

830. The Colour of Organic Compounds. Part IX.* Merocyanines Derived from 2-Hydroxythiazoles and Thiazole-2-thiols.

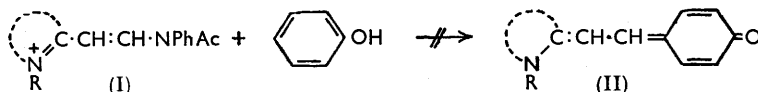
By E. B. KNOTT.

2-Hydroxy-4-phenylthiazole and 4-phenylthiazole-2-thiol, which contain a nucleophilic carbon atom at position 5, react under basic conditions with 2-acetanilidovinyl derivatives of heterocyclic quaternary salts to give merocyanines (VIII; X = O or S). These are strongly polar dyes, particularly when X = S, as indicated by their showing hypsochromic absorption shifts with increase in solvent polarity. They, and the cyanines (IX), obtained on quaternization are photographic desensitizers.

Similar reactions with 2-hydroxy-4-methylthiazole lead to trinuclear dyes, e.g., (X), as a result of the additional reactivity of the 4-methyl group. These complex dyes which contain a cyanine-like resonance system may also be quaternized to give true cyanines (XI).

The absorption characteristics of these dyes are discussed.

THE first step in the formation of cyanines or merocyanines, by base-catalysed condensation of 2-acetanilidovinyl derivatives (I) of heterocyclic quaternary salts with compounds containing a reactive methyl or methylene group is essentially an electrophilic attack by the 2-carbon atom of the vinyl group on the nucleophilic methyl or methylene group or on the anion of the latter. It is analogous to the attack by diazonium salts on reactive methyl¹ or methylene² groups, or by oxidized photographic colour developer, which is a quinone 1,4-bis-*NN*-dialkylimmonium cation.³ In searching for new nucleophilic ring systems containing an active hydrogen atom, for incorporation in a merocyanine molecule, it was of interest to study systems which are known to react with diazonium salts or oxidized colour developer. Foremost amongst these are phenolic compounds, which contain a nucleophilic carbon atom in the position *para* to the hydroxyl group.



It is known that dyes of type (II) can be obtained by the condensation of 2-methyl derivatives of heterocyclic quaternary salts with *p*-hydroxybenzaldehyde, but that they are not formed from 2-acetanilidovinyl derivatives⁴ of the same quaternary salts (I) and phenol. These dyes and derivatives are the only merocyanines known in which the keto-group is not adjacent to the chain between the nuclei.

The lack of reactivity of phenol towards the salt (I) must be a result of an insufficiently high electron-density on the atom in position 4 of the ring. This density can be increased by a number of structural changes, one of which is to replace the benzene ring by a heterocycle. This is applied in normal merocyanine condensations by the use of non-aromatic heterocyclic keto-methylene compounds, many of which form aromatic enolates. In all cases, coupling occurs at position 2 with respect to the carbonyl group. To transfer such coupling to position 4, heterocyclic hydroxy-compounds of type (III) are required.

Such a system exists in 2-hydroxythiazoles (V; X = O) or 2-hydroxyimidazoles (VI; X = O) unsubstituted in the 5-position. It is known⁵ that there is a high electron

* Part VIII, *J.*, 1956, 1360.

¹ König, *Ber.*, 1924, **57**, 1292; Wahl and Lebris, *Compt. rend.*, 1952, **234**, 631.

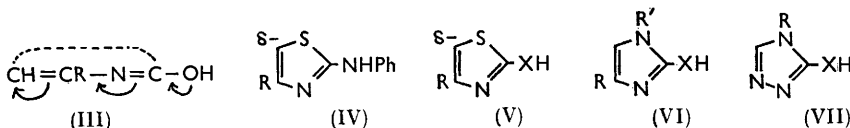
² Knorr, *Annalen*, 1887, **238**, 183.

³ Tong and Glesmann, *J. Amer. Chem. Soc.*, 1957, **79**, 583.

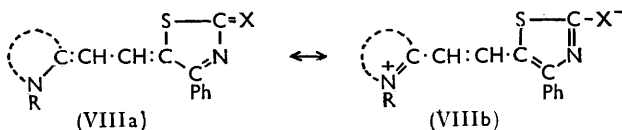
⁴ (a) Kiprianov and Petrunkin, *J. Gen. Chem. (U.S.S.R.)*, 1940, **10**, 600, 613; (b) Kiprianov and Timschenko, *ibid.*, 1947, **17**, 1468; (c) Knott, *J.*, 1951, 3038; (d) Brooker, Keyes, and Heseltine, *J. Amer. Chem. Soc.*, 1951, **73**, 5350.

⁵ Pullman and Metzger, *Bull. Soc. chim. France*, 1948, 1021.

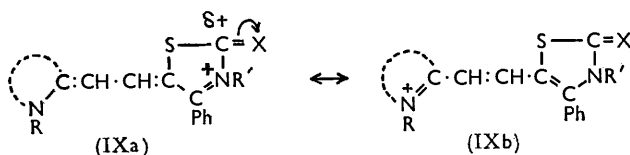
density at position 5 in thiazole itself and that 2-hydroxy-4-phenylthiazole (V; X = O, R = Ph) will couple in the 5-position with diazonium salts; ⁶ also ⁷ that 2-anilinothiazoles (IV) couple with oxidized colour-developer. 2-Hydroxy-4-phenylthiazole also couples with the latter to give an unstable blue dye.



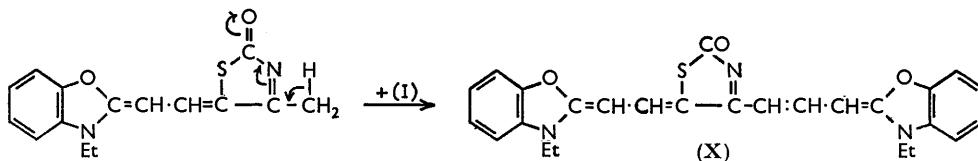
Although the imidazoles (VI; R = Ph, R' = Me, X = O) and triazoles (VII; X = O or S) showed no reactivity towards a compound (I), the thiazole (IV; R = Me) readily gave intensely coloured solutions under strongly basic conditions (sodium ethoxide in ethanolic pyridine), and the analogue (V; R = Ph, X = O) gave stable dyes (VIIIa \leftrightarrow VIIIb; X = O) under such conditions.



Similarly 4-phenylthiazole-2-thiol (V; R = Ph, X = S) gave the analogous thiones (VIII; X = S), under less basic conditions in pyridine-triethylamine. A higher vinylogue of the dye (VIII; X = O) was obtained from 2-(4-acetanilidobuta-1,3-dienyl)-3-ethylbenzothiazolium iodide. All these dyes are easily quaternized by alkyl esters to give true cyanines (IXa \leftrightarrow IXb).



The condensation of 2-2'-acetanilidovinyl-3-ethylbenzoxazolium iodide with 2-hydroxy-4-methylthiazole, in the presence of alcoholic sodium ethoxide and pyridine gave, initially, a yellow solution, this colour being expected by analogy with the 4-phenyl analogue. The colour was, however, rapidly degraded on further heating and replaced by an intense, blue-green. The dye which was then isolated gave blue solutions in pyridine. Analogous dyes were obtained from benzothiazolium and 1,3,3-trimethylindoleninium salts.



Since the only structural change was the replacement of the 4-phenyl by the 4-methyl group in the thiazole ring, it was presumed that the latter group, when present in the initial yellow, normal dye, became nucleophilic and condensed with a second molecule of 2-2'-acetanilidovinyl-3-ethylbenzoxazolium iodide to give the trinuclear dye (X). Analyses of the isolated dye (X) and its analogues confirmed this, but in each case one molecule of ethanol was tenaciously held. Treatment of the dye (X) with methyl iodide gave the true cyanine (XIa, b), solutions of which are easily bleached by light.

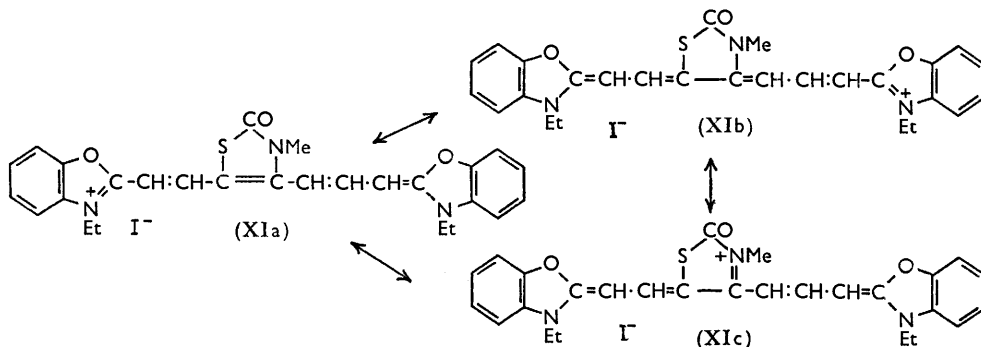
⁶ Ganapathi and Venkataraman, *Proc. Indian Acad. Sci.*, 1945, **22**, A, 343.

⁷ Dr. J. R. Thirtle, Eastman Kodak Co., personal communication.

The cyanine (XI) is a higher vinylogue of a series of dyes obtained by Nys⁸ by a different method.

Analogous experiments with compound (I) and 4-methylthiazole-2-thiol gave intensely and deeply coloured solutions, the colour of which degraded rapidly. In one experiment, 2-2'-acetanilidovinyl-3-ethylbenzoxazolium iodide and the thiazolethiol (V; R = Me, X = S) in pyridine with triethylamine gave an intensely purple solution, fading to orange and yielding 3,3'-diethyloxacarbocyanine iodide in low yield.

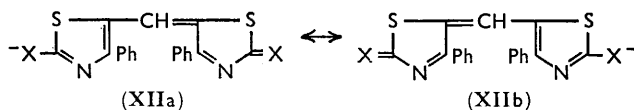
The Absorption of the Dyes.—(a) *Merocyanines* (VIII). Consideration of the two extreme resonance structures of these dyes (VIIIa, b) shows that, whereas in the classical structure (VIIIa) both heterocycles are non-aromatic, in the dipolar structure both rings, in the benzazole and quinoline series, are now stabilized by aromatic resonance. Consequently, as in the case of the related dyes⁴ (II), it would be expected that the merocyanines (VIII) would be strongly polar. It would also be expected that the thione (VIII; X = S) would be more strongly polar than the oxo-compound (VIII; X = O)



by virtue of the stronger +M effect of the C=S group. Both these forecasts were confirmed by the solvatochromic behaviour of the dyes (see Table). They all show hypsochromic shifts with increasing solvent polarity. These shifts are particularly pronounced for the thione dyes, which indicates^{4d} their higher degree of polarity, as do their lower extinction coefficients (compared with those of the oxygen analogues).

Since the gain in resonance stabilization of the right-hand nucleus in moving from (VIIIa) to (VIIIb) is lower than in the case of the carbocyclic analogues (II), the magnitude of the shifts is also lower.

It is of interest that for the dye (VIII; X = O) the strongly basic 1-ethyl-1,2(or 1,4)-dihydroquinolinylidene dyes give a much greater total shift than the less basic nuclei. This would be expected as a result of their greater polarity. In the series (VIII; X = S)



this pattern is not observed. Here the dihydroquinoline dye shows a more complex spectrum, but the maximum shift is smaller than for the other dyes which show a constant shift. The reason for this is not known.

In order to determine the degree of energetic asymmetry of these dyes by Brooker's deviation method⁹ it is necessary to obtain the absorption peak of the oxonols, the anion of which is (XII; X = O or S). Since the merocyanines (VIII) are the structural hybrids of (XII) and the appropriate trimethincyanine, the calculated absorption peak of merocyanines (VIII) at the isoenergetic point is the mean of the peaks of (XII) and the trimethincyanine. Any deviation from this value to the shorter wavelength side is a measure

⁸ Nys, B.P. 789,077.

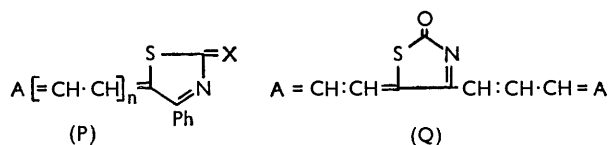
⁹ Brooker *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 1881; 1951, **73**, 5332.

of the loss of energetic symmetry of the hybrid. In fairly drastic conditions of synthesis the oxonol (XII; X = O) was obtained.

The Table shows the deviations given by the merocyanines (VIII). It will be noted that in pyridine (VIII; X = O) shows *negative* deviations in all cases, these being greatest for the strongly basic nuclei. In 50% aqueous pyridine the first three dyes show no deviation, whilst the quinolines show positive deviations. In pyridine-water (1 : 2) all show positive deviations. The reason for the negative deviation is obscure. It could imply that, for some reason, the oxonol absorption is at shorter wavelengths than it should be. This might well be a result of a twisting of both phenyl residues out of the plane of the molecule, although the effect of the presence of the phenyl groups on the absorption is not known. The analogue of (XII) from 2-hydroxy-4-methylthiazole could not be obtained.

Since all the absorption peaks of the dyes (VIII; X = S) lie to longer wavelengths than the calculated isoenergetic peak for compounds (VIII; X = O), it is clear that the replacement of oxygen by sulphur has a profound bathochromic effect on absorption.

Absorption of merocyanines (VIII) and (X).



A in dye	X	Pyr *		Pyr-H ₂ O (1 : 1)		Pyr-H ₂ O (1 : 3)		Total shift (λ)	Iso-energetic max. (mμ)	Deviation Pyr	Deviation Pyr-H ₂ O (1 : 3)
		λ _{max.} (mμ)	10 ⁻⁴ ε	λ _{max.} (mμ)	10 ⁻⁴ ε	λ _{max.} (mμ)	10 ⁻⁴ ε				
A in dye (P)											
3-Methylthiazolidin-2-	O	504	8.7	492	5.4	485	5.0	-19	492	-12	+7
	S	580	5.2	535	4.3	500	2.6	-80			
3-Ethylbenzoxazolin-2-	O	518	8.5	513	6.25	507	5.7	-11	512	-6	+5
	S	596	4.35	550	2.85	516	?	-80			
		522	2.4	530	2.7						
3-Ethylbenzothiazol-in-2-	O	553	9.4	547	7.95	542	7.05	-11	547	-6	+5
	S	634	8.5	580	4.85	560	4.2	-74			
1-Ethyl-1,2-dihydro-quinolin-2-	O	592	7.95	560	6.6	550	6.05	-42	571	-21	+21
	S	564i									
		655i	4.55	616	4.8	607	5.1	-48?			
		621	6.9	567	3.6	563	4.1				
		577i	2.6								
1-Ethyl-1,4-dihydro-quinolin-4-	O	653	8.1	595	5.5	580	4.5	-73	622	-31	+42
		608i									
A in dye (Q)											
3-Ethylbenzoxazolin-2-		625	8.1	657	8.8	661	10.0	+36			
		465	3.0	459	3.2	457	3.3				
3-Ethylbenzothiazol-in-2-		684	8.9	715	9.7	725	10.0	+41			
		499	3.65	494	3.1	497	2.9				
1,3,3-Trimethyl-indolenin-2-		640	5.9	680	7.25	685	8.5	+45			
		492	2.5	492	2.9	492	2.75				

* Pyr = Pyridine. i = Inflection.

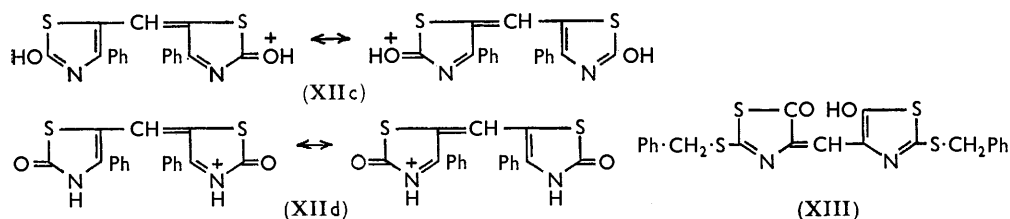
Similar shifts have been noted in other merocyanines by Nys¹⁰ and in cyanines by Wizinger.¹¹ It is believed to be a function of the greater free-energy change involved in the process C=S → ⁺C-S⁻ than in C=O → ⁺C-O⁻, *i.e.*, the stronger +M effect of the C=S group than of the C=O group. In terms of the energy picture of extreme and excited structures, it means that there is a greater energy jump as the electron leaves the negatively charged sulphur atom in the dipolar extreme structure (VIIIb), to give an excited structure

¹⁰ Nys, *Compt. rend. 27th Congr. internat. Chim. Ind. (Brussels), 1954, Vol. 3; Ind. Chim. belge, 1955, 20, Spec. No. 635.*

¹¹ Wizinger, *Ind. Chim. belge, 1955, 20, Spec. No. 670; Wizinger and Ulrich, Helv. Chim. Acta, 1956, 39, 207, 217.*

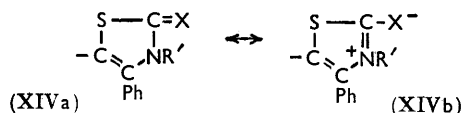
than when it leaves an oxygen atom. It is analogous to the deeper absorption of cyanines or merocyanines containing strongly basic ($-M$) nuclei, *e.g.*, 1-alkyldihydro-pyridines or -quinolines.¹² The bathochromic effect of increasing such energy differences is forecast by the "steeper the deeper" rule of Brooker and Sklar¹³ (see also Knott¹⁴).

The oxonol anion (XII) gives magenta solutions in methanol (λ_{\max} , 538 $m\mu$, ϵ 4.9×10^4), which change to orange (λ_{\max} , 466 $m\mu$, ϵ 1.9×10^4) as the oxonol is released. This strong hypsochromic shift is normal and is a result of the loss of energetic symmetry of the molecule. However, if strong acid is then added to the solution the magenta colour returns (λ_{\max} , 540 $m\mu$, ϵ 3.5×10^4) and is permanent. The molecular species giving this colour must be cationic and a result of proton addition to the oxonol. The depth of colour of the solutions also indicates a symmetrical molecule. Possible structures are (XIIc and d). That the cation is best represented by (XIIc) is indicated by experiments of proton addition to other oxonols. Only in one case was a deepening of colour observed on addition of strong acid and that was with compound (XIII). The latter and the dye (XII) were the only oxonols of the series which contain aromatic heterocycles. Since in forms (XIIc)



aromatic stabilization is retained, but not in (XII d), the former structure is the more likely.

(b) *Cyanines* (IX). These dyes are interesting in that they all show much shorter wavelength absorption than the parent merocyanines. This hypsochromic effect of quaternization is clearly a result of an increase in the energetic asymmetry of the hybrid. In structure (IXa) neither ring has aromatic stabilization; the adjacency of the positively charged nitrogen atom to the electrophilic $C=X$ carbon atom results in a high-energy



structure. In structure (IXb), aromatic resonance in the left-hand nucleus is present, whilst the right-hand nucleus is stabilized by amide resonance (XIVa \leftrightarrow b) and aromatic resonance in (XIVb). An energetically, highly asymmetric hybrid would, therefore, be expected.

(c) *Trinuclear merocyanines* (X) and *cyanines* (XI). These merocyanines (X) contain a crossed-conjugation system with the major extreme structures, (X), (Xa), and (Xb). The resonance systems consist of two merocyanine types (X \leftrightarrow Xa) and (X \leftrightarrow Xb) and a cyanine type (Xa \leftrightarrow Xb). The system (X \leftrightarrow Xa) is the same as is present in the simple merocyanine (VIIIa \leftrightarrow b; X = O), which, as has been shown, is one of low asymmetry. On the other hand, the system (X \leftrightarrow Xb) will be of considerably higher asymmetry since, unlike the position in (Xa), the dipolar extreme structure is not stabilized by aromatic resonance in the central ring. The short-wavelength peak of a compound (X) can, therefore, be ascribed to the transition (X \leftrightarrow Xa), modified by (X \leftrightarrow Xb). The modification will be a hypsochromic shift of this peak from its position for the related

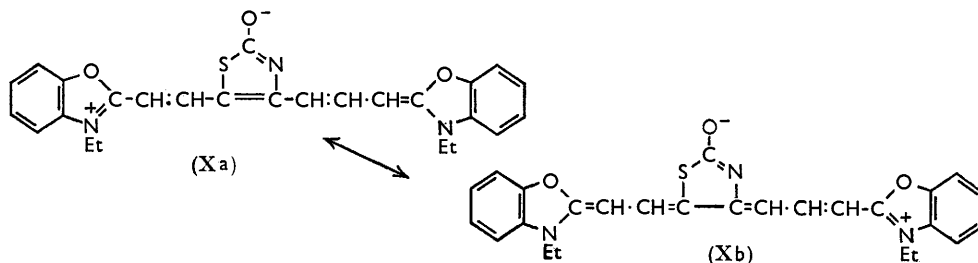
¹² Brooker, White, and Sprague, *J. Amer. Chem. Soc.*, 1951, **73**, 1087.

¹³ Brooker (with Sklar), *Rev. Mod. Phys.*, 1942, **14**, 275.

¹⁴ Knott, *l.*, 1951, 1024.

simple merocyanine (VIII). This effect is depicted in (Xc), an important excited structure of the hybrid. The effect of replacing a 4-phenyl group [as in (VIII)] by the 3-ethylbenzoxazolin-2-ylideneprop-1-enyl group [as in (X)], which has a strong $-M$ effect, is to stabilize (Xc) and cause a hypsochromic shift.¹⁴

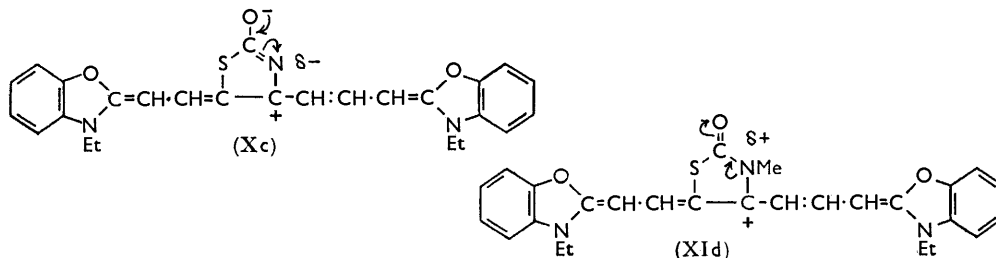
The relatively low sensitivity of the position of this second peak to changes in solvent polarity (Table), compared with that of (VIII), may well be a function of opposition by the



system ($X \leftrightarrow Xb$) to electron movement into the central ring by the main system ($X \leftrightarrow Xa$).

The long-wavelength band of compound (X) must be ascribed to the system ($Xa \leftrightarrow Xb$). This is a non-degenerate system, structure (Xa) being, for reasons given above, of lower energy than (Xb). It is, perhaps, unexpected that, with a charge-transfer system, this long-wavelength peak associated with it is sensitive to solvent environment, a bathochromic shift occurring with increasing solvent polarity. It may be a result of a decrease in non-degeneracy, arising because the increasing solvent polarity stabilizes structure (Xb) more than (Xa).

That ($Xa \leftrightarrow Xb$) does represent the hybrid responsible for the long-wavelength peak is indicated by a comparison of the spectra in methanol of compound (X) with its quaternized product, the cyanine (XI). The peaks of (X) also appear in (XI), the longer



wavelength peak of (X) being shifted bathochromically and the shorter wavelength peak hypsochromically on quaternization. Both these shifts were expected¹⁴ for the following reasons.

As indicated for the quaternized merocyanines (IX), the effect of quaternization is to impart a high degree of energetic asymmetry to the system ($c \leftrightarrow a$). As in comparison of (IX) with the parent (VIII), so also in comparison of (XI) with (X), the wavelength of the short-wavelength peak should be shortened.

The only structural difference between the resonance systems ($Xa \leftrightarrow Xb$) and ($XIa \leftrightarrow XIb$) is in the central ring, the group attached to the central carbon atom of the chain. The most significant structure in each case in which this chain-carbon atom is charged is (Xc) and (XIId) respectively. Structure (Xc) is stabilized by the electron shifts shown by the curved arrows, and these shifts give a hypsochromic shift. On the other hand the related shifts in (XIa) will make this structure less stable and function bathochromically. The long-wavelength peak of (XI) would, therefore, be expected to be at longer wavelength than that of (X).

EXPERIMENTAL

2-Hydroxy-4-phenylthiazole, which can be obtained by a variety of methods, was prepared conveniently as follows. Phenacyl bromide (20 g.), isopropyl thioncarbamate (11 g.), and ethanol (50 c.c.) were refluxed together on a steam-bath for 15 min. The required compound separated rapidly and, after cooling to 5°, was collected and washed with ethanol. It (15.1 g., 85.5%) formed flat, white needles, m. p. 212—214°, from benzene (lit., m. p. 204°).

4-Phenyl- and 4-methyl-thiazole-2-thiol were prepared according to directions of Miolati,¹⁵ and 2-hydroxy-4-methylthiazole according to those of Tscherniac.¹⁶

Merocyanines (VIII; X = O).—5-[2-(3-Ethylbenzothiazolin-2-ylidene)-ethylidene]-4-phenyl- Δ^3 -thiazol-2-one. 2-2'-Acetanilidovinyl-3-ethylbenzothiazolium iodide (4.5 g.), 2-hydroxy-4-phenylthiazole (1.8 g.), pyridine (10 c.c.), and a solution from sodium (0.23 g.) in ethanol (5 c.c.) were heated together on a steam-bath for 5 min. The solution became magenta, the solids dissolved, and then the whole solidified. The dye was collected, washed with propan-2-ol, and then obtained in 77.5% yield (2.8 g.) as flat, maroon needles [from pyridine (75 c.c.)-ethanol (50 c.c.)] decomposing above 275° (Found: C, 65.6; H, 4.3; N, 7.65; S, 17.7. C₂₀H₁₆N₂OS₂ requires C, 65.9; H, 4.4; N, 7.7; S, 17.6%).

5-[2-(1-Ethyl-1,2-dihydroquinolin-2-ylidene)-ethylidene]-4-phenyl- Δ^3 -thiazol-2-one was obtained similarly from 2-2'-acetanilidovinyl-1-ethylquinolinium iodide (4.44 g.). The dye did not crystallize so it was precipitated with ether. The solid was boiled with ethanol (30 c.c.), the whole chilled, and the dye (2.65 g.) washed with ethanol. The dye was then extracted with benzene in a Soxhlet thimble, 0.8 g. (22.5%) crystallizing from the benzene solution. Finally it was obtained from pyridine-benzene as bronze or blue needles, decomposing from 260° (Found: C, 73.5; H, 5.1; N, 7.75; S, 8.85. C₂₂H₁₈N₂OS requires C, 73.75; H, 5.05; N, 7.8; S, 8.95%).

The isomeric 5-[2-(1-ethyl-1,4-dihydroquinolin-2-ylidene)-ethylidene]-4-phenyl- Δ^3 -thiazol-2-one was obtained similarly, the dye being precipitated as a tar on addition of ether to the reaction mixture. It crystallized when boiled in ethanol and then formed green crystals (1.25 g., 35%), m. p. 250°, from pyridine-benzene (Found: C, 73.9; H, 4.95; N, 7.6; S, 8.9%).

5-[2-(3-Ethylbenzoxazol-2-ylidene)-ethylidene]-4-phenyl- Δ^3 -thiazol-2-one was obtained similarly from 2-2'-acetanilidovinyl-3-ethylbenzoxazolium iodide, and was precipitated by ether. It (3.0 g., 86%) was obtained as flat, red needles, m. p. 246—247°, by concentrating its solution in methanol (Found: C, 69.1; H, 4.7; N, 7.85; S, 9.25. C₂₀H₁₆N₂O₂S requires C, 69.0; H, 4.6; N, 8.05; S, 9.2%).

5-[2-(3-Methylthiazolidin-2-ylidene)-ethylidene]-4-phenyl- Δ^3 -thiazol-2-one was obtained from 2-2'-acetanilidovinyl-3-methylthiazolinium iodide (3.9 g.) and was precipitated by ether. On recrystallizing from methanol it (1.8 g., 59.5%) formed brick-red needles falling to a powder on drying, and decomposing from 261° (Found: C, 59.8; H, 4.85; N, 9.4; S, 21.05. C₁₃H₁₄N₂OS₂ requires C, 59.6; H, 4.65; N, 9.3; S, 21.2%).

5-[4-(3-Ethylbenzothiazolin-2-ylidene)but-2-enylidene]-4-phenyl- Δ^3 -thiazol-2-one was obtained similarly from 2-(4-acetanilidobuta-1,3-dienyl)-3-ethylbenzothiazolium iodide (4.76 g.). The dye was precipitated with ether and then extracted with benzene in a Soxhlet thimble. It (1.55 g., 79.5%) formed steel-blue flakes, m. p. 220°, from pyridine-ethanol (Found: C, 67.95; H, 4.7; N, 7.1; S, 16.3. C₂₂H₁₈N₂OS₂ requires C, 67.75; H, 4.6; N, 7.2; S, 16.4%).

Merocyanines (VIII; X = S).—These were obtained by the use of triethylamine as base.

5-[2-(3-Ethylbenzoxazol-2-ylidene)-ethylidene]-4-phenyl- Δ^3 -thiazol-2-thione. 2-2'-Acetanilidovinyl-3-ethylbenzoxazolium iodide (2.2 g.), 4-phenylthiazole-2-thiol (1.0 g.), pyridine (5 c.c.), and triethylamine (0.75 c.c.) were heated on a steam-bath for 5 min. Ethanol (20 c.c.) was added to the deep purple solution, causing a change in colour to red. The dye then crystallized, leaving an intensely yellow liquor. The dye (0.5 g., 27%) formed fine green flakes, decomp. from 240°, from pyridine-ethanol. Its solutions in benzene and chloroform are blue (Found: C, 65.7; H, 4.6; N, 7.55; S, 17.3. C₂₀H₁₆N₂OS₂ requires C, 65.9; H, 4.4; N, 7.7; S, 17.6%).

5-[2-(3-Ethylbenzothiazolin-2-ylidene)-ethylidene]-4-phenyl- Δ^3 -thiazol-2-thione was formed in a similar way from 2-2'-acetanilidovinyl-3-ethylbenzothiazolium iodide (2.25 g.). The dye was precipitated with ether, and then dissolved in warm acetic acid (25 c.c.) to give a reddish solution

¹⁵ Miolati, *Gazzetta*, 1893, **23**, I, 579.

¹⁶ Tscherniac, *J.*, 1919, **115**, 1075.

of the dye salt, and the solution was diluted with water (1 l.). Undissolved carbocyanine was filtered off and the filtrate set aside for the dye to crystallize. The procedure was repeated and gave 0.9 g. (24%) of green crystals, decomposing from 245° (Found: C, 63.1; H, 4.2; N, 7.25; S, 24.3. $C_{20}H_{16}N_2S_3$ requires C, 63.2; H, 4.2; N, 7.35; S, 25.3%).

5-[2-(3-Methylthiazolidin-2-ylidene)-ethylidene]-4-phenyl- Δ^3 -thiazol-2-thione was obtained similarly, the dye solidifying during the reaction. It (0.4 g., 25%) formed soft, green needles, m. p. 256° (decomp.), from pyridine-methanol (Found: C, 56.25; H, 4.55; N, 8.55; S, 29.9. $C_{15}H_{14}N_2S_2$ requires C, 56.55; H, 4.4; N, 8.8; S, 30.2%).

Cyanines (IX).—All the merocyanines (VIII; X = O or S) were readily quaternized by methyl or ethyl iodide when refluxed (1–2 g.) with the halide (25 c.c.) until the colour associated with the merocyanine had disappeared. It required from 2 to 8 hr.

3-Ethyl-2-[2-(3-methyl-2-oxo-4-phenylthiazolin-5-yl)vinyl]benzothiazolium iodide, which separated during the 8-hours' refluxing, was extracted with hot benzene to remove any unchanged dye base. It formed rust-coloured flakes, m. p. 257°, from methanol in 75% yield (Found: C, 50.0; H, 3.85; I, 25.3; N, 5.65; S, 12.05. $C_{21}H_{19}IN_2OS_2$ requires C, 49.8; H, 3.75; I, 25.1; N, 5.55; S, 12.65%).

3-Ethyl-2-[2-(3-ethyl-2-oxo-4-phenylthiazolin-5-yl)vinyl]benzothiazolium iodide was obtained in 76% yield as green-brown flakes, m. p. 252°, from methanol (Found: C, 50.6; H, 3.9; I, 24.6; N, 5.1; S, 12.3. $C_{22}H_{21}IN_2OS_2$ requires C, 50.8; H, 4.05; I, 24.4; N, 5.4; S, 12.3%).

3-Ethyl-2-[2-(3-methyl-2-oxo-4-phenylthiazolin-5-yl)vinyl]benzothiazolium iodide was obtained in 90% yield as brown flakes, m. p. 216°, from ethanol (Found: I, 25.6. $C_{21}H_{19}IN_2O_2S$ requires I, 25.9%).

3-Ethyl-2-[4-(3-ethyl-2-oxo-4-phenylthiazolin-5-yl)buta-1,3-dienyl]benzothiazolium iodide formed black flakes, m. p. 272–273°, from ethanol-ether (Found: I, 23.0. $C_{24}H_{23}IN_2OS_2$ requires I, 23.2%).

3-Ethyl-2-[2-(3-ethyl-4-phenyl-2-thiothiazolin-5-yl)vinyl]benzoxazolium iodide was obtained from ethanol-ether in 95% yield as flat, orange-red needles, m. p. 197° (effervescence), losing solvent at 80° (Found: I, 24.7. $C_{22}H_{21}IN_2OS_2$ requires I, 24.4%).

Trinuclear Merocyanines (X).—5-[2-(3-Ethylbenzoxazolin-2-ylidene)ethylidene]-4-[2-(3-ethylbenzoxazolin-2-ylidene)prop-1-enyl]- Δ^3 -thiazol-2-one. 2-2'-Acetanilidovinyl-3-ethylbenzoxazolium iodide (8.7 g., 0.02 mole), 2-hydroxy-4-methylthiazole (1.15 g., 0.01 mole), pyridine (20 c.c.), and a solution from sodium (0.46 g.) in ethanol (10 c.c.) were heated together on a steam-bath for 1 hr. Ether was added to the blue-green solution in order to precipitate the dye as a tar. The latter was boiled with ethanol to give the crystalline dye. It (1.35 g., 27%) formed golden flakes, m. p. 207°, from pyridine-ethanol (Found: C, 67.0; H, 6.05; N, 8.15; S, 6.25. $C_{26}H_{23}N_3O_3S_2C_2H_5\cdot OH$ requires C, 67.0; H, 5.75; N, 8.35; S, 6.35%).

5-(3-Ethylbenzothiazolin-2-ylidene)-4-[3-(3-ethylbenzothiazolin-2-ylidene)prop-1-enyl]- Δ^3 -thiazol-2-one was obtained similarly in low yield. The tar precipitated by ether from the reaction mixture was boiled with ethanol to give the crystalline dye. The latter was extracted with benzene in a Soxhlet thimble. The dye, which separated from the benzene solution, recrystallized from pyridine-ethanol as green needles, m. p. 192° (previous sintering) (Found: N, 7.75; S, 18.0. $C_{26}H_{23}N_3OS_3C_2H_5\cdot OH$ requires N, 7.85; S, 17.95%).

5-[2-(1,3,3-Trimethylindolen-2-ylidene)-ethylidene]-4-[3-(1,3,3-trimethylindolen-2-ylidene)prop-1-enyl]- Δ^3 -thiazol-2-one was worked up as for the benzothiazole analogue. The benzene extract was concentrated and chilled and the crystals formed were washed free from a red dye with cold propan-2-ol. They formed brassy aggregates, m. p. 177°, from a little benzene-ethanol (Found: C, 73.0; H, 7.2; N, 7.7; S, 5.95. $C_{30}H_{31}N_3OS_2C_2H_5\cdot OH$ requires C, 72.8; H, 7.0; N, 7.95; S, 6.05%).

Trinuclear Cyanine (XI).—3-Ethyl-2-<3-[5-[2-(3-ethylbenzoxazolin-2-ylidene)-ethylidene]-3-methyl-2-oxothiazolidin-4-ylidene]prop-1-enyl>benzoxazolium iodide was obtained by refluxing the dye base (0.5 g.) in methyl iodide (20 c.c.) for 90 min. The dark green powder had m. p. 167° after recrystallization from methanol-ether (Found: I, 21.25. $C_{27}H_{26}IN_3O_3S$ requires I, 21.2%).

5-(2-Hydroxy-4-phenylthiazol-5-ylmethylene)-2-oxo-4-phenyl- Δ^3 -thiazoline (XII; X = O).—2-Hydroxy-4-phenylthiazole (1.8 g.), ethyl orthoformate (5 c.c.), triethylamine (1.5 c.c.), and acetic anhydride (5 c.c.) were heated on a steam-bath for 12 hr. A deep magenta colour developed as the solid dissolved and a second solid crystallised. The latter was collected and washed with methanol. It (0.8 g.) formed soft, white needles, m. p. 335–340°, from pyridine-ethanol. The needles reddened in air and dissolved to a magenta solution in concentrated acids

(Found: C, 62.5; H, 3.6; N, 7.6; S, 17.2. $C_{19}H_{12}N_2O_2S_2$ requires C, 62.7; H, 3.3; N, 7.7; S, 17.6%). This compound is therefore isomeric with the required *oxonol*. The reddened needles became colourless on being heated.

The magenta filtrates were treated with an excess of ether to precipitate the triethylamine salt of the oxonol. The latter was then mixed with hot methanol to dissolve the salt, leaving a yellow powder of free oxonol. The latter was dissolved in a little methanolic triethylamine, and the solutions were combined. To the hot solution, acetic acid was added until the magenta colour had been replaced by orange-red. The free oxonol then crystallized on seeding of the solution. It formed orange needles, m. p. 325—330°, shrinking and subliming from 250° (Found: C, 62.7; H, 3.55; N, 7.9; S, 17.5%).

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RESEARCH LABORATORIES, KODAK LTD.,
WEALDSTONE, HARROW, MIDDLESEX.

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