 482 mμ in ethanolic triethylamine.

**3-Ethoxycarbonylmethyl-5-[3-ethoxy-3-(3-ethoxycarbonylmethyl-4-hydroxy-2-thiothiazolin-5-yl)-1-methylprop-2-enylidene]-2-thiothiazolid-4-one**.—3-Ethoxycarbonylmethyl-5'-ethoxyethylidenerhodanine (VII; R' = OEt, R'' = CH<sub>2</sub>-CO<sub>2</sub>Et) (5.8 g., 0.02 mole) was added to a hot solution from sodium (0.23 g.) in ethanol (10 ml.), and the solution refluxed on a steam-bath for 5 min. The sodium salt (IX) crystallized from the blue solution; it (4.1 g., 74%) formed green flakes, m. p. 197°, from ethanol (Found: C, 43.1; H, 4.6; N, 4.95; Na, 4.2; S, 23.6. C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>NaO<sub>7</sub>S<sub>4</sub> requires C, 43.3;

H, 4.3; N, 5.05; Na, 4.15; S, 23.1%),  $\lambda_{\max}$ . 616 m $\mu$  in ethanol. The *free acid*, liberated by concentrated hydrochloric acid from the ethanolic solution of the sodium salt, formed pale yellow needles, m. p. 159°, from ethanol containing a drop of concentrated hydrochloric acid (Found: C, 45.3; H, 4.75; N, 5.4; S, 23.9. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>7</sub>S<sub>4</sub> requires C, 45.05; H, 4.5; N, 5.25; S, 24.05%), p*K* 4.1, colour change pH 4.9—3.3.

3-*Allyl-5-p-hydroxybenzylidene-2-thiothiazolid-4-one*.—*p*-Hydroxybenzaldehyde (6.1 g., 1 mole), 3-allylrhodanine (8.65 g., 1 mole), ethanol (10 ml.), and piperidine (0.2 ml.) were heated on a steam-bath for 1—2 min. until solid. The *compound* (11.9 g., 86%) formed orange needles, m. p. 167—169°, from benzene—light petroleum (Found: C, 56.6; H, 4.15; N, 4.95; S, 22.95. C<sub>13</sub>H<sub>11</sub>NO<sub>2</sub>S<sub>2</sub> requires C, 56.3; H, 4.0; N, 5.05; S, 23.1%).

3-*Ethyl-5-(4-hydroxy-1-naphthylmethylene)-2-thiothiazolid-4-one* (XVI; R = Et). Sodium (0.23 g.) was dissolved in ethanol (10 ml.) and 1-naphthol (1.44 g., 0.01 mole) and 5-ethoxymethylene-3-ethylrhodanine (2.17 g., 0.01 mole) were added. The mixture was refluxed for 5 min. and the purple solution treated with concentrated hydrochloric acid (1 ml.) in ethanol (5 ml.) until the colour changed to orange and the whole solidified. It was dissolved in hot ethanolic triethylamine, white flocks were filtered off, and the hot filtrate was acidified. The *compound* (1.75 g., 55.5%) formed orange threads, m. p. 250° and softening at 243° (Found: C, 61.3; H, 4.23; N, 4.3; S, 20.1. C<sub>16</sub>H<sub>13</sub>NO<sub>2</sub>S<sub>2</sub> requires C, 61.0; H, 4.1; N, 4.45; S, 20.3%),  $\lambda_{\max}$ . 438 m $\mu$  in chloroform, 552 m $\mu$  in ethanolic triethylamine. The white flocks (0.3 g.) formed white threads, decomposing above 330°, from dimethylformamide (Found: C, 68.5; H, 3.55; S, 14.05. C<sub>13</sub>H<sub>8</sub>O<sub>2</sub>S requires C, 68.0; H, 3.5; S, 13.95%).

An analogous reaction with 2-naphthol gave only the nitrogen-free analogue of the above, as pale yellow threads, decomposing above 335°, from dimethylformamide (Found: C, 68.1; H, 3.25; S, 14.5%).

3-*Ethyl-5-(2-hydroxy-4-phenylthiazol-5-ylmethylene)-2-thiothiazolid-4-one* (XVII; R = Et, R' = Ph, X = O).—5-Ethoxymethylene-3-ethylrhodanine (2.17 g., 0.01 mole) and 2-hydroxy-4-phenylthiazole (1.77 g., 0.01 mole) were added to a solution from sodium (0.23 g.) in ethanol (5 ml.), and the whole was refluxed for 5 min. Acetic acid (1.5 ml.) was added to the deep-red solution. The whole solidified. The *product* was collected and washed with ethanol; it (2.9 g., 83.5%) formed yellow threads, m. p. 274°, from ethanol (Found: C, 52.05; H, 3.5; N, 8.05; S, 27.8. C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub> requires C, 51.75; H, 3.45; N, 8.05; S, 27.6%),  $\lambda_{\max}$ . 438 m $\mu$  in chloroform, 506 m $\mu$  in ethanolic triethylamine; p*K* 6.5, colour change pH 7.5—5.5. 3-*Ethyl-5-(2-hydroxy-4-methylthiazol-5-ylmethylene)-2-thiothiazolid-4-one* (XVII; X = O, R' = Me, R = Et) (2.3 g., 80.5%) was obtained analogously from 2-hydroxy-4-methylthiazole (1.15 g., 0.01 mole). It formed soft, chrome-yellow flakes, decomposing from 275° onwards, when its hot solution in ethanolic triethylamine was acidified (Found: C, 41.7; H, 3.35; N, 9.85; S, 33.7. C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub> requires C, 41.9; H, 3.5; N, 9.8; S, 33.75%),  $\lambda_{\max}$ . 423 m $\mu$  in chloroform, 505 m $\mu$  in ethanolic triethylamine. 3-*Ethyl-5-(2-mercapto-4-methylthiazol-5-ylmethylene)-2-thiothiazolid-4-one* (XVII; X = S, R = Et, R' = Me) was obtained in low yield by the above procedure from 4-methylthiazole-2-thiol. It formed magenta needles, decomposing from 230°, when its solution in ethanolic triethylamine was acidified (Found: C, 40.1; H, 3.4; N, 8.95; S, 42.5. C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>OS<sub>4</sub> requires C, 40.0; H, 3.3; N, 9.3; S, 42.4%),  $\lambda_{\max}$ . 461 m $\mu$  in chloroform, 518 m $\mu$  in ethanolic triethylamine.

5-(2,2-Dicyanovinyl)-3-ethyl-4-hydroxythiazoline-2-thione (XXIII; R = Et, R' = CN).—5-Ethoxymethylene-3-ethylrhodanine (6.5 g., 0.03 mole), malononitrile (2.0 g., 0.03 mole), ethanol (25 ml.), and triethylamine (4.5 ml., 0.03 mole) reacted exothermically. The yellow solution was heated for 5 min. on a steam-bath and then diluted with water (100 ml.). The clear solution was chilled and concentrated hydrochloric acid (20 ml.) gradually added. Crystallization set in and, after the mass had been chilled overnight, the crystals were collected (6.3 g., 88%). The *compound* can be recrystallized with difficulty, usually giving a poor recovery of solvated crystals. A sample from *n*-butyl alcohol formed brown crystals, m. p. 95—97° (Found: C, 50.5; H, 5.7; N, 13.3; S, 20.95. C<sub>9</sub>H<sub>7</sub>N<sub>3</sub>OS<sub>2</sub>.C<sub>4</sub>H<sub>9</sub>OH requires C, 50.2; H, 5.45; N, 13.5; S, 20.6%),  $\lambda_{\max}$ . 433 m $\mu$  in chloroform, 457 m $\mu$  in ethanolic triethylamine.

5-(2-Cyano-2-ethoxycarbonylvinyl)-3-ethyl-4-hydroxythiazoline-2-thione (XXIII; R = Et, R' = CO<sub>2</sub>Et). 5-Ethoxymethylene-3-ethylrhodanine (XV; R = Et) (2.2 g., 1 mole), ethyl cyanoacetate (1.1 ml., 1 mole), ethanol (10 ml.), and triethylamine (1.5 ml., 3 moles) were heated on a steam-bath for 5 min. Water (100 ml.) was added followed by concentrated hydrochloric acid (10 ml.). An orange tar was precipitated. The liquor was decanted, the tar washed with water and dissolved in cold ethanol (25 ml.). Water was then run in until the solution became faintly cloudy. As crystal-

lization proceeded more water was dripped in. The thick crystalline meal (1.4 g.) gave pale yellow crystals, m. p. 128—130° (soft from 117°) from acetic acid (Found: C, 44.0; H, 4.8; N, 8.9; S, 20.75.  $C_{11}H_{12}N_2O_3S_2 \cdot H_2O$  requires C, 43.7; H, 4.65; N, 9.25; S, 21.2%);  $\lambda_{max}$ . 430 m $\mu$  in chloroform, 455 m $\mu$  in ethanolic triethylamine.

3-Ethyl-5-[3-(3-ethyl-4-hydroxy-2-thiothiazolin-5-yl)-2-nitroprop-2-enylidene]-2-thiothiazolid-4-one (Triethylammonium Salt) (XXIX; R = Et).—5-Ethoxymethylene-3-ethylrhodanine (XV; R = Et) (6.5 g., 0.03 mole), nitromethane (2 ml., 0.04 mole), ethanol (30 ml.), and triethylamine (4.5 ml., 0.03 mole) were heated on a steam-bath for 10 min. Ether (30 ml.) was run in gradually to give green-red crystals. From ethanol the compound (5.25 g., 70%) formed flat, green-brown needles, m. p. 201° (decomp. with effervescence) (Found: C, 45.1; H, 5.75; N, 10.95; S, 25.55.  $C_{19}H_{28}N_4O_4S_4$  requires C, 45.25; H, 5.55; N, 11.1; S, 25.4%);  $\lambda_{max}$ . 534 m $\mu$  in ethanolic triethylamine.

3-Ethyl-4-hydroxy-5-(2-nitroprop-1-enyl)thiazoline-2-thione (XXVIII; R = Et, R' = Me).—Nitroethane (1.8 ml., 0.24 mole) was added to a solution from sodium (0.46 g.) in ethanol (25 ml.). The sodium salt formed a thick meal when the mixture was agitated violently. 5-Ethoxymethylene-3-ethylrhodanine (XV; R = Et) (4.34 g., 0.02 mole) was added and the whole was heated on a steam-bath for 5 min. The addition of ether (50 ml.) then precipitated the sodium salt as a scarlet powder. From ethanol-ether the salt (4.6 g., 86%) formed a scarlet powder, m. p. 128—129° (Found: C, 35.45; H, 3.5; N, 10.4; Na, 8.4; S, 24.1.  $C_8H_9N_2NaO_3S_2$  requires C, 35.8; H, 3.35; N, 10.45; Na, 8.6; S, 23.9%). The free acid was obtained as yellow grains on the addition of acetic acid to an aqueous solution of the sodium salt. On being recrystallized from benzene, however, it decomposed to give alkali-insoluble maroon needles, m. p. 231—233° (Found: C, 48.0; H, 4.6; N, 6.8; S, 31.65.  $C_8H_9NOS_2$  requires C, 48.25; H, 4.55; N, 7.05; S, 32.2%).

3-Ethoxycarbonylmethyl-4-hydroxy-5-(2-nitrobut-1-enyl)thiazoline-2-thione (XXVIII; R =  $CH_2 \cdot CO_2Et$ , R' = Et).—Sodium (0.23 g.) was dissolved in ethanol (15 ml.) and 1-nitropropane (1 ml., 0.011 mole) added. The solid sodium salt was well dispersed. 3-Ethoxycarbonylmethyl-5-ethoxymethylenetherodanine (XV; R =  $CH_2 \cdot CO_2Et$ ) (2.76 g., 0.01 mole) was added and the whole was heated for 5 min. on a steam-bath. The intensely orange solution was then treated gradually with ether (50 ml.) as crystallization proceeded. The dark red needles fell to a red powder (2.5 g., 73.5%) on standing. The compound formed a red, crystalline powder, m. p. 152—154°, from ethanol-ether (Found: C, 38.5; H, 4.1; N, 8.15; S, 18.4.  $C_{11}H_{13}N_2NaO_5S_2$  requires C, 38.8; H, 3.8; N, 8.25; S, 18.85%).

5-( $\alpha$ -Cyano-4-nitrostyryl)-3-ethyl-4-hydroxythiazoline-2-thione (XXIII; R = Et, R' = *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>) (Sodium Salt).—5-Ethoxymethylene-3-ethylrhodanine (XV; R = Et) (4.34 g., 0.02 mole) and *p*-nitrophenylacetone nitrile (3.24 g., 0.02 mole) were added to a solution from sodium (0.46 g.) in ethanol (25 ml.). A purple colour developed and, when the solution was heated, the dye separated as the sodium salt. After 2 min. the solution was chilled and ether (25 ml.) was added. The green crystals (6.1 g., 86%) were sufficiently pure for dye reactions. A sample, from ethanol-ether, formed green crystals shrinking at 208—210° (Found: C, 47.3; H, 3.2; N, 11.6; Na, 6.2; S, 19.55.  $C_{14}H_{10}N_3NaO_3S_2$  requires C, 47.25; H, 3.1; N, 11.85; Na, 6.5; S, 19.1%);  $\lambda_{max}$ . 549 m $\mu$  in ethanol.

Anhydro-3-ethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-2-methylthio-4-oxothiazolinium Hydroxide (III; A = Al, X = S, R = Et).—(a) 3-Ethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-2-thiothiazolid-4-one<sup>5</sup> (3.33 g.) was dissolved in a solution from sodium (0.23 g.) in ethanol (25 ml.). Methyl iodide (1.5 ml.) was added and the mixture refluxed on a steam-bath for 2 hr. The grey-green crystals which had then separated were washed with ethanolic triethylamine. The compound (2.75 g., 79%) was obtained as maroon crystals, m. p. 268° (decomp. with effervescence), softening from 180° (Found: C, 54.9; H, 3.8; N, 3.9; S, 18.35.  $C_{16}H_{13}NO_4S_2$  requires 55.3; H, 3.75; N, 4.05; S, 18.45%);  $\lambda_{max}$ . 530 m $\mu$  in chloroform.

(b) The above oxonol (1.1 g.) and methyl sulphate (1 ml.) were fused together at 170° for about 3 min. until fusion was complete. This was best carried out in a boiling-tube, the solid being ground with a glass rod. The tar was dissolved in a little dimethylformamide and chilled to give compound (III; A = Al; X = S, R = Et) (0.3 g.). The filtrate, after being diluted with much water, gave a solid on prolonged storage. This product (0.8 g.) formed ochre needles, decomposing from 260°, on acidification of its red solution in ethanolic triethylamine. It was 3-ethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)thiazolidine-2,4-dione (V; R = Et) (Found: C, 56.65; H, 3.6; N, 4.3; S, 10.2.  $C_{15}H_{11}NO_5S$  requires C, 56.75; H, 3.45; N, 4.4; S, 10.1%). The analogous 3-ethoxycarbonylmethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)thiazolidine-2,4-dione (V; R =  $CH_2 \cdot CO_2Et$ )



was obtained directly in 56% yield from the quaternization reaction in boiling ethanol. It was obtained as bronze flakes, m. p. 282—292°, when its solution in ethanolic triethylamine was acidified (Found: C, 54.4; H, 3.75; N, 3.5; S, 8.75.  $C_{17}H_{13}NO_7S$  requires C, 54.35; H, 3.5; N, 3.7; S, 8.55%);  $\lambda_{\max}$ . 504 m $\mu$  in ethanolic triethylamine.

*Anhydro-3-ethoxycarbonylmethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-2-methylthio-4-oxothiazolinium Hydroxide* (III; A = A1, X = S, R = CH<sub>2</sub>·CO<sub>2</sub>Et).—The alkylation of the oxonol (I; A = A1, X = S, R = CH<sub>2</sub>·CO<sub>2</sub>Et) with hot methyl iodide in ethanolic sodium ethoxide does not yield compound (III; A = A1, X = S, R = CH<sub>2</sub>·CO<sub>2</sub>Et), as it is readily hydrolysed to compound (V; R = CH<sub>2</sub>·CO<sub>2</sub>Et) under these conditions. It was obtained as follows. The oxonol (2.55 g.) was dissolved in a solution from sodium (0.15 g.) in methanol (25 ml.). Methyl iodide (3 ml.) was added at room temperature and the mixture set aside for 24 hr. It solidified after 2 hr. Isopropyl alcohol (25 ml.) was added and the green threads (1.6 g., 60%) were collected. This material formed bronze-green threads, m. p. 212—214°, from ethanol (Found: C, 53.55; H, 3.7; N, 3.2; S, 15.9.  $C_{18}H_{15}NO_6S_2$  requires C, 53.3; H, 3.7; N, 3.45; S, 15.8%),  $\lambda_{\max}$ . 530 m $\mu$  in chloroform.

*Anhydro-3-ethyl-5-(3-hydroxy-1-oxoinden-2-ylmethylene)-2-methylthio-4-oxothiazolinium Hydroxide* (III; A = A3, X = S, R = Et).—The oxonol (see above) (3.17 g., 0.01 mole) was dissolved in a hot solution of sodium (0.23 g.) in methanol (50 ml.). Methyl iodide (1.5 ml., 0.024 mole) was added and the solution was refluxed for 30 min. A solid commenced to separate after 10 min. The mixture was chilled, and the solid was collected and washed with ethanol. The compound (2.8 g., 84.5%) formed orange needles, m. p. 251—252° (soft, 245°), from dimethylformamide-ethanol (Found: C, 57.2; H, 3.95; N, 3.8; S, 19.15.  $C_{10}H_{13}NO_3S_2$  requires C, 57.75; H, 3.95; N, 4.25; S, 19.35%);  $\lambda_{\max}$ . 506 m $\mu$  in chloroform.

*Anhydro-3-ethoxycarbonylmethyl-5-(4-hydroxy-2-oxochromen-3-ylmethylene)-2-methylthio-4-oxothiazolinium Hydroxide* (III; A = A2, X = S, R = CH<sub>2</sub>·CO<sub>2</sub>Et).—The oxonol<sup>5</sup> (1.0 g., 1 mole) and methyl sulphate (0.3 ml., 1.2 moles) were fused at 155° for 5 min. The tar was washed with ether and boiled up with ethanol (20 ml.). The mixture was chilled and the grains (0.85 g., 87%) were collected; they formed orange needles, m. p. 241—242°, from dimethylformamide-ethanol (Found: C, 52.9; H, 4.05; N, 3.25; S, 15.5.  $C_{18}H_{15}NO_6S_2$  requires C, 53.3; H, 3.7; N, 3.45; S, 15.8%),  $\lambda_{\max}$ . 492 m $\mu$  in chloroform.

*Anhydro-3-ethyl-5-( $\alpha$ -cyano-4-nitrostyryl)-4-hydroxy-2-methylthiothiazolinium Hydroxide* (XXVI).—The sodium salt of compound (XXIII; R = Et, R' = *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>) (1.0 g., 1 mole), methanol (25 ml.), and methyl iodide (1 ml., 4 moles) were refluxed for 1 hr. The purple colour had by then largely faded and crystals had separated. These crystals (0.95 g., 97%) were washed with methanol and were sufficiently pure for further condensation. A sample from dimethylformamide formed steel-grey crystals, decomposing above 268° (Found: C, 51.65; H, 3.95; N, 12.1; S, 18.65.  $C_{15}H_{13}N_3O_3S_2$  requires C, 51.9; H, 3.75; N, 12.1; S, 18.45%);  $\lambda_{\max}$ . 505 m $\mu$  in chloroform.

*Anhydro-3-ethoxycarbonylmethyl-5-[3-ethoxy-3-(3-ethoxycarbonylmethyl-4-hydroxy-2-thiothiazolin-5-yl)-1-methylprop-2-enylidene]-2-methylthio-4-oxothiazolinium Hydroxide* (X).—The trimethine-oxonol (IX) (2.8 g., 0.005 mole) was covered with methanol (5 ml.) and heated with methyl sulphate (0.5 ml., 0.02 mole) on a steam-bath for 1—1½ min. until the solid had dissolved and the colour of the solution had changed from blue to magenta. Ether (50 ml.) was added and the mixture chilled overnight. The solid was collected, and washed with ether and water. It formed dark-bronze crystals, m. p. 90—105°, and was sufficiently pure for further reaction (Found: C, 44.7; H, 4.65; N, 4.8; S, 22.9.  $C_{21}H_{26}N_2O_7S_4$  requires C, 45.1; H, 4.75; N, 5.1; S, 23.4%);  $\lambda_{\max}$ . 531 m $\mu$  in chloroform.

*Complex Oxonols* (VI). *General Procedure*.—The oxonol (I) (0.01 mole) and methyl sulphate (0.015—0.045 mole) in a boiling tube were immersed in a steam- or oil-bath (100—170°) for 30 sec. to 5 min. and the mixture ground with a glass rod until the mass had fused to a tar. In some cases crystallization set in. The quaternary salt was washed with ether, the reactive methylene component (B) (0.015 mole), pyridine or ethanol (25 ml.), and triethylamine (0.03 mole) were added, and the solution heated on a steam-bath for 5 min. The solution was then acidified with concentrated hydrochloric acid (0.02 mole) in those cases where ethanol was used as the solvent, or with 2N-hydrochloric acid where pyridine was used as a solvent. The complex dye then usually precipitated or crystallized. It was purified by the addition of concentrated hydrochloric acid to its solution in hot ethanolic triethylamine until the colour shifted hypsochromically to yellow.

*3-Ethoxycarbonylmethyl-5-[3-ethoxycarbonylmethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-4-oxothiazolidin-2-ylidene]-2-thiothiazolid-4-one* (VI; R = R' = CH<sub>2</sub>·CO<sub>2</sub>Et, A = A1, B = B1,

X = Y = S).—The oxonol (I; A = A1, R = CH<sub>2</sub>-CO<sub>2</sub>Et, X = S) (1.0 g.) and methyl sulphate (1 ml.) were fused together at 170° for 5 min. and reacted with 3-ethoxycarbonylmethylrhodanine (0.65 g.). The dye (0.5 g., 34%) formed maroon platelets, m. p. 268° (decomp. from 255°) (Found: C, 50.3; H, 3.65; N, 4.65; S, 16.7. C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>9</sub>S<sub>3</sub> requires C, 50.0; H, 3.5; N, 4.85; S, 16.65%); λ<sub>max</sub>. 593, 633 mμ in alcoholic triethylamine, pK 4.5, colour change pH 5.5—3.5.

3-Ethoxycarbonylmethyl-5-[3-ethoxycarbonylmethyl-5-(4-hydroxy-2-oxochromen-3-ylmethylene)-4-oxothiazolidin-2-ylidene]-2-thiothiazolid-4-one (VI; A = A2, B = B1, X = Y = S, R = R' = CH<sub>2</sub>-CO<sub>2</sub>Et).—The oxonol (I; R = CH<sub>2</sub>-CO<sub>2</sub>Et, A = A2) (1 g.) and methyl sulphate (0.3 ml.) were fused at 170° for 30 sec. and made to react with 3-ethoxycarbonylmethylrhodanine (0.65 g.). The dye (0.75 g., 51%) was obtained as orange threads, m. p. 283° with previous softening (Found: C, 50.2; H, 3.75; N, 4.65; S, 16.55. C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>9</sub>S<sub>2</sub> requires C, 50.0; H, 3.5; N, 4.85; S, 16.65%). Its triethylammonium salt was obtained as small, magenta needles, m. p. 218—219°, by the addition of ether to its solution in ethanolic triethylamine (Found: C, 53.2; H, 5.3; N, 6.35; S, 9.75. C<sub>30</sub>H<sub>35</sub>N<sub>3</sub>O<sub>9</sub>S<sub>2</sub> requires C, 53.0; H, 5.15; N, 6.2; S, 9.45%); λ<sub>max</sub>. 512 mμ in ethanolic triethylamine.

3-Ethyl-5-[3-ethyl-5-(3-hydroxy-1-oxoinden-2-ylmethylene)-4-oxothiazolidin-2-ylidene]-2-thiothiazolid-4-one (VI; A = A3, B = B1, X = Y = S, R = R' = Et).—The oxonol (I; A = A3, R = Et) (1.05 g.) and methyl sulphate (0.7 ml.) were fused at 145° for 5 min. and condensed with 3-ethylrhodanine (0.7 g.). The complex dye (1.4 g., 95%) formed a black, crystalline powder of indefinite m. p. (Found: C, 54.0; H, 3.8; N, 6.1; S, 21.95. C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S<sub>3</sub> requires C, 54.15; H, 3.6; N, 6.3; S, 21.65%); λ<sub>max</sub>. 466 mμ in chloroform, 543 mμ in ethanolic triethylamine, pK 0.5, colour change pH 0.2—0.7.

5-[3-Ethoxycarbonylmethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-4-oxothiazolidin-2-ylidene]-3-ethyl-2-thio-oxazolid-4-one (VI; A = A1, B = B1, X = S, Y = O, R' = Et, R = CH<sub>2</sub>-CO<sub>2</sub>Et). The oxonol (I; A = A1, X = S, R = CH<sub>2</sub>-CO<sub>2</sub>Et) (1.0 g.) and methyl sulphate (1 ml.) were quaternized at 165° for 5 min. and condensed with 3-ethyl-2-thio-oxazolid-4-one (0.5 g.). The dye (1.1 g., 86%) was obtained as rusty-red flakes, softening from 225° (Found: C, 52.85; H, 3.8; N, 5.45; S, 12.55. C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub> requires C, 52.6; H, 3.6; N, 5.6; S, 12.75%), λ<sub>max</sub>. 475 (435) mμ in chloroform, 546 mμ in ethanolic triethylamine. The isomeric 5-[3-ethoxycarbonylmethyl-5-(4-hydroxy-2-oxochromen-3-ylmethylene)-4-oxothiazolidin-2-ylidene]-3-ethyl-2-thio-oxazolid-4-one (VI; A = A2, etc.) was obtained in 43% yield as orange threads, m. p. 301—302° (Found: C, 52.6; H, 3.95; N, 5.3; S, 12.55%); λ<sub>max</sub>. 444 mμ in chloroform, 490 mμ in ethanolic triethylamine.

3-Ethyl-5-[3-ethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-4-oxo-oxazolid-2-ylidene]-2-thiothiazolid-4-one (VI; A = A1, B = B1, X = O, Y = S, R = R' = Et). The oxonol (I; A = A1, X = O, R = Et) (0.95 g.) and methyl sulphate (0.5 ml.) were fused at 160° for 30 sec. The quaternary salt and 3-ethylrhodanine (0.5 g.) yielded a tar which crystallized on being heated with ethanol. The dye (0.2 g., 15%) formed an orange powder of indefinite m. p. (Found: C, 58.1; H, 3.75; N, 6.3; S, 14.6. C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub> requires C, 57.75; H, 3.6; N, 6.3; S, 14.75%).

5-[3-Ethoxycarbonylmethyl-4-(4-hydroxy-2-oxochromen-3-ylmethylene)-4-oxothiazolidin-2-ylidene]-2-ethylthiothiazol-5-one (VI; A = A2, B = B3, R = CH<sub>2</sub>-CO<sub>2</sub>Et).—The oxonol (I; A = A2, R = CH<sub>2</sub>-CO<sub>2</sub>Et, X = S) (1.3 g.) and methyl sulphate (0.5 ml.) were fused together at 170° for 30 sec. and made to react with 2-ethylthiothiazol-5-one, obtained by heating *N*-dithioethoxycarbonylglycine (1.2 g.) with acetic anhydride (10 ml.) at 130° for 30 min. and removing the solvents. The dye (0.2 g., 11%) formed a bronze-black powder, m. p. 276° (effervescence) (Found: C, 51.05; H, 3.7; N, 5.6; S, 19.05. C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>7</sub>S<sub>3</sub> requires C, 51.0; H, 3.5; N, 5.4; S, 18.55%); λ<sub>max</sub>. 470 mμ in chloroform, 508 mμ in ethanolic triethylamine.

2-Diphenylamino-5-[3-ethyl-5-(3-hydroxy-1-oxoinden-2-ylmethylene)-4-oxothiazolidin-2-ylidene]-thiazolin-4-one (VI; A = A3, B = B3, X = S, R = Et).—The oxonol (I; A = A3, X = S, R = Et) (1.05 g.) and methyl sulphate (0.7 ml.) were fused together at 145° for 5 min. and reacted with 2-diphenylaminothiazol-4-one (0.9 g.). The dye (1.75 g., 96%) formed green crystals, m. p. 271—272°, from pyridine-ethanol (Found: C, 65.5; H, 4.05; N, 7.7; S, 11.75. C<sub>30</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub> requires C, 65.3; H, 3.8; N, 7.6; S, 11.6%), λ<sub>max</sub>. 546 mμ in chloroform.

2-Dicyanomethylene-3-ethoxycarbonylmethyl-5-(4-hydroxy-2-oxochromen-3-ylmethylene)thiazolid-4-one (IV).—This compound was obtained in 93% yield as orange crystals, m. p. 202°, from ethanol (Found: N, 9.95; S, 7.45. C<sub>20</sub>H<sub>13</sub>N<sub>3</sub>O<sub>6</sub>S requires N, 9.95; S, 7.55%).

3-Allyl-5-(3-allyl-5-4'-hydroxybenzylidene-4-oxothiazolidin-2-ylidene)-2-thiothiazolid-4-one (XVII).—3-Allyl-5-*p*-hydroxybenzylidenerhodanine (1.4 g.) and methyl sulphate (0.6 ml.) were fused together on a steam-bath for 15 min. The orange tar solidified on being stirred. 3-Allylrhodanine (0.9 g.), pyridine (5 ml.), and triethylamine (1.6 ml.) were added and the solution was

heated for 15 min. on a steam-bath. The addition of 2N-hydrochloric acid precipitated an orange tar which was washed with water and dissolved in hot ethanol (50 ml.). Triethylamine (5 ml.) and water (100 ml.) were added and the magenta solution was distilled on a steam-bath. As the ethanol and triethylamine distilled the dye crystallized as magenta threads which were collected when the colour of the solution changed from magenta to yellow. The process was repeated to give 0.3 g. (14.5%) of brick-red threads, m. p. 252—253° (Found: C, 54.8; H, 4.0; N, 6.6; S, 23.4.  $C_{19}H_{16}N_2O_3S_3$  requires C, 54.8; H, 3.85; N, 6.75; S, 23.1%);  $\lambda_{max}$  463 m $\mu$  in chloroform, 534 m $\mu$  in aqueous-ethanolic (1:2) triethylamine, pK 8.5, colour change pH 9.2—7.8.

**3-Ethyl-5-[3-ethyl-5-(2-hydroxy-4-phenylthiazol-5-ylmethylene)-4-oxothiazolidin-2-ylidene]-2-thiothiazolid-4-one (XIX).**—The dye (XVII; X = O, R' = Ph, R = Et) (1.75 g.) and methyl sulphate (0.6 ml.) were fused at 140° for 5 min. and condensed with 3-ethylrhodanine (0.9 g.). The dye (0.55 g., 23%), purified by the method described above for the 4-hydroxybenzylidene analogue, formed soft, rose-red threads decomposing from 310° (Found: C, 50.15; H, 3.7; N, 8.65; S, 27.05.  $C_{20}H_{17}N_3O_3S_4$  requires C, 50.5; H, 3.6; N, 8.55; S, 26.95%);  $\lambda_{max}$  487 m $\mu$  in chloroform, 559 m $\mu$  in ethanolic triethylamine, pK 6.3, colour change pH 7.2—5.5.

**2-[5-(2-Cyano-2-ethoxycarbonylvinyl)-3-ethyl-4-hydroxythiazolin-2-ylidene]-4-ethyl-5-thiothiazolid-4-one (XXIV).**—The dye (XXIII; R' = CN, R = Et) (1.34 g.) and methyl sulphate (0.6 ml.) were heated on a steam-bath for 5 min. to yield a solid quaternary salt. With 3-ethylrhodanine (0.9 g.) it gave 0.65 g. (32%) of complex dye forming pale-green aggregates shrinking at 167° with loss of water (Found: C, 45.2; H, 4.55; N, 9.6; S, 22.5.  $C_{16}H_{17}N_3O_4S_3 \cdot H_2O$  requires C, 44.7; H, 4.45; N, 9.8; S, 22.35%);  $\lambda_{max}$  424 m $\mu$  in chloroform, 553 m $\mu$  in ethanolic triethylamine. The presence of water of crystallization rather than of amide formation from the CN-group was shown by its i.r. spectrum.

**5-[5-( $\alpha$ -Cyano-4-nitrostyryl)-3-ethyl-4-hydroxythiazolin-2-ylidene]-3-ethyl-2-thiothiazolid-4-one (XXVII).**—The dye (XXVI) (1.0 g.), 3-ethylrhodanine (0.5 g.), dimethylformamide (10 ml.), and triethylamine (0.5 ml.) were heated on a steam-bath for 5 min. Acetic acid (3 ml.) and ethanol (20 ml.) were added to the deep-blue solution. The dye (1.2 g., 90%) crystallized, was dissolved in hot ethanolic triethylamine and the solution acidified with concentrated hydrochloric acid. Dark-green crystals, m. p. 234° (efferv.), were formed (Found: C, 49.9; H, 3.45; N, 12.0; S, 20.6.  $C_{19}H_{16}N_4O_4S_3$  requires C, 49.55; H, 3.5; N, 12.15; S, 20.9%);  $\lambda_{max}$  517 m $\mu$  in chloroform, 606 m $\mu$  in ethanolic triethylamine.

**4-Ethoxycarbonylmethyl-2-[3-ethoxycarbonylmethyl-5-[3-ethoxy-3-(4-ethoxycarbonylmethyl-3-hydroxy-5-thiothiazolin-2-yl)-1-methylprop-2-enylidene]-4-oxothiazolidin-2-ylidene]-5-thiothiazolid-3-one (XI).**—Compound (X) (1.1 g.), 3-ethoxycarbonylmethylrhodanine (0.5 g.), pyridine (5 ml.), and triethylamine (0.3 ml.) heated for 5 min. on a steam-bath gave 0.45 g. (31%) of dye as yellow crystals, m. p. 158—160° (Found: C, 45.25; H, 4.4; N, 5.85; S, 22.95.  $C_{27}H_{31}N_3O_{10}S_5$  requires C, 45.2; H, 4.3; N, 5.85; S, 22.3%);  $\lambda_{max}$  441 m $\mu$  in chloroform, 665 m $\mu$  in ethanolic triethylamine.

**3-Ethoxycarbonylmethyl-5-[3-ethoxycarbonylmethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-4-oxothiazolidin-2-ylidene-ethylidene]-2-thiothiazolid-4-one (VIII; A = A1, R = R'' = CH<sub>2</sub>·CO<sub>2</sub>Et, X = S, R' = H)** was obtained from the betaine (III; A = A1, R = CH<sub>2</sub>·CO<sub>2</sub>Et) and compound (VII; R'' = CH<sub>2</sub>·CO<sub>2</sub>Et, R' = H)<sup>6</sup> in 12.5% yield as green threads, m. p. ca. 250° (Found: C, 51.6; H, 4.0; N, 4.8; S, 15.75.  $C_{26}H_{22}N_2O_9S_3$  requires C, 51.8; H, 3.65; N, 4.65; S, 15.95%);  $\lambda_{max}$  494 m $\mu$  in chloroform, 650 (442) m $\mu$  in ethanolic triethylamine. **3-Ethoxycarbonylmethyl-5-[2-[2-ethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-4-oxothiazolidin-2-ylidene]-1-ethylthioethylidene]-2-thiothiazolid-4-one (VIII; A = A1, R = Et, R'' = CH<sub>2</sub>·CO<sub>2</sub>Et, X = S, R' = SEt)**, from the betaine (III, A = A1, R = Et) and compound (VII; R'' = CH<sub>2</sub>·CO<sub>2</sub>Et, R' = SEt)<sup>6</sup> in 40% yield, formed green crystals, decomposing at 270—280° (Found: C, 51.9; H, 4.15; N, 4.5; S, 21.4.  $C_{26}H_{24}N_2O_7S_4$  requires C, 51.6; H, 4.0; N, 4.65; S, 21.2%);  $\lambda_{max}$  556 m $\mu$  in chloroform, 700 (452) m $\mu$  in ethanolic triethylamine.

**3-Ethoxycarbonylmethyl-5-[1-ethoxy-2-[3-ethoxycarbonylmethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-4-oxothiazolidin-2-ylidene]ethylidene]-2-thiothiazolid-4-one (VIII; A = A1, R = R'' = CH<sub>2</sub>·CO<sub>2</sub>Et, X = S, R' = OEt).**—This compound was obtained from the betaine (III; A = A1, R = CH<sub>2</sub>·CO<sub>2</sub>Et) and compound (VII; R'' = CH<sub>2</sub>·CO<sub>2</sub>Et, R' = OEt) in 25% yield, and formed maroon threads softening at ca. 250° (Found: C, 52.05; H, 4.15; N, 4.0; S, 14.85.  $C_{26}H_{26}N_2O_{10}S_3$  requires C, 52.0; H, 4.0; N, 4.35; S, 14.85%);  $\lambda_{max}$  531 m $\mu$  in chloroform, 658 (436) m $\mu$  in ethanolic triethylamine, pK 5.6, colour change pH 6.6—4.6.

**3-Ethoxycarbonylmethyl-5-[1-ethoxy-2-[3-ethoxycarbonylmethyl-5-(4-hydroxy-2-oxochromen-3-ylmethylene)-4-oxothiazolidin-2-ylidene]ethylidene]-2-thiothiazolid-4-one (VIII; A = A2, R = R'' =**

$\text{CH}_2\cdot\text{CO}_2\text{Et}$ ,  $\text{X} = \text{S}$ ,  $\text{R}' = \text{OEt}$ .—This compound, obtained from the betaine (III;  $\text{A} = \text{A}_2$ ,  $\text{R} = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ) and compound (VII;  $\text{R}' = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ,  $\text{R}' = \text{OEt}$ ) in 62% yield, formed maroon crystals, m. p. ca. 242° (Found: C, 52.05; H, 4.3; N, 4.3; S, 15.0.  $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_{10}\text{S}_3$  requires C, 52.0; H, 4.0; N, 4.35; S, 14.85%);  $\lambda_{\text{max}}$ , 502 m $\mu$  in chloroform, 564 m $\mu$  in ethanolic triethylamine.

*Complex Holopolar Dyes* (XIII).—The oxonol (I) (0.01 mole) was quaternized as before and heated for 5 min. on a steam-bath with the reactive methyl quaternary salt (0.01 mole) in pyridine (25 ml.) and triethylamine (0.03 mole). The dye crystallized during the reaction, on cooling or on the addition of ethanol (50 ml.). It was usually recrystallized from pyridine-ethanol.

*Anhydro-[3-ethyl-2-benzothiazole][3-ethoxycarbonylmethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-4-oxo-2-thiazoline]methinecyanine Hydroxide* (XIII;  $\text{A} = \text{A}_1$ ,  $\text{B} = 3$ -ethyl-2-benzothiazolium,  $\text{R} = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ).—This compound was obtained from the betaine (III;  $\text{A} = \text{A}_1$ ,  $\text{R} = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ) and 3-ethyl-2-methylbenzothiazolium iodide in 29% yield as bronze threads, m. p. 261—262° (Found: C, 60.3; H, 4.15; N, 4.9; S, 11.9.  $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_6\text{S}_2$  requires C, 60.75; H, 4.1; N, 5.25; S, 12.0%);  $\lambda_{\text{max}}$ , 661, 617 m $\mu$  in pyridine, 641, 596 m $\mu$  in pyridine-water (1:2), 507 m $\mu$  in acetic acid-HCl. The hydrochloride (as XII) was obtained by dissolving the dye base in acetic acid, adding concentrated hydrochloric acid until the colour shifted from blue to orange-red, and running in ether. It formed maroon crystals, m. p. 250—254° (Found: Cl, 6.1.  $\text{C}_{27}\text{H}_{23}\text{ClN}_2\text{O}_6\text{S}_2$  requires Cl, 6.2%).

*Anhydro-[1-methyl-4-quinoline][3-ethoxycarbonylmethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-4-oxo-2-thiazoline]methinecyanine Hydroxide* (XIII;  $\text{A} = \text{A}_1$ ,  $\text{B} = 1$ -methyl-4-quinolinium,  $\text{R} = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ).—This compound was obtained from the betaine (III;  $\text{A} = \text{A}_1$ ,  $\text{R} = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ) and 1,4-dimethylquinolinium toluenesulphonate in 26% yield. It formed bronze crystals, m. p. 276°, from dimethylformamide-ethanol (Found: C, 65.3; H, 4.4; N, 5.15; S, 6.45.  $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_6\text{S}$  requires C, 65.4; H, 4.3; N, 5.45; S, 6.25%);  $\lambda_{\text{max}}$ , 743 m $\mu$  in pyridine, 675 m $\mu$  in pyridine-water (1:2) and 512 m $\mu$  in acetic acid-hydrochloric acid.

*Anhydro-[3-ethyl-2-benzoxazole][3-ethoxycarbonylmethyl-5-(4-hydroxy-1-oxoisochromen-3-ylmethylene)-4-oxo-2-thiazoline]methinecyanine Hydroxide* (XIII;  $\text{A} = \text{A}_1$ ,  $\text{B} = 3$ -ethylbenzoxazolium,  $\text{R} = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ).—This was obtained in 13% yield as green threads, m. p. 275° (Found: C, 62.65; H, 4.3; N, 5.25; S, 6.3.  $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_7\text{S}$  requires C, 62.5; H, 4.25; N, 5.4; S, 6.2%);  $\lambda_{\text{max}}$ , 646, 600 m $\mu$  in pyridine, 631, 587 m $\mu$  in pyridine-water (1:2) and 496 m $\mu$  in acetic acid-hydrochloric acid.

*Anhydro-[3-ethyl-2-benzothiazole][3-ethoxycarbonylmethyl-5-(4-hydroxy-2-oxochromen-3-ylmethylene)-4-oxo-2-thiazoline]methinecyanine Hydroxide* (XIII;  $\text{A} = \text{A}_2$ ,  $\text{B} = 3$ -ethyl-2-benzothiazolium,  $\text{R} = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ).—This was obtained from the betaine (III;  $\text{A} = \text{A}_2$ ,  $\text{R} = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ) and 3-ethyl-2-methylbenzothiazolium iodide in 35% yield, as dark-red crystals, m. p. 285—286° (Found: C, 60.4; H, 4.2; N, 5.1; S, 12.3.  $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_6\text{S}_2$  requires C, 60.75; H, 4.1; N, 5.25; S, 12.0%);  $\lambda_{\text{max}}$ , 549 m $\mu$  in pyridine, 528 m $\mu$  in pyridine-water (1:2) and 463 m $\mu$  in acetic acid-hydrochloric acid.

*Anhydro-[1-ethyl-2-benzoxazole][3-ethoxycarbonylmethyl-5-(4-hydroxy-2-oxochromen-3-ylmethylene)-4-oxo-2-thiazoline]methinecyanine Hydroxide* (XIII;  $\text{A} = \text{A}_2$ ,  $\text{B} = 3$ -ethyl-2-benzoxazolium,  $\text{R} = \text{CH}_2\cdot\text{CO}_2\text{Et}$ ).—This compound was obtained in 30% yield as rose needles or magenta aggregates, m. p. 283° (Found: C, 62.25; H, 4.35; N, 5.2; S, 6.1.  $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_7\text{S}$  requires C, 62.5; H, 4.25; N, 5.4; S, 6.2%);  $\lambda_{\text{max}}$ , 534 m $\mu$  in pyridine, 516 m $\mu$  in pyridine-water (1:2) and 452 m $\mu$  in acetic acid-hydrochloric acid.

*Anhydro-[3-ethyl-2-benzothiazole][3-ethyl-5-(3-hydroxy-1-oxoinden-2-ylmethylene)-4-oxo-2-thiazoline]methinecyanine Hydroxide* (XIII;  $\text{A} = \text{A}_3$ ,  $\text{B} = 3$ -ethyl-2-benzothiazolium,  $\text{R} = \text{Et}$ ).—This compound, obtained from the betaine (III;  $\text{A} = \text{A}_3$ ,  $\text{R} = \text{Et}$ ) and 3-ethyl-2-benzothiazolium iodide in 91% yield, formed maroon threads, m. p. indef., from dimethylformamide-ethanol (Found: C, 65.25; H, 4.6; N, 5.9; S, 13.85.  $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_3\text{S}_2$  requires C, 65.25; H, 4.35; N, 6.1; S, 13.9%);  $\lambda_{\text{max}}$ , 578 m $\mu$  in pyridine, 561 m $\mu$  in pyridine-water (1:2).

*Anhydro-[3-allyl-5-4'-hydroxybenzylidene-4-oxo-2-thiazoline][3-ethyl-2-benzothiazole]methinecyanine Hydroxide* (XX).—This compound was obtained in 31% yield from quaternized 3-allyl-5-*p*-hydroxybenzylidenerhodanine and 3-ethyl-2-methylbenzothiazolium iodide. The crude product, which probably contained some hydriodide (as XII), was ground with pyridine containing a little strong ammonia. It formed green crystals, m. p. ca. 275° (Found: N, 6.3; S, 15.1.  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_2$  requires N, 6.65; S, 15.25%);  $\lambda_{\text{max}}$ , 578 m $\mu$  in pyridine-water (1:2).

*Anhydro-[3-ethyl-2-benzothiazole][3-ethyl-5-(2-hydroxy-4-phenylthiazol-5-ylmethylene)-4-oxo-2-thiazoline]methinecyanine Hydroxide* (XXI).—This compound, obtained in 25% yield from

compound (XVII; X = O, R' = Ph, R = Et) by quaternization and condensation with 3-ethyl-2-methylbenzothiazolium iodide, formed green-brown crystals, m. p. 255—256°, from pyridine-isopropyl alcohol (Found: C, 60.65; H, 4.35; N, 8.35; S, 19.2.  $C_{25}H_{21}N_3O_2S_3$  requires C, 61.0; H, 4.25; N, 8.55; S, 19.55%);  $\lambda_{max}$ . 628 m $\mu$  in pyridine, 596 m $\mu$  in pyridine-water (1:2), 495 m $\mu$  in acetic acid-hydrochloric acid.

*Anhydro-[3-ethyl-2-benzothiazole][3-ethyl-5-(2,2-dicyanovinyl)-4-hydroxy-2-thiazole]methine-cyanine Hydroxide (XXV).*—This compound was obtained in 64% yield as bronze threads or crystals, m. p. 278—279°, from dimethylformamide-ethanol, by quaternizing compound (XXIII; R' = CN, R = Et) (2.4 g.) with methyl sulphate (1.3 ml.) (10 min. at 100°) and condensing the quaternary salt with 3-ethyl-2-methylbenzothiazolium iodide (3.1 g.) (Found: C, 55.0; H, 4.85; N, 13.55; S, 15.0.  $C_{19}H_{16}N_4OS_2 \cdot 2H_2O$  requires C, 54.8; H, 4.8; N, 13.45; S, 15.35%);  $\lambda_{max}$ . 555 m $\mu$  in pyridine, 539 m $\mu$  in pyridine-water (1:2), 511 m $\mu$  in acetic acid-hydrochloric acid.

*Anhydro-{3-ethyl-2-benzothiazole}{3-ethoxycarbonylmethyl-5-[3-ethoxy-3-(3-ethoxycarbonylmethyl-4-hydroxy-2-thiothiazolin-5-yl)-1-methylprop-2-enylidene]-4-oxo-2-thiazoline}methinecyanine Hydroxide (XIV).*—The betaine (X) was condensed with 3-ethyl-2-methylbenzothiazolium iodide to give the complex dye in 26% yield as green crystals, m. p. 223°, from pyridine-ethanol (Found: C, 53.1; H, 5.1; N, 6.1; S, 18.55.  $C_{30}H_{33}N_3O_7S_4$  requires C, 53.3; H, 4.9; N, 6.2; S, 18.95%);  $\lambda_{max}$ . 688 m $\mu$  in pyridine, 682 m $\mu$  in pyridine-water (1:2).

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