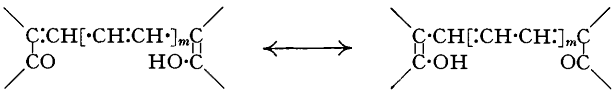
238. *A Trimethincyanine; a Trimethinoxonol and Some Compounds related to Trimethinoxonols; Some Di- and Tetra-methin*mero*cyanines.*

By Frances M. Hamer and Barbara S. Winton.

A trimethincyanine and a trimethinoxonol are described, also five anilinoallylidene compounds, intermediate in structure to oxonols, and three corresponding acetanilido-derivatives. Seven dimethin*mero*cyanines and five tetramethin*mero*cyanines are also described. Absorption maxima of methyl-alcoholic solutions are recorded, those of the anilinoallylidene compounds being of acidified and basified solutions.

Neocyanines, the first trinuclear dyes which we synthesised, were shown to be structurally related to tri- and penta-methincyanines, and the absorption maximum of each was compared with those of one or two dyes of the former class and one of the latter (Hamer, Rathbone, and Winton, *J.*, 1947, 1434; 1948, 1872). Subsequently, trinuclear dyes of a new type were synthesised, each of which was correlated with one trimethinoxonol and with one or two dimethin*mero*cyanines; with trinuclear dyes of yet another type, each was related to a trimethincyanine and to a di- and a tetra-methin*mero*cyanine (*idem*, this vol., p. 1113). The preparations of a trimethincyanine, of these dinuclear *mero*cyanines, of a trimethinoxonol, and of substances structurally related to trimethinoxonols, form the subject of the present paper.

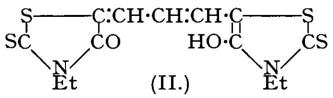
" Oxonol " is a useful trivial name introduced by Brooker, and may conveniently be included in the systematic nomenclature. Oxonols are characterised by possessing two cyclic nuclei, linked by an odd-numbered methin chain, comprising structure (I). Symmetrical methinoxonols



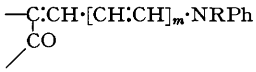
(I*a*.) (I*b*.)

(I; *m* = 0), containing two phenylmethylpyrazolone residues, were described many years ago (Knorr, *Annalen*, 1887, **238**, 137; Stolz, *J. pr. Chem.*, 1897, **55**, 145; Claisen, *Annalen*, 1897, **297**, 1), as also such compounds having two ketodihydrothionaphthen nuclei (Friedländer and Kielbasinski, *Ber.*, 1911, **44**, 3098; Friedländer and Risse, *Ber.*, 1914, **47**, 1919). In the patent literature there is disclosed the use of certain symmetrical methinoxonols and tri-, penta-, and hepta-methinoxonols (I; *m* = 0, 1, 2, or 3) as photographic filter dyes (Gaspar, B.P. 506,385/1937). More recent scientific literature contains an account of one series of oxonols in which two 3-ketodihydrothionaphthen nuclei are linked by methin, trimethin, and pentamethin chains, respectively (Sveschnikov and Levkoev, *J. Gen. Chem. Russia*, 1940, **10**, 274).

Of one desired unsymmetrical, and four symmetrical, oxonols it was only found possible to prepare (II), which was obtained by condensing 3-ethylrhodanine with β-anilinoacraldehyde anil hydrochloride, in the presence of triethylamine in alcohol. The intense blue of its ammoniacal salt changed to red on acidification.

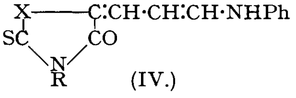


(II.)

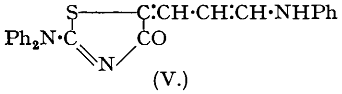


(III.)

By condensing a cyclic compound having a reactive ketomethylene group with suitable anils, compounds intermediate in structure to oxonols and comprising the skeleton (III) may be prepared. Compounds of this kind having one methin group (III; *m* = 0) were discovered earliest (Dains and Brown, *J. Amer. Chem. Soc.*, 1909, **31**, 1148; Dains, Thompson, and Asendorf, *ibid.*, 1922, **44**, 2310), and those with a trimethin chain (III; *m* = 1) have been described in the patent literature (Kodak Ltd., B.P. 470,725/1935). Five of the latter type have now been prepared, for comparison with intermediates having the branched chain $\cdot C{<}^{CH:}_{CH\cdot NHPh}$ which were used in preparing trinuclear dyes (Hamer, Rathbone, and Winton, this vol., p. 1113).



(IV.)

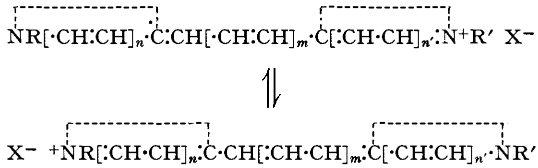


(V.)

These are (IV; R = Et, X = O, S, or NPh, respectively; R = $CH_2\cdot CO_2H$, X = S) and (V), the first three of which are examples in the patent. With dye (IV; X = S), having the

$CH_2\cdot CO_2H$ group, and with dye (V) having the NPh_2 group, the absorption maxima of methyl-alcoholic solutions containing sulphuric acid lay at wave-lengths longer by 55 A. and 225 A., respectively, than did those of the corresponding methyl-alcoholic solutions containing ammonia. With the other three compounds represented by (IV), the addition of acid or alkali to the methyl-alcoholic solution did not affect the position of the absorption maximum. In the case of three *acetyl* derivatives of (IV; R = Et, X = O, S, or NPh, respectively), the absorption maxima lay at wave-lengths shorter (by 500—695 A.) than did those of the corresponding anilino-compounds themselves, as recorded also for pairs of acetanilido- and anilino-compounds which are cyanine intermediates (Brooker, White, Keyes, Smyth, and Oesper, *J. Amer. Chem. Soc.*, 1941, **63**, 3192).

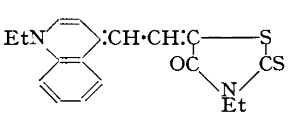
Intermediate between the oxonols, with structure (I), and the cyanines, in which two heterocyclic nitrogen-containing nuclei are linked by an odd-numbered methin chain comprising structure (VI; *m* = 0, 1, 2, 3, etc.; *n* and *n′* = 0 or 1), is another class of dye, which was discovered independently by Kendall (B.P. 426,718/1933) and by Brooker (Kodak Ltd., B.P. 450,958/1934). They comprise structure (VII; *m* = 0, 1, 2, 3; *n* = 0 or 1), in which an even-numbered methin chain links a heterocyclic nitrogen-containing nucleus to a cyclic ketomethylene residue. For these non-ionic compounds, which are prepared from cyanine intermediates, one of us (F. M. H.) suggested the term *mero*cyanine (μερος = part) and this has proved acceptable as a general term (Levkoev, Sveschnikov, and Durmaschkina, *J. Gen. Chem. Russia*, 1940, **10**, 773; Brooker, White, Keyes, Smyth, and Oesper, *loc. cit.*; Stammers and I.C.I. Ltd., B.P. 587,481/1944). Its inclusion in the systematic nomenclature is now required, in order to name our new types of trinuclear dyes (Hamer, Rathbone, and Winton, this vol., p. 1113). In naming *mero*cyanines it seemed logical to follow the pattern of the simplified names used for cyanine dye bases, as suggested by Dr. J. T. Hewitt, F.R.S. (Hamer, *J.*, 1940, 799), rather than that of the systematic names used for the cyanines themselves (Fisher and Hamer, *J.*, 1937, 907; Beilenson and Hamer, *J.*, 1942, 98).

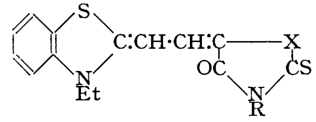

(VIa.) $\mathrm{NR[\cdot CH{:}CH]_n\cdot C{:}CH[\cdot CH{:}CH]_m\cdot C[{:}CH\cdot CH]_{n'}{:}N^+R'\ X^-}$

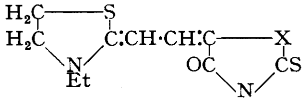
$\rightleftharpoons$

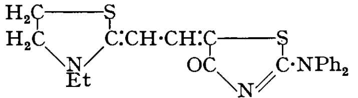
(VIb.) $\mathrm{X^-\ {}^+NR[{:}CH\cdot CH]_n{:}C\cdot CH[{:}CH\cdot CH]_m{:}C[\cdot CH{:}CH]_{n'}\cdot NR'}$


(VII.) $\mathrm{NR[\cdot CH{:}CH]_n\cdot C[{:}CH\cdot CH]_m{:}C\cdot CO}$


(VIII.)

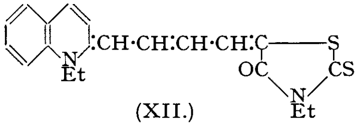

(IX.)


(X.)

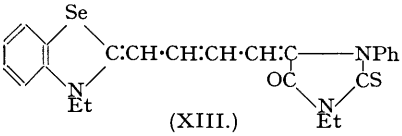

(XI.)

Eight *dimethin*mero*cyanines* were made, namely (VIII), (IX; R = Et, X = O; R = Et, X = S; R = $CH_2\cdot CO_2H$, X = S), the 5-chloro-derivative of (IX; R = Et, X = S), (X; X = O or S), and (XI). Six of these dyes were prepared from the appropriate β-acetanilidovinyl quaternary salt, whilst (X; X = S) was prepared from a β-anilinovinyl salt, and the 5-chloro-derivative of (IX; R = Et, X = S) was prepared by condensing a quaternary salt having a reactive methyl group with an acetanilidoallylidene compound (III; *m* = 1, R = Ac).

Five *tetramethin*mero*cyanines* were prepared, namely (XII), (XIII), and the higher vinylene homologues of (IX; N = Et; X = S and NPh, respectively), and of (X; X = S). The preparation of eleven tetramethin*mero*cyanines is given in the patent literature (Kodak Ltd., B.P. 450,958/1934), where the appropriate acetanilidobutadienyl salt was condensed with the heterocyclic methylene compound, by means of triethylamine in alcohol, one dye thus prepared being the higher vinylene homologue of (IX; X = S). In view of the observed instability of these acetanilido-compounds (Hamer, *J.*, 1949, 32), our method consisted in using triethylamine in acetic anhydride as condensing agent, the starting point being the anilinobutadienyl salt. Each tetramethin*mero*cyanine was liable to be accompanied by the corresponding pentamethincyanine, which in two instances was present in considerable amount; the types could, however, be separated by benzene, in which only the former is soluble. The higher vinylene homologue of (X; X = S) was accompanied by a by-product, having about its own solubility in various organic solvents; the latter was left undissolved when the *tetramethin*mero*cyanine* was taken up by hydrochloric acid and was identified as the acetyl derivative of (IV; R = Et, X = S). The process whereby this 3-ethyl-5-(γ-acetanilidoallylidene)rhodanine is formed from 3-ethylrhodanine with 2-(4′-anilino-1′ : 3′-butadienyl)-Δ^2-thiazoline ethiodide and triethylamine in acetic anhydride is obscure. The compounds comprise photographic sensitisers. Tests were carried out on gelatino-bromide plates except where otherwise stated.



(XII.)



(XIII.)

EXPERIMENTAL.

[2-(4-*Methyl*-3-*ethylthiazole*)][2-(3-*ethyl*-6 : 7-*benzbenzthiazole*)]*trimethincyanine Iodide*.—4-Methyl-2-β-acetanilidovinylthiazole ethiodide (2·07 g.; 1 mol.) and 2-methyl-6 : 7-benzbenzthiazole ethiodide (1 mol.) were mixed with ice-cold alcohol (45 c.c.) and triethylamine (2·2 mols.) and kept at 0° for 5 days. The washed cyanine (2·47 g.) was twice boiled out with methyl alcohol (2 × 20 c.c.). The solids which crystallised (0·16 + 0·17 g.) were added to the residue (1·86 g.), and the whole recrystallised from methyl alcohol (200 c.c.), giving a 72% yield. After a second recrystallisation (100 c.c. per g.), the yield of *iodide* was 63% (Found : I, 24·95. $C_{22}H_{23}N_2IS_2$ requires I, 25·05%). The dark green crystals had no definite m. p.; shrinking began at about 180° and violent decomposition occurred between 230° and 240°. The absorption maximum was at 5660 A. Sensitisation was from 4500 to 6500 A. with a maximum at 5900 A.

Bis-[5-(3-*ethylrhodanine*)]*trimethinoxonol* (II).—A mixture of β-anilinoacraldehyde anil hydrochloride (5·17 g.; 1 mol.), 3-ethylrhodanine (4 mols.), absolute alcohol (40 c.c.), and triethylamine (2 mols.) was boiled under reflux for 6 hours. The reaction mixture was cooled, filtered to remove any by-product, and the filtrate shaken with aqueous ammonia (*d* 0·885; 400 c.c.) which had been saturated with ammonium chloride, and with benzene (800 c.c.). At first both layers were blue but after standing for a few days they lost this colour, the ammonium salt of the dye separating as a tar, which subsequently hardened. It was filtered off and washed with benzene. To free it from ammonium chloride, it was thrice extracted with acetone (3 × 20 c.c.). Evaporation of the solvent from the deep blue extract left the bronze ammonium salt (2·99 g.). The salt was ground with aqueous ammonia (5 c.c., *d* 0·965, per g.), and the mixture added to boiling water (400 c.c. per g.); the hot filtrate was treated with concentrated hydrochloric acid (8 c.c. per g.), and the precipitated *oxonol* was filtered off and washed, being obtained in 12% yield (Found, after drying in a vacuum at 60—80° : S, 35·55. $C_{13}H_{14}O_2N_2S_4$ requires S, 35·8%). The black solid began to shrink at about 160° and gradually decomposed, resulting in a brown drop by 210°, but it had no definite m. p. A methyl-alcoholic solution containing ammonia had its absorption maximum at 6100 A. On acidification the colour changed from blue to red but this red soon faded to yellowish. The dye desensitised, without sensitising, and gave chemical fog.

4-*Keto*-2-*thio*-3-*ethyl*-5-(γ-*anilinoallylidene*)*tetrahydro-oxazole* (IV; R = Et, X = O).—4-Keto-2-thio-3-ethyltetrahydro-oxazole (0·72 g.; 2 mols.), β-anilinoacraldehyde anil hydrochloride (0·65 g.; 1 mol.), and piperidine (0·50 c.c.; 2 mols.), dissolved in absolute ethyl alcohol (100 c.c.), were allowed to react at room temperature for 18 hours. The crystals were filtered off and washed (61% yield). After recrystallisation from pyridine (9 c.c.) and water (4·5 c.c.), the yield was 54% (Found, after drying in a vacuum at 60—80° : S, 11·8. $C_{14}H_{14}O_2N_2S$ requires S, 11·7%). The deep orange crystals had m. p. 244° (decomp.). Whether a methyl-alcoholic solution contained ammonia or sulphuric acid, the absorption maximum was at 4460 A., the curve for the acid solution being more rounded than the other. The *dye* sensitised a gelatino-chloride plate to 6100 A., with the maximum at 5200 A. (cf. examples 3 and 6 of B.P. 470,725).

4-*Keto*-2-*thio*-3-*ethyl*-5-(γ-*acetanilidoallylidene*)*tetrahydro-oxazole*.—The foregoing compound (1·62 g.; 1 mol.), acetic anhydride (8 c.c.), and triethylamine (1 mol.) were boiled together under reflux for 5 minutes, as in B.P. 470,725, example 6. The washed product (1·70 g.) was twice recrystallised from acetic acid (18 c.c. per g.) and obtained in 67% yield. The *acetyl* derivative was dried in a vacuum at 80—100° and analysed by the method of Carius, which procedure was adopted throughout this work, except where otherwise stated (Found : S, 10·15. $C_{16}H_{16}O_3N_2S$ requires S, 10·15%). The pale yellow crystals had m. p. 240° with previous softening; in the patent, 247—249° (decomp.) is given. The absorption maximum was at 3775 A. The substance sensitised a gelatino-chloride plate to 5000 A. with the maximum at 4100 A.

3-*Ethyl*-5-(γ-*anilinoallylidene*)*rhodanine* (IV; R = Et, X = S).—3-Ethylrhodanine (1·61 g.; 1 mol.), β-anilinoacraldehyde anil hydrochloride (1 mol.), triethylamine (1 mol.), and absolute alcohol (20 c.c.) were boiled together for 2 minutes. The washed crystals (78% yield) were recrystallised from methyl alcohol (250 c.c. per g.). The 60% yield fell to 57% on a second recrystallisation from methyl alcohol with charcoal (0·2 g. per g.) (Found : S, 22·35. $C_{14}H_{14}ON_2S_2$ requires S, 22·1%). The red crystals melted at 207°. A methyl-alcoholic solution containing ammonia had its absorption maximum at 4775 A. and one containing sulphuric acid at 4795 A. The *rhodanine* sensitised a chloride plate to 6100 A. with the maximum at 5400 A. and with some decrease of the original blue sensitivity (cf. example 2 of B.P. 470,725).

3-*Ethyl*-5-(γ-*acetanilidoallylidene*)*rhodanine*.—3-Ethyl-5-(γ-anilinoallylidene)rhodanine was acetylated with acetic anhydride and triethylamine, as in B.P. 470,725. The washed crystals, after recrystallisation from pyridine (10 c.c. per g.), gave a 77% yield (Found: S, 19·4. $C_{16}H_{16}O_2N_2S_2$ requires S, 19·3%). The yellow crystals deepened in colour from 170° and had m. p. 222·5°. The m. p. recorded in the patent is 225·5—226·5°. The absorption maximum was at 4115 A. The *acetyl* derivative decreased the blue sensitivity of a gelatino-chloride plate and sensitised weakly from 4400 to 5400 A., with the maximum at 4900 A.

1-*Phenyl*-3-*ethyl*-5-(γ-*anilinoallylidene*)-2-*thiohydantoin* (V; R = Et, X = NPh.).—As in example 8 of B.P. 470,725, equimolecular quantities of 1-phenyl-3-ethyl-2-thiohydantoin (2·20 g.), β-anilinoacraldehyde anil hydrochloride, and triethylamine, in absolute alcohol (15 c.c.), were boiled together for 30 minutes. The washed product (77% yield) was recrystallised from pyridine (10 c.c.) and water (5 c.c.), giving a 60% yield (Found, after drying in a vacuum at 60—80°: S, 9·1. $C_{20}H_{19}ON_3S$ requires S, 9·2%). The bluish-red crystals had m. p. 128—130° (decomp.). A methyl-alcoholic solution, whether containing ammonia or sulphuric acid, had its maximum at 4650 A., but the acid one faded during exposure. The *dye* sensitised a chloride plate to 6000 A., the maximum lying at 5350 A.

1-*Phenyl*-3-*ethyl*-5-(γ-*acetanilidoallylidene*)-2-*thiohydantoin*.—1-Phenyl-3-ethyl-5-(γ-anilinoallylidene)-2-thiohydantoin was acetylated with acetic anhydride and triethylamine, and the washed *acetyl* derivative recrystallised from 50% aqueous pyridine (12 c.c. per g.), giving a 67% yield (Found: S, 8·05. $C_{22}H_{21}O_2N_3S$ requires S, 8·2%). The yellow crystals had m. p. 212—214°, whereas in B.P. 470,725 the m. p. is given as 247—249° (decomp.). The absorption maximum was at 4155 A. The substance sensitised a gelatino-chloride plate to 5100 A., with the maximum at 4500 A.

3-*Carboxymethyl*-5-(γ-*anilinoallylidene*)*rhodanine* (IV; R = $CH_2{\cdot}CO_2H$, X = S).—3-Carboxymethylrhodanine (0·96 g.; 2 mols.), β-anilinoacraldehyde anil hydrochloride (1 mol.), absolute alcohol (10 c.c.), and triethylamine (4 mols.) were mixed at room temperature and, after 15 minutes, cooled with ice. The triethylamine salt was filtered off, washed with absolute alcohol (0·67 g. left), and recrystallised from methyl alcohol (5 c.c.). The product (0·60 g.) was taken up in hot methyl alcohol (6 c.c.) and treated with hot acetic acid (6 c.c.), whence a 45% yield of the *acid* was obtained on cooling (Found: S, 20·25. $C_{14}H_{12}O_3N_2S_2$ requires S, 20·05%). The light red crystals had m. p. about 264° (decomp.), with shrinking and darkening from 225°. A methyl-alcoholic solution containing ammonia had its absorption maximum at 4745 A. whilst one containing sulphuric acid had the maximum at 4800 A. The dye sensitised a gelatino-chloride plate from 4500 to 6100 A., the maximum lying at 5500 A., and decreased the blue sensitivity.

2-*Diphenylamino*-4-*keto*-5-(γ-*anilinoallylidene*)-Δ^2-*thiazoline* (V).—2-Diphenylamino-4-keto-Δ^2-thiazoline (0·67 g.; 1 mol.), β-anilinoacraldehyde anil hydrochloride (1 mol.), and triethylamine (2 mols.) in absolute alcohol (5 c.c.) were boiled together for 30 minutes. The washed product (89% yield) was twice recrystallised from methyl alcohol (95 c.c. and 135 c.c. per g.) whereupon the yield was 22% (Found, after drying in a vacuum at 60—80°: S, 8·15. $C_{24}H_{19}ON_3S$ requires S, 8·05%). The orange crystals, with a blue reflex, had m. p. about 257° (decomp.), with darkening from 240°. The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4455 A. and of one containing sulphuric acid at 4680 A. The *thiazoline* sensitised a gelatino-chloride plate to 5500 A., with the maximum at 5000 A.

[4-(1-*Ethyldihydroquinoline*)][5-(3-*ethylrhodanine*)]*dimethin*mero*cyanine* (VIII).—This is mentioned as example 117 of B.P. 450,958. A mixture of 4-β-acetanilidovinylquinoline ethiodide (2·22 g.; 1 mol.), 3-ethylrhodanine (0·81 g.; 1 mol.), absolute alcohol (20 c.c.), and triethylamine (1·0 c.c.; 1·5 mols.) was boiled for 10 minutes. The washed *dye* was recrystallised from pyridine (20 c.c.). The 48% yield was boiled out with methyl alcohol (30 c.c. per g.) and recrystallised from pyridine and water (30 c.c. of each per g.), giving a 43% yield (Found, after drying in a vacuum at 60—80°: S, 18·4. $C_{18}H_{18}ON_2S_2$ requires S, 18·75%). The purple powder had m. p. 226° (decomp.). The principal absorption maximum was at 6140 A., with a secondary one at 5760 A. Sensitisation was from 5600 to 6800 A., with the maximum at 6550 A., and decrease of the blue sensitivity.

[5-(4-*Keto*-2-*thio*-3-*ethyltetrahydro*-*oxazole*)][2-(3-*ethylbenzthiazoline*)]*dimethin*mero*cyanine* (IX; R = Et, X = O).—This is mentioned as example 85 of B.P. 450,958. A mixture of 4-keto-2-thio-3-ethyltetrahydro-oxazole (0·73 g.; 1 mol.), 2-β-acetanilidovinylbenzthiazole ethiodide (1 mol.), triethylamine (2 mols.), and ethyl alcohol (30 c.c.) was boiled for 3 minutes. The washed dye (1·45 g.) was recrystallised from pyridine (15 c.c.) and obtained in 75% yield (Found, after drying in a vacuum at 60—80°: S, 19·5. $C_{16}H_{16}O_2N_2S_2$ requires S, 19·3%). The maroon crystals had m. p. 240° (decomp.), with shrinking from 212°. The absorption maximum was at 5030 A. The *dye* sensitised a gelatino-chloride plate to 5900 A. with the chief maximum at 5500 A., and another at 4750 A. This preparation and the next were carried out by Dr. R. J. Rathbone.

[5-(3-*Ethylrhodanine*)][2-(3-*ethylbenzthiazoline*)]*dimethin*mero*cyanine* (IX; R = Et, X = S).—This *dye* is mentioned as example 88 of B.P. 450,958. Its preparation was like the preceding one but with 3-ethylrhodanine instead of the oxazole derivative. The crude dye (75% yield) was recrystallised from pyridine (40 c.c. per g.), giving a 60% yield (Found: S, 27·8. $C_{16}H_{16}ON_2S_3$ requires S, 27·6%). The bright red crystals had m. p. 265° (decomp.). The absorption maximum was at 5300 A. and the sensitising maximum at 5800 A.

[5-(3-*Carboxymethylrhodanine*)][2-(3-*ethylbenzthiazoline*)]*dimethin*mero*cyanine* (IX; R = $CH_2{\cdot}CO_2H$, X = S).—3-Carboxymethylrhodanine (0·96 g.; 1 mol.), 2-β-acetanilidovinylbenzthiazole ethiodide (1 mol.), triethylamine (1·2 mols.), and ethyl alcohol (8 c.c.) were boiled together for 15 minutes. The crude product (0·75 g.) was recrystallised from pyridine (5 c.c.), then converted into the *acid* by boiling with acetic acid (10 c.c.), resulting in a 25% yield (Found, after drying in a vacuum at 60—80°: S, 25·35. $C_{16}H_{14}O_3N_2S_3$ requires S, 25·45%). The purple powder became scarlet at about 200°, darkened at about

220°, and had m. p. about 273—278° (decomp.). The absorption maximum of a methyl-alcoholic solution containing sulphuric acid was at 5225 A. The dye sensitised to 6400 A., with the maximum at about 5600 A.

[5-(3-*Ethylrhodanine*)][2-(5-*chloro*-3-*ethylbenzthiazoline*)]*dimethin*mero*cyanine*.—5-Acetanilidomethylene-3-ethylrhodanine (1·53 g.; 1 mol.), 5-chloro-2-methylbenzthiazole ethiodide (1 mol.), triethylamine (1·5 mols.), and absolute alcohol (25 c.c.) were boiled together for 3 minutes. The washed product (1·40 g.) was recrystallised from pyridine (80 c.c.) and methyl alcohol (80 c.c.), being obtained in 63% yield (Found, after drying in a vacuum at 60—80°: Cl, 9·3. $C_{16}H_{15}ON_2ClS_3$ requires Cl, 9·3%). The reddish crystals had m. p. 246—248° (decomp.). The absorption maximum was at 5220 A. The *dye* sensitised a gelatino-bromide plate to 6400 A., with maxima at 5800 A. and 5250 A.

[5-(4-*Keto*-2-*thio*-3-*ethyltetrahydro-oxazole*)][2-(3-*ethylthiazolidine*)]*dimethin*mero*cyanine* (X; X = O). —4-Keto-2-thio-3-ethyltetrahydro-oxazole (0·73 g.; 1 mol.), 2-β-acetanilidovinyl-Δ^2-thiazoline ethiodide, triethylamine (1·2 mols.), and ethyl alcohol (8 c.c.) were boiled together for 15 minutes. The washed product (1·05 g.) was recrystallised from aqueous pyridine (2 : 1, 21 c.c.) and obtained in 68% yield. After another such recrystallisation, the yield was 41% (Found, after drying in a vacuum at 60—80°: S, 22·3. $C_{12}H_{16}O_2N_2S_2$ requires S, 22·55%). The yellow powder had m. p. 169°. The absorption maximum was at 4575 A. The *cyanine* sensitised a gelatino-chloride plate to 5500 A., the maximum lying at 5000 A.

[2-(3-*Ethylthiazolidine*)][5-(3-*ethylrhodanine*)]*dimethin*mero*cyanine* (X; X = S).—This was prepared by boiling together for 5 minutes, 2-β-anilinovinyl-Δ^2-thiazoline ethiodide (3·62 g.; 1 mol.), 3-ethylrhodanine, triethylamine (1·5 mols.), and ethyl alcohol (16 c.c.). The washed product (65% yield) was recrystallised from pyridine and methyl alcohol (8 c.c. of each) and obtained in 23% yield. After a second recrystallisation (5 c.c. pyridine; 15 c.c. MeOH per g.) the yield was 20% (Found, after drying in a vacuum at 60—80°: S, 31·8. $C_{12}H_{16}ON_2S_3$ requires S, 32·05%). The crimson powder had m. p. 161°. The absorption maximum was at 4825 A. The *dye* sensitised to 5800 A. with the maximum at 5350 A.

[2-(3-*Ethylthiazolidine*)][5-(2-*diphenylamino*-4-*keto*-Δ^2-*thiazoline*)]*dimethin*mero*cyanine* (XI).—2-Diphenylamino-4-keto-Δ^2-thiazoline (2·69 g.; 1 mol.), 2-β-acetanilidovinyl-Δ^2-thiazoline ethiodide (1 mol.), triethylamine (1·2 mols.), and ethyl alcohol (15 c.c.) were boiled together for 12 minutes. The washed product (72% yield) was boiled out four times with methyl alcohol (4 × 25 c.c.), and the residue recrystallised from a mixture of acetic acid (15 c.c.) and methyl alcohol (30 c.c.). The substance from the first boiling out was rejected and that from the next three (0·30 g.) added to the main bulk (1·80 g.), making a 52% yield (Found, after drying in a vacuum at 60—80°: S, 15·55. $C_{22}H_{21}ON_3S_2$ requires S, 15·75%). The bright yellow *cyanine* had m. p. 279—281° (decomp.). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4600 A. A gelatino-chloride plate was sensitised to 5500 A., the maximum lying at 4950 A.

[2-(1-*Ethylquinoline*)][5-(3-*ethylrhodanine*)]*tetramethin*mero*cyanine* (XII).—To 2-(4′-anilino-1′ : 3′-butadienyl)quinoline ethiodide (4·28 g.; 1 mol.) were added acetic anhydride (200 c.c.), triethylamine (2·75 c.c.; 2 mols.), and 3-ethylrhodanine (3·22 g.; 2 mols.), and the mixture was boiled for 4 minutes. The solid was filtered off, washed with acetic anhydride and with ether (2·33 g. left), and boiled out with light petroleum (b. p. 80—100°; 2400 c.c.). The residue (0·76 g.; 38% yield) was recrystallised from benzene (330 c.c. per g.) and gave a 17% yield (Found, S, 17·4. $C_{20}H_{20}ON_2S_2$ requires S, 17·4%). The greyish blue crystals turned green at about 257° and melted about 270° (decomp.). The principal absorption maximum was at 6575 A., with a secondary one at 6150 A. The *cyanine* sensitised from 6200 to 7400 A., with a maximum at 7000 A., but caused some veil.

[5-(1-*Phenyl*-3-*ethyl*-2-*thiohydantoin*)][2-(3-*ethylbenzselenazoline*)]*tetramethin*mero*cyanine* (XIII).—2-(4′-Anilino-1′ : 3′-butadienyl)benzselenazole ethiodide (4·81 g.) was similarly boiled with acetic anhydride, triethylamine, and 1-phenyl-3-ethyl-2-thiohydantoin. The washed product (2·88 g.) was twice boiled out with light petroleum (b. p. 80—100°; 1200 c.c., 2400 c.c.). The substance which separated from the second extract (0·07 g.) was added to the residue (1·69 g.) and boiled out with benzene (120 c.c.), whence a 13% yield crystallised. After recrystallisation from benzene (210 c.c. per g.), the yield of *cyanine* was 5% [Found, micro-analysis by Drs. Weiler and Strauss: N, 8·75. $C_{25}H_{23}ON_3SSe$ requires S, 8·75%). The dull green crystals had m. p. 277° (decomp.). The absorption maximum was at 5590 A. Sensitisation was from 5100 to 7500 A., with the maximum at 6900 A.

The residue (0·44 g.) from the first benzene recrystallisation was again boiled out with benzene (50 c.c.) and this residue (0·35 g.) was recrystallised from methyl alcohol (125 c.c.; 0·16 g. obtained) (Found: I, 21·25. Calc. for $C_{23}H_{23}N_2ISe_2$: I, 20·9%). This by-product had the properties of the known bis-2-(3-ethylbenzselenazole)pentamethincyanine iodide (Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703).

[5-(3-*Ethylrhodanine*)][2-(3-*ethylbenzthiazoline*)]*tetramethin*mero*cyanine*.—This *dye* was prepared by heating together 2-(4′-anilino-1′ : 3′-butadienyl)benzthiazole ethiodide (4·34 g.), acetic anhydride, triethylamine, and 3-ethylrhodanine. The washed product (2·70 g.) was boiled out with light petroleum (b. p. 80—100°; 2400 c.c.) and the residue (1·30 g.; 35% yield) was thrice recrystallised from benzene (210 c.c. per g.), the yields being 27%, 20%, and 14% (Found: S, 25·95. $C_{18}H_{18}ON_2S_3$ requires S, 25·7%). The greyish-blue crystals had m. p. 238°, with shrinking from 235°. The broad absorption curve had its maximum at 5950 A. Sensitisation was from 6200 to 7300 A., with the maximum at 6900 A., and the original blue sensitivity of the plate was decreased. The preparation of this dye is recorded in B.P. 450,958, example 123.

[5-(1-*Phenyl*-3-*ethyl*-2-*thiohydantoin*)][2-(3-*ethylbenzthiazoline*)]*tetramethin*mero*cyanine*.—This *dye* was prepared from the same anilino-compound (4·34 g.) but with 1-phenyl-3-ethyl-2-thiohydantoin. The washed product (1·89 g.) was boiled out with light petroleum (b. p. 80—100°; 2400 c.c.), and the residue (1·38 g.) boiled out five times with benzene (5 × 20 c.c.). From the first four extracts a 10% yield crystallised. A second recrystallisation from benzene (50 c.c.) gave a 6% yield (Found: S, 14·9. $C_{24}H_{23}ON_3S_2$ requires S, 14·8%). The green crystals decomposed from about 255°. The rounded absorption curve had its maximum at 5650 A. Sensitisation was from 5300 to 7300 A., with fogging and with decrease of the original blue sensitivity.

The dye undissolved at the first benzene extraction was further boiled out with benzene and the residue (0·57 g.) was recrystallised from methyl alcohol (150 c.c. per g.; 0·32 g. obtained) (Found: I, 24·55. Calc. for $C_{23}H_{23}N_2IS_2$: I, 24·5%).

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][5-(3-*ethylrhodanine*)]*tetramethin*mero*cyanine*.—This was prepared from 2-(4′-anilino-1′ : 3′-butadienyl)-Δ^2-thiazoline ethiodide (1·93 g.), 3-ethylrhodanine, acetic anhydride, and triethylamine, by boiling together for 1 minute. The ether-washed product (1·22 g.) was ground with cold concentrated hydrochloric acid solution (20 c.c.), which dissolved the mero*cyanine*. It was precipitated (30% yield) by adding the extract to hot water (100 c.c.) and treating it with excess of ammonia. After two recrystallisations from benzene (50 c.c. per g.) (yields 19% and 11%) and one from 50% aqueous pyridine (20 c.c. per g.), the final yield was 11% (Found: S, 29·25. $C_{14}H_{18}ON_2S_3$ requires S, 29·5%). The steel-blue crystals had no definite m. p.; softening began at about 175° and violent decomp. occurred at about 280°. The absorption maximum was at 5700 A. Sensitisation was from 5400 to 6900 A., with the maximum at 6300 A.

The product left undissolved by hydrochloric acid was again ground with acid (20 c.c.) and then washed with water. The residue (0·60 g.) was twice recrystallised from pyridine (10 c.c. per g.) and gave a 25% yield of yellow crystals, which by analysis (Found: S, 19·45. Calc. for $C_{16}H_{16}O_2N_2S_2$: S, 19·3%), m. p. and mixed m. p., were identified as 3-ethyl-5-(γ-acetanilidoallylidene)rhodanine (cf. p. 1128).

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