476. *Dimethin*merocyanines derived from 2-Substituted Azol-5-ones.*

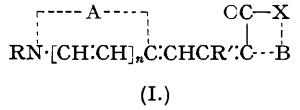
By Per Aubert, E. B. Knott, and L. A. Williams.

A number of *S*-esters (V), including long-chain alkyl esters, of *N*-dithiocarboxyglycine have been prepared, cyclised by the method of Cook, Harris, Heilbron, and Shaw (*J.*, 1948, 1056), and converted into a series of dimethin*mero*cyanines (cf. Cook, Harris, and Shaw, *J.*, 1949, 1435) containing the 2-alkylthiothiazol-5-one nucleus. Analogous *O*-esters (XIV) of *N*-thioncarboxyglycine were readily obtained by the condensation of potassium aminoacetate with ethyl alkoxydithioformates. Cyclisation of these with acetic anhydride gave a series of 2-alkoxythiazol-5-ones (XV), or, in the presence of ethyl orthoformate, 2-alkoxy-4-ethoxymethylenethiazol-5-ones (XVI) both of which were converted into a series of dimethin*mero*cyanines. Similarly *N*-acylthiohydantoic acids were cyclised by phosphorus tribromide to give what are believed to be 2-acylamidothiazol-5-one hydrobromides which also contain a reactive methylene group giving rise to a series of dimethin*mero*cyanines.

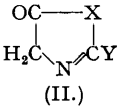
The condensation of *N*-dithiocarbethoxyglycine with secondary amines led to *NN*-disubstituted *N'*-carboxythioureas (XIX) which were cyclised by phosphorus tribromide to 2-di-alkyl(or -aryl)aminothiazol-5-ones which also readily formed dimethin*mero*cyanines.

The series of dimethin*mero*cyanines derived from 2-phenyloxazol-5-one (Cook *et al.*, *loc. cit.*, 1949) was extended.

Because of their usefulness as photographic optical sensitisers the class of dyes known as dimethin*mero*cyanines (I) has been widely investigated. In (I), R is usually alkyl, R′ is hydrogen, alkyl, or aryl, *n* is 0 or 1, and A and B represent the atoms necessary to complete a 5- or 6-membered ring or rings. In the majority of known dyes the ketonic nucleus carries a substituted amino-group adjacent to the ketonic group (*i.e.*, X = NR). Keyes and Brooker (B.P. 518,904), however, obtained a number of dimethin*mero*cyanines containing the 2-phenyloxazol-5-one nucleus (II; X = O, Y = Ph), and recently Cook *et al.* (*J.*, 1949, 1435) obtained similar dyes by a different method and also related dyes from the 2-substituted thiazol-5-one



(I.)



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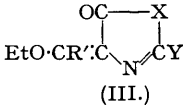

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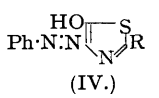


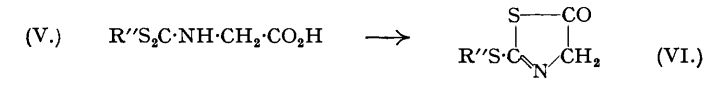
(IV.)

nucleus (II; X = S, Y = Ph, ·S·CH$_2$Ph, ·S·CO$_2$Et) The latter authors prepared their dyes by the known procedure of condensing the 4-ethoxymethylene derivative (III; R′ = H) of (II) with the reactive methyl derivative of the required cyclic quaternary ammonium salt in the presence of alcoholic triethylamine.

In view of the possible photographic application of such dyes a larger number have been synthesised (see Experimental) containing the 2-phenyloxazol-5-one, 2-ethylthiothiazol-5-one, 2-benzylthiothiazol-5-one, and 2-mercaptothiazol-5-one nuclei (cf. II; X = S, Y = SH) (Cook, Heilbron, and Levy, *J.*, 1948, 201). These dyes were obtained both by Cook's method

* Patent applications pending.

and by the more usual method of condensing (II) with the 2-acetanilidovinyl derivative of the cyclic quaternary ammonium salt in alcoholic triethylamine. An extension of the series of dyes was made possible (see Experimental) by the synthesis of a number of further *S*-esters (V) of *N*-dithiocarboxyglycine. Thus, using Körner's method (*Ber.*, 1908, **41**, 1091), the *p*- and *m*-nitrobenzyl esters (V; R″ = ·CH_2·C_6H_4·NO_2) were obtained and cyclised by phosphorus tribromide to the required hydrobromides of 2-*p*- and 2-*m*-nitrobenzylthiothiazol-5-one (VI). It was also possible to make long-chain alkyl esters (V), by refluxing the required alkyl bromide with the potassium salt of *N*-dithiocarboxyglycine. In this way the *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-decyl, *n*-dodecyl, and 3-phenylpropyl esters (V) were readily obtained. The salts of the longer-chain esters possess some surface activity. All of these esters were readily cyclised by

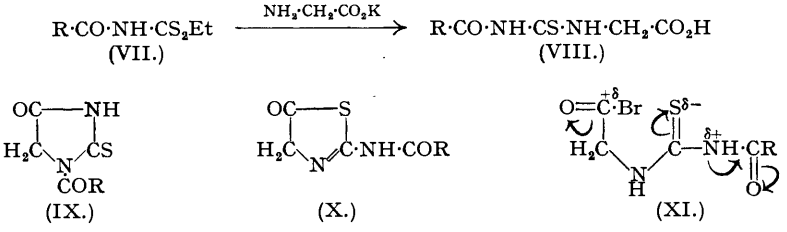


acetic anhydride or phosphorus tribromide to the required thiazol-5-one (VI) or its hydrobromide (VI; R″ = $C_{12}H_{25}$) was characterised by conversion of its hydrobromide into 2-*n*-dodecylthio-5-hydroxy-4-phenylazothiazole (IV; R = S·$C_{12}H_{25}$) by gently warming it with diazoaminobenzene in ethanol (see also Knott and Williams, *J.*, 1951, 1586, for similar reactions of diazoaminobenzene with reactive methyl groups).

All of the above thiazol-5-ones or their 4-ethoxymethylene derivatives were readily converted into dimethin*mero*cyanine dyes. It has also been found that chain-substituted dyes (I; R′ = Me or Et) are readily obtained from the intermediates (III; R′ = Me or Et) prepared by cyclisation of the necessary glycine with acetic anhydride in the presence of ethyl orthoacetate or ethyl orthopropionate. Although these intermediates were not isolated in the thiazol-5-one series, crystalline 4-1′-ethoxyethylidene-2-phenyloxazol-5-one (III; R′ = Me, X = O, Y = Ph) * (cf. " The Chemistry of Penicillin," Princeton Univ. Press, 1949, p. 803, for III, R′ = H) was isolated in good yield.

In view of the strong sensitising properties of many of the foregoing dyes we prepared analogues with other substituents in the 2-position of the thiazol-5-one ring, notably 2-acylamido-, 2-alkoxy-, and 2-*tert.*-amino-groups. The requisite thiazolones were hitherto unknown.

2-*Acylamidothiazol-5-ones* (X).—Wheeler, Nicolet, and Johnson (*Amer. Chem. J.*, 1911, **46**, 456) obtained *N*-acetylthiohydantoic acid (*N*-*N*′-acetylthiocarbamylglycine) (VIII; R = Me) by heating potassium aminoacetate with ethyl acetamidodithioformate (VII; R = Me). They obtained the benzamido-analogue (VIII; R = Ph) by a similar process. On heating these



acids with a mixture of acetic anhydride, acetic acid, sodium acetate, and benzaldehyde they obtained a compound which they formulated as 1-acetyl-5-benzylidenetetrahydro-4-keto-2-thioglyoxaline (the benzylidene derivative of IX; R = Me) since on hydrolysis with cold 10% potassium hydroxide it yielded 5-benzylidenetetrahydro-4-keto-2-thioglyoxaline which was synthesised unambiguously from 2-thiohydantoin and benzaldehyde.

It will be observed that (VIII) is an acylamide of *N*-dithiocarboxyglycine, the *S*-ester of which was used by Cook in the synthesis of 2-alkylthiothiazol-5-ones, and that (VIII) is thus the intermediate required for cyclisation to 2-acylamidothiazol-5-ones. The above work (Wheeler *et al.*) indicates, however, that ring closure occurs between the carboxy-group and the amido-nitrogen atom and not between the former and the sulphur atom. Treatment of (VIII; R = Me) with acetic anhydride under conditions used by Cook for the cyclisation of *N*-dithiocarbalkoxyglycines gave an oil which exhibited only weak colour reactions with an alcoholic-triethylamine solution of a variety of 2-acetanilidovinyl derivatives of cyclic quaternary

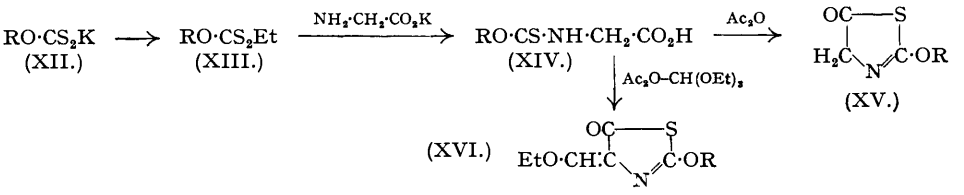
* This compound has already been made by Kendall and Duffin (B.P. 633,736).

ammonium salts. On the other hand treatment of (VIII; R = Me) with phosphorus tribromide in dioxan–ether gave a product, the analysis of which indicated the loss of the elements of water, giving the hydrobromide of (IX) or (X). Similar products were obtained from (VIII; R = Bu^n or Ph). All these hydrobromides slowly decomposed in moist air, fuming strongly. They gave strong colour reactions with the above-mentioned quaternary salts, and a number of dimethin*mero*cyanines were isolated (see Experimental). Attempts to isolate the free bases from the hydrobromides by shaking them with aqueous sodium acetate–ether were unsuccessful, the ethereal layer no longer giving any colour reactions. This method of releasing the bases was successfully employed by Cook *et al.* (*loc. cit.*, 1949) in the case of 2-benzylthiothiazol-5-one.

The apparent instability of the bases of these hydrobromides is considered to favour their being thiazolones (X) rather than tetrahydroketoglyoxalines (IX) since the latter would be expected to be stable. Further evidence against (IX) is the non-formation of insoluble silver salts by the dyes derived from the hydrobromides. Thus the thiol group in (IX) (regarded as a mercapto-derivative) should be capable of salt formation as has been found for similar dyes derived from 2-mercaptothiazol-5-one. From an electronic standpoint it would, moreover, be expected that thiazolone formation would be preferred. Thus it may be assumed that the first step in the cyclisation is the formation of the acid bromide (XI) in which one reactive centre is the electrophilic carbonyl-carbon atom of the COBr residue. For formation of (IX) it is then required that this centre should attack the amido-nitrogen atom which is, however, also electrophilic by virtue of the amide-type resonance in the system. For thiazolone formation the nucleophilic sulphur atom is the second active centre and consequently the formation of a covalent C–S bond appears the more likely. Similar electronic conditions also apply in the condensation of thiourea with α-halogeno-ketones or 2-bromoethylamine, the resultant products in such cases being derivatives of 2-aminothiazole or 2-aminothiazoline and not of a di- or tetra-hydroglyoxaline. In view of the sensitivity of 5-imino-2-thiothiazolidines to alkali (Cook *et al.*, *J.*, 1948, 201) (causing isomerisation to 2 : 4-dithiohydantoin) there appears the possibility that the compound obtained by Wheeler *et al.* (*loc. cit.*) was, in fact, a thiazolidone, the hydrolysing treatment with alkali causing a similar isomerisation to the 2-thiohydantoin derivatives.

The hydrobromide from (VIII; R = Pr^n) condensed readily with diazoaminobenzene to give what is considered to be 2-*n*-butyramido-5-hydroxy-4-phenylazothiazole (IV; R = NH·COPr^n).

2-*Alkoxythiazol-5-ones* (XV).—For the preparation of these derivatives, *N*-thiocarbalkoxyglycines (XIV) were required. They cannot be obtained in the same way as the *N*-dithio-analogues, but are readily obtained according to the following reaction scheme:

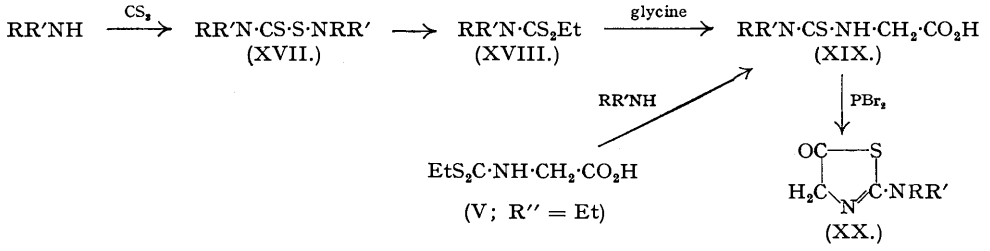


The required alcohol (ROH) was converted into the potassium alkoxydithioformate (alkylxanthate) (XII), esterified with ethyl bromide to give the ethyl alkoxydithioformate (XIII) (omission of this step lowers considerably the yield in the next step), and the latter refluxed with aqueous-alcoholic potassium aminoacetate to give the required *N*-thioncarbalkoxyglycine (XIV) with the elimination of ethanethiol. Twelve alkyl, and also the 3-phenylpropyl, esters were thus prepared; they are all stable, alkali-soluble crystalline solids, the longer-chain esters being surface-active. They are readily cyclised by acetic anhydride at 100—130° to a series of 2-alkoxythiazol-5-ones. The crude oils were used in all cases for the preparation of a series of dimethin*mero*cyanines. 2-Ethoxythiazol-5-one was distilled without decomposition but the product, even after fractionation, had the odour of acetic anhydride and gave low values for nitrogen and sulphur.

By cyclising in the presence of ethyl orthoformate 2-alkoxy-4-ethoxymethylenethiazol-5-ones (XVI) were obtained and the crude products used in dye formation. They are all crystalline products but those with short alkyl chains rapidly decompose and liquefy. The stability increases with increasing chain length and several of these compounds were characterised.

The attempted cyclisation of (XIV) by phosphorus tribromide or phosphorus trichloride in dioxan–benzene did not give the required 2-alkoxythiazol-5-one salt. The crystalline product which resulted was well defined and its nature and properties will be reported separately.

2-tert.-*Aminothiazol-5-ones* (XX).—In view of the failure to bring 2-ethylthiothiazol-5-one into reaction with secondary amines in order to produce 2-*tert.*-aminothiazol-5-ones their synthesis was attempted by the cyclodehydration of *NN*-disubstituted *N'*-carboxymethylthioureas (XIX). In theory these may be obtained by two routes. It is well known (Delépine, *Compt. rend.*, 1902, **134**, 715) that secondary amines (NHRR') condense with carbon disulphide to give salts of *NN*-disubstituted dithiocarbamates (XVII) which are readily esterified by alkyl halides to give (XVIII). Treatment of these esters with glycine would then be expected to give the amide (XIX) but it appears that amide formation does not readily occur in these cases, although it occurs much more readily with *N*-monosubstituted dithiocarbamates (XVIII; R = H).



It was found then that the required substances were smoothly formed by the condensation of the secondary amine in aqueous or aqueous-alcoholic solution with the potassium salt of *N*-dithiocarbethoxyglycine (V; R'' = Et). In this way *N*-(*NN*-diethylthiocarbamyl)glycine (XIX;

R = R' = Et), and the analogues (XIX; R = Ph, R' = Et), (XXI), and (XXII) were obtained. These are cyclised by phosphorus tribromide to oily 2-*tert.*-aminothiazol-5-one hydrobromides which were used directly in dye formation (see Experimental).

Experimental.

Microanalyses are by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.

4-1'-*Ethoxyethylidene-2-phenyloxazol-5-one* (III; R' = Me, X = O, Y = Ph).—Hippuric acid (72 g., 0·4 mol.), ethyl orthoacetate (65 g., 0·4 mol.), and acetic anhydride (80 c.c.) were heated together in an oil-bath at 140—150° for 1 hour and the solvents removed under reduced pressure. The residual red oil crystallised on chilling. It was dissolved in warm ethanol (50 c.c.) and then chilled and the crystals were collected and washed with light petroleum (b. p. 60—80°). The *ketone* (21 g.) formed pink blades, m. p. 110°, from ethanol (Found: N, 5·95. $C_{13}H_{13}O_3N$ requires N, 6·05%).

N-*Dithiocarbalkoxyglycines.*—N-*Dithiocarbonitrobenzyloxyglycines* (V; R'' = $CH_2{\cdot}C_6H_4{\cdot}NO_2$). Potassium hydroxide (11·2 g., 0·2 mol.) was dissolved in water (25 c.c.), the solution was chilled, and glycine (7·5 g., 0·1 mol.) and carbon disulphide (7·6 g., 0·1 mol.) were added. The mixture was shaken until homogeneous (3—4 hours) and *m*-nitrobenzyl bromide (21·6 g., 0·1 mol.) dissolved in ethanol (25 c.c.) was added. After further shaking for 4 hours the yellow solid (not investigated) was filtered off and the filtrate acidified to give an oil which soon crystallised. It was redissolved in 2N-sodium carbonate, and the solution filtered and acidified. The precipitated m-*nitrobenzyl* ester was collected, washed and air-dried. It (14 g.) formed pale yellow needles, m. p. 144°, from benzene (Found: S, 22·5. $C_{10}H_{10}O_4N_2S_2$ requires S, 22·4%). The p-*nitro*-isomer was similarly obtained from *p*-nitrobenzyl chloride (17·15 g., 0·1 mol.). The crude product was crystallised by dissolving it in acetone, adding benzene (2 vols.), and slowly distilling off the acetone. It (20·5 g., 72%) formed pale yellow needles, m. p. 146°, from toluene (Found: S, 22·75%).

N-*Dithiocarbo*-n-*heptyloxyglycine* (V; R'' = n-C_7H_{15}). A solution of potassium hydroxide (56 g., 1·0 mol.) and glycine (37·5 g., 0·5 mol.) in water (100 c.c.) was shaken for 3 hours with carbon disulphide (38 g.). *n*-Heptyl bromide (90 g., 0·5 mol.) and industrial alcohol (100 c.c.) were added and the two-phase mixture was refluxed on the steam-bath for 30 minutes. Before the whole finally became homogeneous a third liquid phase separated. The solution was chilled, water (200 c.c.) was added, the resultant cloudiness removed by ether-extraction, and the aqueous layer acidified. The precipitated oil was extracted with ether, the ethereal solution dried, and the solvent distilled off. The residual oil was dissolved in light petroleum (b. p. 80—100°) (300 c.c.) and the solution chilled. There were obtained 57 g. (46%) of glittering, waxy flakes, m. p. 99°, after a second recrystallisation from light petroleum (Found: S, 25·65. $C_{10}H_{19}O_2NS_2$ requires S, 25·7%).

By proceeding similarly the esters recorded in Table I were obtained.

2-p-*Nitrobenzylthiothiazol-5-one Hydrobromide.*—This was obtained in quantitative yield by dissolving (V; R'' = ·CH_2·C_6H_4·NO_2) (20 g.) in dioxan (80 c.c.) and adding ether (100 c.c.) and then phosphorus tribromide (12 c.c.). The required *salt* separated as an oil which rapidly crystallised. It was finely ground under ether and air-dried (Found: Br, 22·3. $C_{10}H_8O_3N_2S_2$,HBr requires Br, 22·9%). The m-*nitro*-isomer was similarly obtained (Found: Br, 22·4%). They both had indefinite m. p.s.

2-Alkylthio-4-1'-ethoxyethylidenethiazol-5-ones and 2-alkylthio-4-1'-ethoxypropylidenethiazol-5-ones were obtained by heating the *N*-dithiocarbalkoxyglycine (15—20 g.), acetic anhydride (75 c.c.), and ethyl orthoacetate or ethyl orthopropionate (30 c.c.) for 30 minutes in an oil-bath at 130°. Removal of the solvents under reduced pressure gave crude oils which were used directly in dye condensations.

2-n-*Dodecylthio-5-hydroxy-4-phenylazothiazole* (IV; R = ·S·$C_{12}H_{25}$).—To a solution of *N*-dithiocarbo-*n*-dodecyloxyglycine (3·2 g.) in dioxan (10 c.c.) and ether (30 c.c.) was added phosphorus tribromide (2 c.c.), and the whole was refluxed for 3 minutes. The solution was chilled and the required 2-*n*-dodecylthiothiazol-5-one hydrobromide precipitated as an oil by the addition of light petroleum (b. p. 40—60°; 100 c.c.). The oil was washed with ether by decantation and dissolved in ethanol (20 c.c.), and diazoaminobenzene (2 g.) was added. The solution was heated on the steam-bath (*ca.* 1 minute) until effervescence commenced, the flask removed from the bath, and, after being chilled overnight, the *dye* was collected. It (1·4 g.) formed glossy golden plates, m. p. 83°, from light petroleum (b. p. 60—80°) (Found: N, 10·15. $C_{21}H_{31}ON_3S_2$ requires N, 10·4%).

TABLE I.

R'' in (V).	Appearance.	M. p.	Solvent.*	Formula.	Found, S, %.	Reqd., S, %.
n-*Hexyl*	Soft, glistening plates	95°	Ligroin	$C_9H_{17}O_2NS_2$	27·3	27·2
n-*Octyl*	Glossy, waxy plates	100	Light petroleum	$C_{11}H_{21}O_2NS_2$	23·95	24·35
n-*Decyl*	Glittering plates	100	Benzene–light petroleum	$C_{13}H_{25}O_2NS_2$	22·5	22·1
n-*Dodecyl*	Glossy plates	111	Ligroin	$C_{15}H_{29}O_2NS_2$	20·3	20·05
3-*Phenylpropyl*	Waxy plates	122	Benzene–light petroleum	$C_{12}H_{15}O_2NS_2$	24·5	24·8

* Ligroin had b. p. 100—120°. Light petroleum had b. p. 60—80°.

Ethyl n-*Butyramidodithioformate* (VII; R = Pr^n).—Ethyl dithiocarbamate (ethyl aminodithioformate) (Delépine, *Compt. rend.*, 1902, **135**, 975) (25 g.) and butyric anhydride (36 c.c.) were heated at 120° in an oil-bath for 4 hours and the solvents removed under reduced pressure. The residue crystallised on chilling. It was dissolved in methanol at 25° and water run in until slightly turbid. After being seeded and cooled to 5° the *ester* (29·5 g., 75%) separated as long, yellow needles. A sample formed lemon-yellow needles, m. p. 45°, from aqueous methanol (Found: S, 16·55. $C_7H_{13}ONS_2$ requires S, 16·75%).

N-N'-*Butyrylthiocarbamylglycine* (VIII; R = Pr^n).—The above ester (25 g.) was added to a solution of potassium hydroxide (7·5 g.) and glycine (10 g.) in water (30 c.c.) and alcohol (30 c.c.), and the whole refluxed on the steam-bath for 8 hours. The clear solution was concentrated to half volume, water (50 c.c.) added, and the mixture acidified with concentrated hydrochloric acid. The bulky white precipitate was collected, washed with water, and obtained as cream-coloured needles (16 g., 60%), m. p. 180°, from aqueous ethanol (Found: S, 15·95. $C_7H_{12}O_3N_2S$ requires S, 15·7%).

2-*Acylamidothiazol-5-one Hydrobromides.*—The *NN'*-acylthiocarbamylglycine (10 g.) was dissolved in dioxan (50—75 c.c.) and ether (100—150 c.c.), and phosphorus tribromide (518 c.c.) added. The required hydrobromide separated rapidly in *ca.* 95% yield. After 3 hours the solid was collected, washed with ether, and vacuum-dried. They all formed colourless powders which fumed in moist air and gradually decomposed. 2-*Acetamidothiazol-5-one hydrobromide* has m. p. 195° (decomp.) (Found: N, 11·9; Br, 32·9; S, 13·7. $C_5H_6O_2N_2S$,HBr requires N, 11·7; Br, 33·45; S, 13·4%). 2-*Butyramidothiazol-5-one hydrobromide* has m. p. 220° (decomp.) (Found: Br, 29·5. $C_7H_{10}O_2N_2$,HBr requires Br, 30·0%). 2-*Benzamidothiazol-5-one hydrobromide* has m. p. 190° (decomp.) (Found: Br, 24·7. $C_{10}H_8O_2N_2S$,HBr requires Br, 26·6%).

2-*Butyramido-5-hydroxy-4-phenylazothiazole* (IV; R = $NHPr^n$).—2-Butyramidothiazol-5-one hydrobromide (1 g.), diazoaminobenzene (1·35 g.), and ethanol (10 c.c.) were warmed together on the steam-bath until effervescence occurred (1—2 minutes). When the mixture was then set aside the *dye* crystallised and formed golden-orange crystals (0·3 g.), m. p. 251°, from ethanol (Found: N, 19·4. $C_{12}H_{14}O_2N_4S$ requires N, 19·8%).

N-*Thiocarbalkoxyglycines* (XIV).—The potassium alkoxydithioformates (xanthates) were obtained by the method of de la Provostarge and Desains (*Compt. rend.*, 1942, **215**, 593) by dissolving the required alcohol (1 mol.) in carbon disulphide (100—250 c.c.), adding finely powdered potassium hydroxide (1 mol.), and shaking the mixture for 1—2 hours. After chilling, the crude filtered salts were washed with ether and air-dried. They were converted into the esters (ethyl alkoxydithioformates) by addition of ethyl bromide (1 mol.) to a suspension of them (1 mol.) in ethanol and warming if necessary to start the reaction. The thick meal of potassium bromide was dissolved in water, the oily ester extracted with ether and dried, and the ether removed (cf. Salomon, *J. pr. Chem.*, 1872, **6**, 445). The crude oils were used directly in the next step.

The following illustrates the general procedure for the final step. N-*Thioncarbethoxyglycine* (XIV; R = Et). Ethyl ethoxydithioformate (75 g., 0·5 mol.) in alcohol (50 c.c.) was added to a solution of

potassium hydroxide (28 g., 0·5 mol.) and glycine (37·5 g., 0·5 mol.) in water (50 c.c.), and the whole refluxed on the steam-bath for 18 hours, the ethanethiol being allowed to distil off. Water (50 c.c.) was added, and the solution clarified by ether-extraction, concentrated to half volume, and acidified with cold concentrated hydrochloric acid (50 c.c.). The required *ester* (55·5 g., 68%) separated and formed glassy needles, m. p. 101°, from water (Found: C, 37·0; H, 5·0; N, 8·2; S, 19·65. $C_5H_9O_3NS$ requires C, 36·8; H, 5·5; N, 8·6; S, 19·9%).

The esters recorded in Table II were obtained in a similar manner.

2-*Alkoxythiazol-5-ones*.—*N*-Thioncarbalkoxyglycine (10 g.) and acetic anhydride (50 c.c.) were heated for 30 minutes in an oil-bath at 130°, and the solvents removed under reduced pressure. The residual oils were used directly in dye formation. *E.g.*, *N*-thioncarbethoxyglycine (10 g.) and acetic anhydride (50 c.c.) gave an oil which on distillation gave a colourless oil, b. p. 57°/4 mm. (62°/5 mm.), which became light brown on storage (Found: N, 7·65; S, 18·6. $C_5H_7O_2NS$ requires N, 9·65; S, 22·1%). It gave the same dyes as the crude reaction mixture and appears to be the required 2-*ethoxythiazol-5-one* contaminated with acetic anhydride.

TABLE II.

R in (XIV).	Appearance.	M. p.	Solvent.*	Formula.	Found, S, %.	Reqd., S, %.
iso*Propyl*	Long, flat needles	129°	Water	$C_6H_{11}O_3NS$	18·1	18·1
n-*Butyl*	Glossy needles	70—71	,,	$C_7H_{13}O_3NS$	16·95	16·75
n-*Amyl*	Needles	49—50	Light petroleum	$C_8H_{15}O_3NS$	15·75	15·6
tert.-*Amyl* ...	Fine threads	52—54	,,	,,	15·75	,,
n-*Hexyl*	Small needles	62	,,	$C_9H_{17}O_3NS$	6·25 (N)	6·4 (N)
n-*Heptyl*	,,	66	,,	$C_{10}H_{19}O_3NS$	6·15 (N)	6·0 (N)
n-*Octyl*	Fine needles	72	,,	$C_{11}H_{21}O_3NS$	5·8 (N)	5·65 (N)
n-*Decyl*	Glistening plates	63	,,	$C_{13}H_{25}O_3NS$	11·55	11·65
n-*Dodecyl*	Fine needles	67	,,	$C_{15}H_{29}O_3NS$	4·85 (N)	4·6 (N)
n-*Tetradecyl* ...	,,	79	,,	$C_{17}H_{33}O_3NS$	9·5	9·65
n-*Hexadecyl* ...	,,	77	,,	$C_{19}H_{37}O_3NS$	4·05 (N)	3·9 (N)
3-*Phenylpropyl*	Asbestos-like threads	88	Benzene–light petroleum	$C_{12}H_{15}O_3NS$	12·5	12·65

* Light petroleum had b. p. 60—80°.

4-*Ethoxymethylene*-2-*alkoxythiazol-5-ones*.—The *N*-thiocarbalkoxyglycine (0·01 mol.), acetic anhydride (10 c.c.), and ethyl orthoformate (3·5 c.c.) were heated in an oil-bath at 135—140° for 30 minutes, the alcohol being allowed to distil off. Removal of the solvents under reduced pressure left an oil which usually crystallised on chilling. The crude products were used directly in dye formation. The following were characterised:

2-n-*Decyloxy*-4-*ethoxymethylenethiazol*-5-*one*, pale yellow needles, m. p. 50°, from ethanol (Found: N, 4·4. $C_{16}H_{27}O_3NS$ requires N, 4·45%); 2-n-*dodecyloxy*-4-*ethoxymethylenethiazol*-5-*one*, pale yellow needles, m. p. 58°, from ethanol (Found: N, 4·1. $C_{18}H_{31}O_3NS$ requires N, 4·1%); 4-*ethoxymethylene*-2-n-*tetradecyloxythiazol*-5-*one*, soft, pale yellow needles, m. p. 64°, from ethanol (Found: C, 65·1; H, 9·25; N, 3·5; S, 8·65. $C_{20}H_{35}O_3NS$ requires C, 65·0; H, 9·5; N, 3·8; S, 8·7%).

N-(NN-*diethylthiocarbamyl*)*glycine* (XIX; R = R′ = Et).—Potassium hydroxide (6·24 g.) was dissolved in water (20 c.c.), *N*-dithiocarbethoxyglycine (20 g.) and diethylamine (11·8 c.c.) were added, and the whole was refluxed for 15 hours. After cooling, the solution was extracted with ether, and the aqueous layer cautiously acidified with concentrated hydrochloric acid. After chilling and scratching, crystallisation set in. The solid (11·0 g., 52%) after air-drying formed small, buff-coloured crystals, m. p. 105°, from benzene (Found: N, 14·4; S, 16·8. $C_7H_{14}O_2N_2S$ requires N, 14·7; S, 16·85%).

N-(N-*Methyl*-N-*phenylthiocarbamyl*)*glycine* (XIX; R = Ph, R′ = Et).—Potassium hydroxide (3·12 g.) and *N*-dithiocarbethoxyglycine (10 g.) were dissolved in water (16 c.c.) and ethanol (32 c.c.), and after the addition of *N*-ethylaniline (6·8 g.) the whole was refluxed 24 hours on the steam-bath. Water (50 c.c.) was added and the mixture extracted with ether. The aqueous layer was acidified with concentrated hydrochloric acid and the *amide* collected after chilling. It (3·05 g., 21%) formed a buff-coloured crystalline powder, m. p. 138°, from water (Found: N, 11·8. $C_{11}H_{14}O_2N_2S$ requires N, 12·0%).

1-N′-*Carboxymethylthiocarbamylpiperidine* (XXI).—Potassium hydroxide (18·72 g.) and *N*-dithiocarbethoxyglycine (60 g.) were dissolved in water (250 c.c.), to this solution was added piperidine (28·5 g.), and the mixture refluxed for 24 hours. Acidification of the chilled solution gave a bulky precipitate of the *glycine* derivative as a hydrate (18·5 g., 22·6%) which formed colourless needles, m. p. 171°, from water (Found: N, 12·9; S, 14·3. $C_8H_{14}O_2N_2S,H_2O$ requires N, 12·6; S, 14·55%).

4-N′-*Carboxymethylthiocarbamylmorpholine* (XXII).—Obtained similarly from morpholine (29·2 g.), this formed a *hydrate*, colourless needles, m. p. 171° (49·5% yield), from water (Found: N, 12·3; S, 14·2. $C_7H_{12}O_3N_2S,H_2O$ requires N, 12·6; S, 14·4%).

The 2-*tert.*-aminothiazol-5-one hydrobromides were obtained as oils on addition of phosphorus tribromide (1 c.c.) to the above glycines (2 g.) dissolved in dioxan (15 c.c.) and anhydrous ether (45 c.c.). The oils were washed with ether and used directly in the dye condensations.

*Dimethin*mero*cyanines*.¶—The *dyes* recorded in Tables III and IV were prepared by treating, for 5—10 minutes on the steam-bath, an alcoholic solution of triethylamine (1 mol.) and (*a*) the 2-acetanilidovinyl derivative of the required cyclic ammonium salt (1 mol.) with the keto-methylene heterocyclic compound (II) (1 mol.) or (*b*) the reactive methyl derivative of the same ammonium salt (1 mol.) with the 4-ethoxymethylene (or 4-1′-ethoxyethylidene) derivative (III) (1 mol.). When the hydrobromides of the latter were employed two mols. of triethylamine were added.

TABLE III.

Ref. no.	[Heterocyclic nucleus][4-(2-phenyloxazol-5-one)] dimethin*mero*cyanine.	Appearance.	M. p.	S.‡	Formula.	Found, N, %.	Reqd., N, %.
1	[2-(1-Ethylquinoline)] *	Green plates	227°	BL	$C_{22}H_{18}O_2N$	7·85	8·2
2	[2-(3-Ethylbenzoxazole)] *	Red needles	225	BL	$C_{20}H_{16}O_3N_2$	8·35	8·45
3	[2-(3-Ethylbenzothiazole)] *	,,	209 †	BL	$C_{20}H_{16}O_2N_2S$	7·75	8·05
4	[2-(3-Ethylbenzoselenazole)].....	Magenta needles	222	BL	$C_{20}H_{16}O_2N_2Se$	6·8	7·1
5	[2-(1 : 3 : 3-Trimethylindolenine)]	Red needles	198	BL	$C_{22}H_{20}O_2N_2$	7·5	8·15
6	[4-(1-Ethylquinoline)]	Green needles	212	BL	$C_{22}H_{18}O_2N_2$	7·85	8·2
7	[2-(3-Methylthiazoline)] *	Brick-red crystals	212	M	$C_{15}H_{14}O_2N_2S$	9·9	9·8
8	[2-(3-Ethyl-4-methylthiazole)] ...	Steel-grey crystals	209	BL	$C_{17}H_{16}O_2N_2S$	9·05	9·0
9	[2-(3-Methylnaphtho-1′ : 2′-4 : 5-oxazole)]	Red needles	288	PW	$C_{23}H_{16}O_3N_2$	7·2	7·6
10	[2-(3-Ethylnaphtho-2′ : 1′-4 : 5-oxazole)]	,,	250	B	$C_{24}H_{18}O_3N_2$	7·35	7·35
11	[2-(3-Ethylnaphtho-1′ : 2′-4 : 5-thiazole)]	Purple needles	206	B	$C_{24}H_{18}O_2N_2S$	7·0	7·05
12	[2-(3-Ethylnaphtho-2′ : 1′-4 : 5-thiazole)]	,,	260	PW	,,	7·0	7·05
13	[2-(1-Ethyl-7 : 8-benzoquinoline)]	Green needles	139	BL	$C_{26}H_{20}O_2N,C_6H_6$	6·0	5·95
14	[2-(3-Ethyl-4-*p*-methoxyphenylthiazole)]	Red needles	180	B	$C_{23}H_{20}O_3N_2S$	6·8	6·95

* Obtained by Keyes and Brooker (*loc. cit.*). † Cook *et al.*, *loc. cit.*, give m. p. 210°.
‡ Solvent: B = benzene; C = chloroform; E = ethanol; L = light petroleum (b. p. 40—60°); M = methanol; P = pyridine; W = water.

TABLE IV.

Ref. no.	[α-(Heterocyclic nucleus][β-4(2-phenyloxazol-5-one)]-β-methyldimethin*mero*cyanine.	Appearance.	M. p.	S.*	Formula.	Found, N, %.	Reqd., N, %.
15	[α-2-(1-Ethylquinoline)]	Flat, green needles	198°	BL	$C_{23}H_{20}O_2N_2$	7·55	7·85
16	[α-2-(3-Methylthiazoline)]	Brick-red crystals	210	BL	$C_{16}H_{16}O_2N_2S$	9·1	9·35
17	[α-2-(3-Ethylbenzoxazole)]	Orange needles	209	BL	$C_{21}H_{18}O_3N_2$	7·7	8·1
18	[α-2-(3-Ethylbenzothiazole)].....	Red needles	237	B	$C_{21}H_{18}O_2N_2S$	7·9	7·75
19	[α-2-(3-Ethylbenzoselenazole)]	Violet needles	228	B	$C_{21}H_{18}O_2N_2Se$	6·95	6·85
20	[α-2-(3-Ethyl-4-methylthiazole)] ...	Purple needles	232	B	$C_{18}H_{18}O_2N_2S$	8·9	8·6

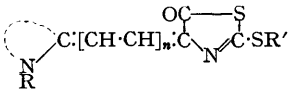
* See footnote, table III.

*Dimethin*mero*cyanines* (cf. Table V) containing the 2-alkylthiothiazol-5-one nuclei were obtained similarly. *mero*Cyanines were also obtained by the standard procedure of treating the thiazolone (II) with the 2-methylthio-derivative of the cyclic ammonium salt in alcoholic triethylamine. *Tetramethin*mero*cyanines* (Table V) were obtained similarly by using the 4-acetanilidobuta-1 : 3-dienyl derivatives of the cyclic ammonium salt.

[α-2-(3-*Ethylbenzoxazole*)][β-4-(2-*n-decylthiothiazol*-5-*one*)]-β-*methyldimethin*mero*cyanine*.—*N*-Dithiocarbo-*n*-decyloxyglycine (1·45 g.), acetic anhydride (15 c.c.), and ethyl orthoacetate (6 c.c.) were heated

¶ In the naming of the dyes the ketonic nucleus is placed in the second bracket irrespective of the alphabetical order of the two nuclei. The nucleus in the first bracket, which is actually a dihydro-derivative of the heterocyclic nucleus, is simplified in all cases. Thus 3-ethylbenzothiazoline is called 3-ethylbenzothiazole, 3-ethylthiazolidine is called 3-ethylthiazoline, etc., as the termination *mero*cyanine indicates the structure. Hamer and Winton (*J.*, 1949, 1126) use both forms. The first dye in Table III is thus [2-(1-ethylquinoline)][4-(2-phenyloxazol-5-one)]dimethin*mero*cyanine.

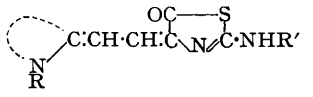
TABLE V.



Ref. no.	Heterocyclic group.	R′.	Appearance.	M. p.	S.‡	Formula.	Found, N, %.	Reqd., N, %.
	[*Heterocyclic group*][4-(2-*alkylthiothiazol*-5-*one*)]*dimethin*mero*cyanine*.							
21	[2-(3-Ethylbenzoxazole)]	H	Yellow prisms	232°	B	$C_{14}H_{12}O_2N_2S_2$	9·1	9·2
22	[2-(3-Ethylbenzothiazole)]	,,	Brown crystals	236	B	$C_{14}H_{12}ON_2S_3$	8·7	8·75
23	[2-(1-Ethylquinoline)]	,,	Black powder	232	B	$C_{16}H_{14}ON_2S_2$	8·65	8·65
24	[2-(3-Ethylbenzoxazole)]	Et	Flat, steel blue needles	156	E	$C_{16}H_{16}O_2N_2S_2$	8·4	8·45
25	[2-(3-Ethylbenzothiazole)] *	,,	Blue-grey prisms	173	B	$C_{16}H_{16}ON_2S_3$	8·2	8·05
26	[2-(3-Ethylbenzoselenazole)]	,,	,,	184	B	$C_{16}H_{16}ON_2S_2Se$	7·05	7·1
27	[2-(3-Methylthiazoline)]	,,	Maroon needles	139	E	$C_{11}H_{14}ON_2S_3$	9·6	9·8
28	[2-(3-Ethylthiazoline)]	,,	Yellow plates	121	E	$C_{12}H_{16}ON_2S_3$	10·75 †	10·65 †
29	[2-(3-Ethyl-4-methylthiazole)]	,,	Green prisms	154	E	$C_{13}H_{16}ON_2S_3$	9·1	9·0
30	[2-(4-*p*-Methoxyphenyl-3-ethylthiazole)]	,,	Maroon needles	182	B	$C_{19}H_{19}O_2N_2S_3$	6·75	6·95
31	[2-(3-Ethylnaphtho-1′ : 2′-4 : 5-thiazole)]	,,	,,	172	B	$C_{20}H_{18}ON_2S_3$	7·1	7·05
32	[2-(1-Ethylquinoline)]	,,	Green needles	163	BE	$C_{18}H_{18}ON_2S_2$	8·4	8·2
33	[4-(1-Ethylquinoline)]	,,	Blue plates	143	E	,,	8·1	8·2
34	[2-(1 : 3 : 3-Trimethylindolenine)]	,,	Red needles	137	BE	$C_{18}H_{20}ON_2S_2$	8·1	8·15
35	[2-(3-Ethylbenzoxazole)]	CH_2Ph	Orange needles	193	E	$C_{20}H_{18}O_2N_2S_2$	7·05	7·1
36	[2-(3-Ethylbenzothiazole)] *	,,	Red needles	179	E	$C_{21}H_{18}ON_2S_3$	6·4	6·85
37	[2-(3-Ethylbenzoselenazole)]	,,	Violet needles	165	E	$C_{21}H_{18}ON_2S_2Se$	5·95	6·1
38	[2-(3-Ethylnaphtho-1′ : 2′-4 : 5-thiazole)]	,,	Purple needles	215	BE	$C_{25}H_{20}ON_2S_2$	5·9	6·0
39	[2-(3-Methylthiazoline)]	,,	Red-green prisms	171	BE	$C_{16}H_{16}ON_2S_3$	7·95	8·05
40	[2-(1-Ethylquinoline)]	,,	Green needles	207	E	$C_{23}H_{20}ON_2S_2$	6·55	6·95
41	[4-(1-Ethylquinoline)]	,,	Blue needles	162	E	$C_{23}H_{20}ON_2S_2$	6·75	6·95
42	[2-(1-Ethylpyridine)]	,,	Purple needles	152	E	$C_{19}H_{18}ON_2S_2$	7·8	7·9
43	[4-(1-Methylpyridine)]	,,	Green crystals	172	E	$C_{18}H_{16}ON_2S_2$	7·9	8·25
44	[2-(3-Methylthiazoline)]	$CH_2{\cdot}C_6H_4{\cdot}NO_2$-*p*	Bronze plates	202	PE	$C_{16}H_{15}O_3N_3S_3$	10·45	10·7
45	[2-(3-Ethylbenzoxazole)]	,,	Purple needles	201	PE	$C_{21}H_{17}O_4N_3S_2$	9·2	9·6
46	[2-(3-Methylthiazoline)]	$CH_2{\cdot}C_6H_4{\cdot}NO_2$-*m*	Steel-blue plates	187	PE	$C_{16}H_{15}O_3N_3S_3$	10·7	10·7
47	[2-(3-Ethylbenzothiazole)]	,,	Green needles	178	PE	$C_{21}H_{17}O_3N_3S_3$	9·4	9·25
48	[2-(3-Ethylbenzoxazole)]	,,	Red crystals	192	PE	$C_{21}H_{17}O_4N_3S_2$	9·4	9·6
49	[2-(3-Ethylbenzoxazole)]	C_6H_{13}-*n*	Red-brown platelets	148	E	$C_{20}H_{24}O_2N_2S_2$	16·6 †	16·5 †
50	,,	C_7H_{15}-*n*	Rust-red crystals	133	E	$C_{21}H_{26}O_2N_2S_2$	15·4 †	15·9 †
51	[2-(3-Ethylbenzoselenazole)]	,,	Glassy, violet needles	112	E	$C_{21}H_{26}ON_2S_2Se$	6·1	6·05
52	[2-(3-Methylthiazoline)]	C_8H_{17}-*n*	Purple needles	81	E	$C_{17}H_{26}ON_2S_3$	26·3 †	25·95 †
53	[2-(3-Ethylthiazoline)]	,,	Orange crystals	86	E	$C_{18}H_{28}ON_2S_3$	25·25 †	25·0 †
54	[2-(3-Ethylbenzoxazole)]	,,	Glossy orange crystals	130	E	$C_{22}H_{28}O_2N_2S_2$	6·75	6·75
55	[2-(3-Ethylbenzothiazole)]	,,	Red needles	81	BM	$C_{22}H_{28}ON_2S_3$	22·2 †	22·2 †
56	[2-(3-Ethyl-5-chlorobenzothiazole)]	,,	Purple needles	156	B	$C_{22}H_{27}ON_2Cl$	20·3·†	20·6 †
57	[2-(3-Ethylbenzoselenazole)]	,,	Violet needles	88	BM	$C_{22}H_{28}ON_2S_2Se$	6·05	5·85
58	[2-(3-Ethylbenzoxazole)]	$C_{10}H_{21}$-*n*	Orange powder	106	E	$C_{24}H_{32}O_2N_2S_2$	5·95	6·2
59	,,	$C_{12}H_{25}$-*n*	Rust powder	103	M	$C_{26}H_{36}O_2N_2S_2$	13·55	13·55
60	,,	$[CH_2]_3{\cdot}Ph$	Red prisms	170	E	$C_{23}H_{22}O_2N_2S_2$	15·05 †	15·2 †
	[*Heterocyclic group*][4-(2-*alkylthiothiazol*-5-*one*)]mero*cyanine* (n = 0).							
61	[2-(1-Methylquinoline)]	CH_2Ph	Dark-green crystals	144	BL	$C_{20}H_{16}ON_2S_2$	7·75	7·7
62	[2-(3-Methylbenzothiazole)]	,,	Yellow needles	193	BL	$C_{18}H_{14}ON_2S_3$	7·45	7·55
	[*Heterocyclic group*][4-(2-*alkylthiothiazol*-5-*one*)]*tetramethin*mero*cyanine* (n = 2).							
63	[2-(3-Ethylbenzothiazole)]	Et	Blue crystals	179	E	$C_{18}H_{18}ON_2S_3$	25·8 †	25·65 †

* See also Cook *et al.* (*loc. cit.*). † Sulphur (not nitrogen). ‡ See footnote to Table III.

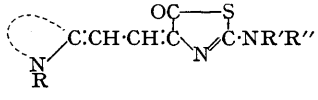
TABLE VI.



Ref. no.	[(Heterocyclic group)][4-(2-acylamidothiazol-5-one)]dimethin-*mero*cyanine.	R′.	Appearance.	M. p.	S‡.	Formula.	Found, N, %.	Reqd., N, %.
64	[2-(1-Ethylquinoline)]	COMe	Green needles	253°	B	$C_{18}H_{17}O_2N_3S$	12·35	12·4
65	[4-(1-Ethylquinoline)]	,,	Green powder	226	E	,,	12·1	12·4
66	[2-(3-Ethylbenzoxazole)]	,,	Red needles	264	C	$C_{16}H_{15}O_3N_3S$	12·8	12·75
67	[2-(3-Ethylbenzothiazole)]	,,	Green-brown needles	228	B	$C_{16}H_{15}O_2N_3S_2$	12·3	12·15
68	[2-(3-Ethylthiazoline)]	,,	Orange crystals	252	B	$C_{12}H_{15}O_2N_3S_2$	14·05	14·15
69	[2-(3-Ethylbenzoselenazole)]	,,	Green crystals	239	C	$C_{16}H_{15}O_2N_3SSe$	10·7	10·7
70	[2-(3-Ethylbenzoxazole)]	$COPr^n$	Brick-red needles	212	E	$C_{18}H_{19}O_3N_3S$	12·1	11·75
71	[2-(3-Methylthiazoline)]	,,	Orange prisms	229	M	$C_{13}H_{17}O_2N_3S$	13·4	13·5
72	[2-(3-Ethylbenzoxazole)]	COPh	Brick-red needles	262	E	$C_{21}H_{17}O_3N_3S$	10·6	10·75
73	[2-(3-Methylthiazoline)]	,,	Orange needles	242	E	$C_{16}H_{15}O_2N_3S$	11·9	12·2

‡ See footnote to Table III.

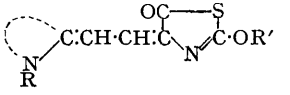
TABLE VIII.



Ref. no.	[(Heterocyclic group)][4-(2-*tert.*-aminothiazol-5-one)]dimethin-*mero*cyanine.	NR′R″.	Appearance.	M. p.	S.‡	Formula.	Found, N, %.	Reqd., N, %.
102	[2-(1-Ethylquinoline)]	NEt_2	Green needles	158°	E	$C_{20}H_{23}ON_3S$	11·2	11·7
103	[4-(1-Ethylquinoline)]	,,	Green crystals, golden reflex	163	E	,,	11·6	11·7
104	[2-(3-Ethylbenzoxazole)]	,,	Brick-red needles	163	E	$C_{18}H_{21}O_2N_3S$	12·3	12·2
105	[2-(3-Ethylbenzothiazole)]	,,	Maroon plates	156	E	$C_{18}H_{21}ON_3S_2$	9·2	9·3
106	[2-(3-Ethylbenzoselenazole)]	,,	Orange-red crystals	153	E	$C_{18}H_{21}ON_3SSe$	10·1	10·3
107	[2-(3-Ethyl-naphtho-1′ : 2′-4 : 5-thiazole)]	,,	Maroon needles	167	E	$C_{22}H_{23}ON_3S_2$	9·8	10·2
108	[2-(3-Ethyl-4-methylthiazole)]	,,	Green needles	158	E	$C_{15}H_{21}ON_3S_2$	13·0	13·0
109	[2-(3-Ethylthiazoline)]	,,	Orange prisms	118	EW	$C_{14}H_{21}ON_3S_2,H_2O$	12·8	12·9
110	[2-(1 : 3 : 3-Trimethylindolenine)]	,,	Red plates, golden reflex	167	E	$C_{20}H_{25}ON_3S$	11·7	11·8
111	[2-(3-Ethylbenzoxazole)]	NPhEt	Orange prisms	183	E	$C_{22}H_{21}O_2N_3S$	10·6	10·7
112	[2-(3-Ethylbenzothiazole)]	,,	Brick-red plates	178	E	$C_{22}H_{21}ON_3S_2$	10·2	10·3
113	[2-(3-Ethylbenzoxazole)]	$N<[CH_2]_5$	Brick-red prisms	192	E	$C_{19}H_{21}O_2N_3S$	12·1	11·8
114	[2-(3-Ethylbenzothiazole)]	,,	Maroon plates	155	E	$C_{19}H_{21}ON_3S_2$	11·5	11·35
115	[2-(3-Ethylbenzoxazole)]	$N<([CH_2]_2)_2O$	Orange powder	218	E	$C_{18}H_{19}O_3N_3S$	11·6	11·7

‡ See footnote to Table III.

TABLE VII.



Ref. no.	[(Heterocyclic group)][4-(2-alkoxythiazol-5-one)]dimethin*mero*cyanine.	R′.	Appearance.	M. p.	S.‡	Formula.	Found, N, %.	Reqd., N, %.
74	[2-(3-Methylthiazoline)]	Et	Brown needles	209°	B	$C_{11}H_{14}O_2N_2S_2$	10·3 23·65 *	10·35 23·7 *
75	[2-(3-Ethylthiazoline)]	,,	Orange needles	136	E	$C_{12}H_{16}O_2N_2S_2$	9·8	9·85
76	[2-(1 : 3 : 3-Trimethylindolenine)]	,,	Glossy, red plates	170	M	$C_{18}H_{20}N_2S$	8·5	8·55
77	[2-(1-Ethylquinoline)]	,,	Blue needles	145	M	$C_{18}H_{18}O_2N_2S$	8·4	8·1
78	[4-(1-Ethylquinoline)]	,,	Grey-green crystals	183	M	,,	8·2	8·1
79	[2-(3-Ethylbenzoxazole)]	,,	Golden plates or hard prisms	192	E	$C_{16}H_{16}O_3N_2S$	8·2	8·35
80	[2-(3-Ethylbenzothiazole)]	,,	Violet needles	188	E	$C_{16}H_{16}O_2N_2S$	7·6	7·95
81	[2-(3-Ethylbenzoselenazole)]	,,	Garnet needles	192	B	$C_{16}H_{16}O_2N_2SSe$	7·05	7·05
82	[2-(3-Ethylnaphtho-1′ : 2′-4 : 5-thiazole)]	,,	Purple needles	202	B	$C_{20}H_{18}O_2N_2S_2$	7·6	7·35
83	[2-(3-Ethylnaphtho-1′ : 2′-4 : 5-oxazole)]	,,	Orange needles	248	E	$C_{20}H_{18}O_3N_2S$	7·6	7·65
84	[2-(3-Ethyl-4-methylthiazole)]	,,	Garnet plates	173	E	$C_{13}H_{16}O_2N_2S_2$	9·2	9·45
85	[2-(3-Ethylbenzoxazole)]	Pr^i	Orange needles	184	E	$C_{17}H_{18}O_3N_2S$	8·35	8·5
86	[2-(3-Methylthiazoline)]	,,	Flat, brown needles, blue reflex	180	E	$C_{12}H_{16}O_2N_2S_2$	9·75	10·0
87	[2-(3-Ethylbenzothiazole)]	,,	Red needles	163	E	$C_{17}H_{18}O_2N_2S_2$	8·15	8·1
88	[2-(3-Ethylbenzoxazole)]	Bu^n	Orange needles	150	M	$C_{18}H_{20}O_3N_2S$	8·4	8·15
89	[2-(3-Methylthiazoline)]	,,	Flat, brown needles, blue reflex	172	E	$C_{13}H_{18}O_2N_2S$	9·35	9·4
90	[2-(3-Methylthiazoline)]	*n*-C_5H_{11}	Flat, brown needles, blue reflex	128	M	$C_{14}H_{20}O_2N_2S_2$	9·0	9·0
91	,, ...	*tert.*-C_5H_{11}	Flat, red-brown platelets	136—138	E	$C_{14}H_{20}O_2N_2S_2$	9·35	9·0
92	,, ...	*n*-C_6H_{13}	Yellow powder	117	E	$C_{15}H_{22}O_2N_2S_2$	8·5	8·6
93	,, ...	*n*-C_7H_{15}	Orange cryst.	115	E	$C_{16}H_{24}O_2N_2S_2$	8·45	8·25
94	[4-(1-Ethylquinoline)]	,,	Black plates	111	E	$C_{23}H_{28}O_2N_2S$	6·75	7·05
95	[2-(3-Methylthiazoline)]	*n*-C_8H_{17}	Flat, yellow needles	114—116	M	$C_{17}H_{26}O_2N_2S_2$	8·1	7·9
96	[2-(3-Ethylbenzoselenazole)]	,,	Red needles	138	E	$C_{22}H_{28}O_2N_2SSe$	6·2	6·05
97	[2-(3-Methylthiazoline)]	*n*-$C_{10}H_{21}$	Orange powder	115	E	$C_{19}H_{30}O_2N_2S_2$	7·3	7·35
98	,, ...	*n*-$C_{12}H_{25}$	Yellow powder	111	E	$C_{21}H_{34}O_2N_2S_2$	7·05	6·85
99	,, ...	*n*-$C_{14}H_{29}$	Glistening, yellow cryst.	117	E	$C_{23}H_{38}O_2N_2S_2$	6·35	6·4
100	,, ...	*n*-$C_{16}H_{33}$	Gold yellow crystals	106—107	E	$C_{25}H_{42}O_2N_2S_2$	5·7	6·0
101	,, ...	$[CH_2]_3$·Ph	Flat, brown needles	159	E	$C_{18}H_{20}O_2N_2S_2$	7·85	7·8

* Sulphur (not nitrogen).

‡ See footnote to Table III.

together in an oil-bath at 120° for 30 minutes. The solvents were removed under reduced pressure, 2-methylbenzoxazole ethiodide (1·45 g.), ethanol (10 c.c.), and triethylamine (1 c.c.) were added, and the whole was heated for 5 minutes on the steam-bath. The solvent was boiled off and the residue scratched to start crystallisation. The triethylamine hydriodide was removed with a little cold methanol, and the *dye* was then obtained as soft, orange needles, m. p. 68°, from ethanol (Found : N, 5·95. $C_{25}H_{34}O_2N_2S_2$ requires N, 6·1%). The *β-ethyl* homologue was similarly obtained by using orthopropionate and formed soft, orange needles, m. p. 96°, from ethanol (Found : N, 6·25. $C_{26}H_{36}O_2N_2S_2$ requires N, 5·95%).

[α-2-(3-*Ethylnaphtho*-1′ : 2′-4 : 5-*thiazole*)][*β*-4-(2-*ethylthiothiazol*-5-*one*)]-*β*-*methyldimethin*mero*cyanine* was similarly obtained, formed violet needles, m. p. 209°, from benzene (Found : N, 6·8. $C_{21}H_{20}ON_2S_3$ requires N, 6·8%), and had an absorption max. at 540 mμ. in methanol.

Absorption Data.—These are recorded below.

Ref. no.	$\lambda_{max.}$	Ref. no.	$\lambda_{max.}$	Ref. no.	$\lambda_{max.}$	Ref. no.	$\lambda_{max.}$	Ref. no.	$\lambda_{max.}$
1	538 (567i)	24	500 (474i)	47	530 (505i)	70	489 (472i)	93	444
2	492	25	527 (500i)	48	492 (475i)	71	476 (464)	94	568
3	522 (493i)	26	528 (505i)	49	494 (463i)	72	498 (478i)	95	444
4	525 (495i)	27	463 (448)	50	491 (465i)	73	486 (468)	96	500
5	492 (465i)	28	470	51	532 (510i)	74	445	97	445
6	620 (580)	29	528 (502i)	52	478 (463)	75	452	98	444
7	474 (450)	30	530 (505i)	53	479 (464)	76	473	99	445
8	530 (502i)	31	548 (515i)	54	489 (465i)	77	530 (500i)	100	444
9	506	32	546	55	529 (498i)	78	568 (607)	101	445
10	506	33	591 (620i)	56	528 (498i)	79	460	102	560
11	529	34	500 (490)	57	531 (500)	80	499	103	588
12	539 (506i)	35	490 (476i)	58	492 (472i)	81	505	104	480
13	531 (505)	36	530 (508i)	59	490 (476i)	82	541	105	519
14	531 (505)	37	531 (508i)	60	492 (470i)	83	485	106	517
15	566	38	545 (520i)	61	485	84	518	107	560
16	475 (455)	39	472 (462)	62	400	85	467	108	542
17	490 (462i)	40	549	63	640 (596i)	86	446	109	469
18	515 (495i)	41	593 (620i)	64	555 (600)	87	494	110	481
19	518 (492i)	42	510	65	593 (630)	88	469	111	482
20	514 (484i)	43	533	66	488 (462i)	89	450	112	518
21	493	44	478 (460)	67	528 (500i)	90	440	113	480
22	522	45	493 (470i)	68	480 (464)	91	443	114	519
23	551 (582i)	46	478 (465)	69	528 (500i)	92	444	115	479

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