Some Reactions of 5-Oxothiazolinium mero*Cyanine Dyes.*

By R. A. Jeffreys.

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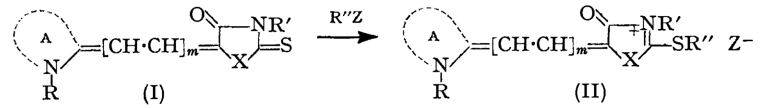
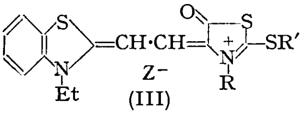
Several reactions, in basic media, of 5-oxothiazolinium *mero*cyanines, of which (III; R and R′ = alkyl) is typical, are described. When a substance of type (III) is condensed with primary amines a complex sequence of reactions takes place, and open-chain derivatives of α-amino(thiolcrotonic acid) (VI; VII*a*, *b*), the expected 2-iminothiazolid-5-one dyes (VIII), or 1 : 3-substituted-2-thiohydantoin dyes (IX), or combinations of these, are isolated. The 2-iminothiazolid-5-one dyes isomerize to 2-thiohydantoins in basic media. When a compound of type (III) is refluxed with alcoholic triethylamine, a number of decomposition products are formed, but only the thiazolid-2 : 5-dione *mero*cyanine was isolated. Formation of open-chain dyes (VI) explains the low yields of trinuclear dyes obtained from (III) and heterocyclic intermediates.

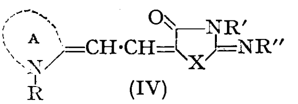
It is well known that *mero*cyanine dyes (I; X = S or NR) derived from rhodanine or from 1 : 3-substituted 2-thiohydantoin are quaternized by fusion with alkyl esters to form cationic dyes (II) (Kendall, B.P. 487,051; Fry and Kendall, B.P. 489,335; Brooker, U.S.P. 2,454,629). It is also established that 5-oxothiazolinium isomers of (II; X = S), *e.g.*, (III), are readily prepared from alkyl esters and *mero*cyanines derived from 2-alkylthiothiazol-5-one or 3-alkyl-2-thiothiazolid-5-one (Knott and Jeffreys, *J.*, 1952, 4762); further, these monocyclic compounds are assumed to be intermediates in the preparation of complex trinuclear dyes by Doyle, Lawrence, and Kendall (B.P. 622,775). The quaternary salts possess a reactive substituent at $C_{(2)}$ in the oxo-heterocyclic ring: they are much more soluble in polar solvents than the parent dyes, and decompose slowly in solution.



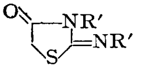
(I) (II)



(III)



(IV)

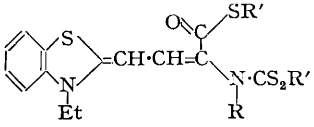


(V)

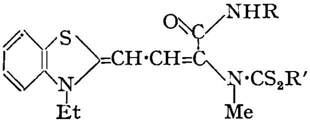
For comparison with 5-oxothiazolinium *mero*cyanines (III), the corresponding dyes containing a tetrahydro-4-oxoglyoxalinium (as in II; X = NR) or a 4-oxothiazolinium (as in II; X = S) ring system were condensed with primary amines. The products, as claimed by Kendall (*loc. cit.*) and Brooker (*loc. cit.*), were closely related to their parent dyes (I), the 2-thio-group being replaced by a 2-alkyl(or 2-aryl)imino-group (as in IV; X = NR or S). The structures of the tetrahydroglyoxaline dyes follow from their analysis, and those of the thiazolid-4-one dyes were confirmed by alternative syntheses from 2-2′-acetanilidovinyl compounds and 2-iminothiazolid-4-ones (V; R′ = Et or Ph). One molar equivalent of alkanethiol was evolved during these reactions.

The compound formed in one reaction was the salt of an iminoglyoxaline dye, probably because of the strong nucleophilic character of the guanidine grouping. Basifying the dye solution caused a hypsochromic shift of the absorption maximum of 24 mμ, by permitting amide-type resonance in the oxo-heterocyclic ring again, with increased energetic asymmetry of the dye.

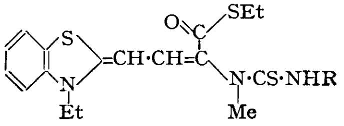
Several types of dyes were produced when 5-oxothiazolinium dyes including (III), reacted with amines, and the evolution of alkanethiol was much less than one molar equivalent. In a typical reaction of (III; R = Et, R′ = Me) with ethylamine the products had absorption maxima at 463 and 515 mμ respectively. The former corresponded, by analysis, to the α-amino(thiolcrotonic ester) derivative (VI; R = Et, R′ = Me). This structure was confirmed by preparation of the analogous dye (VI; R = Me, R′ = Et) from a 5-oxothiazolinium quaternary salt and triethylamine in ethanethiol. Formation of these compounds accounted for the small yield of alkanethiol, for this is used in fission of the ring. The empirical formula of the second dye was that of (VIII or IX; R = R′ = Et). Its identity with the product from the reaction between 2-2′-acetanilidovinylbenzothiazole ethiodide and 1 : 3-diethyl-2-thiohydantoin proved it to be (IX; R = R′ = Et).



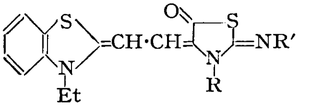
(VI)



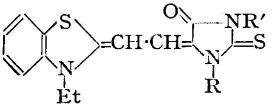
(VII*a*)



(VII*b*)



(VIII)



(IX)

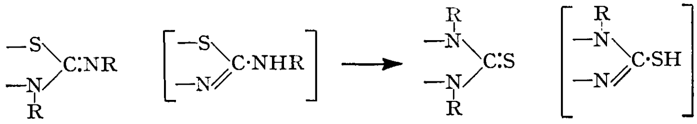
Reaction of dye (III; R = Me, R′ = Et) with methylamine provided two dyes. One was a 2-thiohydantoin dimethin*mero*cyanine (IX; R = R′ = Me), the structure being confirmed by an alternative synthesis from 1 : 3-dimethyl-2-thiohydantoin (Cook and Cox, *J.*, 1949, 2343). The absorption maximum (462 mμ) of the second was sufficiently close to that of (VI) to imply an open-chain structure. In alcoholic solution this dye readily cyclized, particularly in the presence of triethylamine, to the thiohydantoin (IX; R = R′ = Me). Its analysis indicated the structure (VII*a*; R = Me, R′ = Et) or (VII*b*; R = Me). It is known, however, that whereas thiohydantoic esters are cyclized in acid, *N*-ethoxycarbonyl derivatives of α-amino-acid amides are cyclized easily in alkaline solution and are hydrolysed by acids (Ware, *Chem. Reviews*, 1950, **46**, 412, 420). The dye was therefore assigned structure (VII*a*); it was formed by initial attack of the amine on (III), ring scission occurring between the $C_{(5)}$ and the S atom. No reaction occurred between (VI) and amines.

Similarly, 5-oxothiazolinium dyes with other —*M* nuclei in place of the benzothiazole system reacted with primary amines to form dyes analogous to (VI) and (IX), although in several experiments only one *mero*cyanine was isolated.

In two instances the expected 2-iminothiazolid-5-one *mero*cyanines were obtained. When the 5-oxothiazolinium quaternary salt (III) reacted with aniline, the product was the 2-anilo-dye (VIII; R = Me, R′ = Ph). Likewise, an ethylenebisiminothiazolid-5-one *mero*cyanine was obtained from ethylenediamine and a thiazoline analogue of (III). Heating these dyes with sodium carbonate in aqueous pyridine caused rearrangement to the thiohydantoin isomers. Under these conditions, the formation of an intermediate similar to (VII*a*) was impossible. It is probable that the iminothiazolid-5-one dyes were isolated because of their insolubility, precipitation occurring before rearrangement could take place.

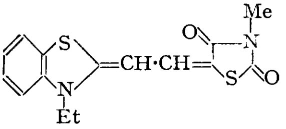
A general mechanism for the reaction can now be postulated. A base having removed the dye (III) anion, the amine replaces the –SR group attached to the thiazolidone ring, providing a 2-imino-dye. This, if sufficiently insoluble, crystallizes out; otherwise it rearranges to a 2-thiohydantoin dye. The other dyes isolated (VI; VII*a*; VII*b*) are produced by a ring scission between $C_{(5)}$ and S before or after the iminothiazolidone dye is formed.

There are various known cases in which the fragment (X*a* or *b*) of a heterocyclic ring rearranges rapidly to the isomeric fragment (XI*a* or *b*) under mild alkaline conditions (Busch and Limpach, *Ber.*, 1911, **44**, 560; Heilbron, *J.*, 1949, 2100; Cook and Heilbron, *Rec. Trav. chim.*, 1950, **69**, 361; Cavallito, Martini, and Nachod, *J. Amer. Chem. Soc.*, 1951, **73**, 2544) without the isolation of an intermediate. Cook and his co-workers (*J.*, 1948, 1060; 1949, 2367; 1950, 1893, 1898, 1947) have shown that, together with other products, 2-thiohydantoins are formed when amines react with 2-alkylthiothiazol-5-ones.


(X*a*) (X*b*) (XI*a*) (XI*b*)

Reaction between (III) and *cyclo*hexylamine in the presence of triethylamine, provided a yellow dye, having $\lambda_{max.}$ 426 mμ, whose empirical formula corresponded to the structure (VII*a*; $R = C_6H_{11}$, $R' = Et$) or (VII*b*; $R = C_6H_{11}$). Unlike the α-aminocrotonamide derivative previously isolated, this compound was not cyclized in neutral, acid, or basic media, and was assigned structure (VII*b*). The compression in this compound may account for the hypsochromic shift of $\lambda_{max.}$ compared with that of (VII*a*; $R = Me$, $R' = Et$). There is, however, no significant reduction of the molecular extinction coefficient.

Since (III) reacted with ethanethiol in the presence of a base, a similar reaction was attempted with ethanol. Sytnik, Levkoev, Deichmeister, and Zhilina (*J. Gen. Chem., U.S.S.R.*, 1952, **22**, 1228) have shown that the 4-oxothiazolinium dyes (II; $X = S$) decompose in aqueous alcohol to thiazolid-2 : 4-dione *mero*cyanines such as (XII), although Van Dormael (*Bull. Soc. chim. Belg.*, 1949, **58**, 403) claimed that open chain α-mercapto-carboxyamides (XIII) were formed. The 5-oxo-isomer formed a number of products, the only isolatable one being the thiazolid-2 : 5-dione *mero*cyanine (XIV). A previous example of a dye with this $+M$ heterocycle was described by Aubert, Knott, and Jeffreys (*J.*, 1951, 2195).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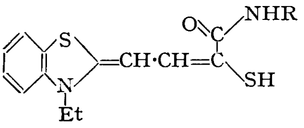
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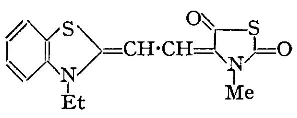

(XIV)

5-Oxothiazolinium salts may be condensed, in basic media, with quaternary salts of heterocyclic bases possessing a reactive methyl group, or with oxomethylene compounds, to give complex trinuclear dyes (Knott and Jeffreys, *loc. cit.*; Doyle *et al.*, *loc. cit.*). In many of these reactions it was observed that, after the solution had cooled, and the main dye product had crystallized out, the mother-liquor was strongly yellow. Concentration of this solution provided a syrup from which was isolated the dye (VI). The formation of this dye, from (III) and ethanethiol evolved in the reaction, explains the somewhat low yields of complex dyes.

EXPERIMENTAL

Absorption max. are recorded for methanol solutions unless otherwise stated. Light petroleum had b. p. 60—80°.

3-n-*Heptyl*-1-*methyl*-2-*thiohydantoin*.—Methylaminoacetonitrile (5·0 g.) in ether (10 c.c.) was added to cooled, stirred *n*-heptyl *iso*thiocyanate (10·1 g.) in ether (10 c.c.) under nitrogen, according to the procedure of Cook and Cox (*loc. cit.*). After 1 hr., the oil which had formed was separated from the ethereal layer and refluxed for 1 hr. with 2N-hydrochloric acid (100 c.c.). The resulting *thiohydantoin* was extracted, dried, and distilled (10 g.); it had b. p. 190°/2 mm. (Found: N, 12·3. $C_{11}H_{20}ON_2S$ requires N, 12·3).

Similar reactions gave 3-*ethyl*-1-*methyl*-2-*thiohydantoin*, needles [from ligroin (b. p. 60—80°)], m. p. 67° (Found: N, 17·7. $C_6H_{10}ON_2S$ requires N, 17·7%), 1 : 3-*diethyl*-2-*thiohydantoin*, needles (from ligroin), m. p. 68° (Found: N, 16·2. $C_7H_{12}ON_2S$ requires N, 16·3%), 3-cyclo*hexyl*-1-*methyl*-2-*thiohydantoin*, leaflets (from *iso*propanol), m. p. 156° (Found: N, 13·2.

$C_{10}H_{16}ON_2S$ requires N, 13·2%), and *ethylenebis*-3-(1-*methyl*-2-*thiohydantoin*), needles (from pyridine–ethanol), m. p. 201° (Found : N, 19·5; S, 22·5. $C_{10}H_{14}O_2N_4S_2$ requires N, 19·6; S, 22·4%) [prepared from ethylene di*iso*thiocyanate (Yakubovich and Klimova, *J. Gen. Chem., U.S.S.R.*, 1939, **9**, 1777)].

*Intermediate Dimethin*mero*cyanines*.—These were prepared by standard methods from the 2-2′-acetanilidovinyl heterocyclic quaternary salt and oxomethylene compound, with triethylamine to remove the acid liberated. Unless otherwise stated, the *dyes* (see Tables 1 and 2) formed needles on recrystallization.

4-(3-*Ethylbenzothiazolin*-2-*ylidene-ethylidene*)-2-*ethylthio*-3-*methyl*-5-*oxothiazolinium Methyl Sulphate* (III; R = Me, R′ = Et, Z = $MeSO_4$).—4-(3-Ethylbenzothiazolin-2-ylidene-ethylidene)-2-ethylthiothiazol-5-one (Aubert, Knott, and Williams, *J.*, 1951, 2192; Cook, Harris, and Shaw, *J.*, 1949, 1435) (1·74 g., 1 mol.) and methyl sulphate (0·7 g., 1·1 mol.) were fused together at 130° for 30 min. The *product*, which solidified on cooling, crystallized from methanol–ether as brick-red needles (1·9 g.), m. p. 174° (decomp.), $\lambda_{max.}$ 536 mμ (Found : N, 5·9; S, 26·9. $C_{18}H_{22}O_5N_2S_4$ requires N, 5·9; S, 27·0%).

Other quaternized dimethin*mero*cyanines (II, and analogues of III) were obtained by fusing the appropriate dimethin*mero*cyanine (1 mol.) with an alkyl ester (1—1·1 mols.) at 120—140° for periods up to 2 hr. or until maximum water solubility was achieved (Kendall *et al.*, *loc. cit.*; Brooker, *loc. cit.*; Knott and Jeffreys, *loc. cit.*). The quaternary salts were not always purified.

2-*Anilo*-5-(3-*ethylbenzoxazolin*-2-*ylidene-ethylidene*)*tetrahydro*-1-*methyl*-4-*oxo*-3-*phenylglyoxaline* (IV; ring A = 3-ethyl-2-benzoxazoline; X = NMe, R′ = R″ = Ph).—5-(3-Ethylbenzoxazolin-2-ylidene-ethylidene)-1-methyl-3-phenyl-2-thiohydantoin (Table 1, dye 1) (0·94 g.) and methyl toluene-*p*-sulphonate (0·47 g.) were fused together at 140° for 2 hr. To the cooled glass were added aniline (0·26 g.), triethylamine (0·35 c.c.), and ethanol (6 c.c.). The solution was refluxed for 10 min., and then cooled. The *dye* was filtered off, washed with a little ethanol, and recrystallized from benzene–light petroleum as dark blue prisms (0·7 g.), m. p. 191°, $\lambda_{max.}$ 430 mμ (Found : N, 12·9. $C_{27}H_{24}O_2N_4$ requires N, 12·85%).

TABLE 1. 5-(3-*Ethyl*-A-2-*ylidene-ethylidene*)-1-*methyl*-3-R′-2-*thiohydantoins* (I; *m* = 1, X = NMe), *prepared from 2-2′-acetanilidovinyl heterocyclic quaternary salts and 2-thiohydantoins.*

No.	Heterocycle A	R′	Appearance	M. p.	$\lambda_{max.}$ (mμ; MeOH)	Formula	Found (%) N	Found (%) S	Reqd. (%) N	Reqd. (%) S
1	Benzoxazoline	Ph	Orange [a]	252°	490	$C_{21}H_{19}O_2N_3S$	11·1	8·6	11·15	8·5
2	Benzothiazoline	Ph	Maroon [a]	275	519	$C_{21}H_{19}ON_3S_2$	10·7	—	10·7	—
3	Benzoxazoline	Me	Orange-red [a]	256	480	$C_{16}H_{17}O_2N_3S$	13·4	—	13·3	—
4	Benzothiazoline	Me	Maroon [a]	235	518	$C_{16}H_{17}ON_3S_2$	12·7	19·2	12·7	19·3
5	Thiazolidine [c]	n-C_7H_{15}	Orange [b]	173	469	$C_{17}H_{27}ON_3S_2$	11·8	—	11·9	—
6	Benzoxazoline	n-C_7H_{15}	Orange [b]	164	480	$C_{22}H_{29}O_2N_3S$	10·6	—	10·5	—
7	Benzothiazoline	n-C_7H_{15}	Red [b]	165	518	$C_{22}H_{29}ON_3S_2$	10·1	—	10·1	—
8	Benzothiazoline [d]	Et	Magenta prisms [e]	197	515	$C_{18}H_{21}ON_3S_2$	11·7	18·0	11·7	17·8
9	Benzothiazoline	Et	Magenta leaflets [e]	214	518	$C_{17}H_{19}ON_3S_2$ [f]	12·1	18·5	12·2	18·5
10	Benzothiazoline	*cyclo*-C_6H_{11}	Red leaflets [g]	208	517	$C_{21}H_{25}ON_3S_2$	10·5	16·1	10·5	16·0
11	Bisbenzothiazoline	$-CH_2\cdot CH_2-$	Red leaflets [h]	305	524 [j]	$C_{32}H_{32}O_2N_6S_4$	12·8	19·5	12·7	19·4
12	Bisthiazolidine	$-CH_2\cdot CH_2-$	Orange-brown [i]	>360	472 [j]	$C_{24}H_{32}O_2N_6S_4$	14·7	22·7	14·9	22·7

[a] From pyridine–methanol. [b] From ethanol. [c] 3-Methyl analogue. [d] X = NEt. [e] From benzene–light petroleum. [f] Found : C, 59·3; H, 5·5. $C_{17}H_{19}ON_3S_2$ requires C, 59·2; H, 5·5%. [g] From benzene. [h] From pyridine. [i] From nitrobenzene. [j] In pyridine.

5-(3-*Ethylbenzothiazolin*-2-*ylidene-ethylidene*)*tetrahydro*-1-*methyl*-2-*methylimino*-4-*oxo*-3-*phenylglyoxaline* (IV; ring A = 3-ethyl-2-benzothiazoline, X = NMe, R′ = Ph, R″ = Me).—Obtained from 5-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-1-methyl-3-phenyl-2-thiohydantoin (Table 1, dye 2) (1·96 g.) and methyl toluene-*p*-sulphonate (0·93 g.) by fusion together for 2 hr. at 140°, followed by 10 minutes' refluxing with methylamine (0·46 c.c. of 33% alcoholic solution), triethylamine (0·7 c.c.), and ethanol (10 c.c.), the *dye* recrystallized from pyridine–methanol as rust-coloured needles (1·1 g.), m. p. 190°, $\lambda_{max.}$ 506 mμ (Found : C, 67·6; H, 5·6; N, 14·4; S, 8·3. $C_{22}H_{22}ON_4S$ requires C, 67·7; H, 5·6; N, 14·4; S, 8·2%).

*5-(3-Ethylbenzoxazolin-2-ylidene-ethylidene)dihydro-1 : 3-dimethyl-2-methylamino-4-oxoglyoxalinium Toluene-*p*-sulphonate.*—Obtained from 5-(3-ethylbenzoxazolin-2-ylidene-ethylidene)-1 : 3-dimethyl-2-thiohydantoin (Table 1, dye 3) (1·57 g.) and methyl toluene-*p*-sulphonate (0·93 g.) by fusion together for 90 min. at 140°, followed by 10 minutes' refluxing with methylamine (0·46 c.c. of 33% alcoholic solution), triethylamine (0·7 c.c.), and ethanol (10 c.c.), the *dye* (1·8 g.) formed water-soluble, mustard-coloured leaflets, m. p. 211°, from ethanol–ether, $\lambda_{max.}$ 537 mμ (Found : N, 11·8; S, 6·7. $C_{24}H_{28}O_5N_4S$ requires N, 11·6; S, 6·6%). On treatment of it with aqueous sodium carbonate, the free base ($\lambda_{max.}$ 433 mμ) was obtained, which was not purified owing to its instability.

*Ethyl α-(*N*-Dithioethoxycarbonyl-*N*-methylamino)-γ-(3-ethylbenzoxazolin-2-ylidene)thiolcrotonate* (benzoxazole analogue of VI; R = Me, R′ = Et).—The quaternary salt from 4-(3-ethylbenzoxazolin-2-ylidene-ethylidene)-2-ethylthiothiazol-5-one (3·3 g.) and methyl sulphate (1·9 g.) was refluxed in ethanethiol (30 c.c.) with triethylamine (1·4 c.c.) for 2 hr. The solvent was removed, and a little ethanol added. The *product* (2·7 g.) obtained by chilling the solution recrystallized from ethyl acetate–light petroleum as orange prisms, m. p. 159°, $\lambda_{max.}$ 432 mμ (Found : C, 56·0; H, 6·0; N, 6·85; S, 23·3. $C_{19}H_{24}O_2N_2S_3$ requires C, 55·9; H, 5·9; N, 6·9; S, 23·5%).

This ester was refluxed for periods up to 36 hr. with severally a molar quantity and an excess of methylamine and diethylamine in ethanol, also in the presence of triethylamine and of acetic acid, but no reaction took place.

*Ethyl α-(*N*-Dithioethoxycarbonyl-*N*-methylamino)-γ-(3-ethylbenzothiazolin-2-ylidene)thiolcrotonate* (VI; R = Me, R′ = Et).—4-(3-Ethylbenzothiazolin-2-ylidene-ethylidene)-2-ethylthio-3-methyl-5-oxothiazolinium methyl sulphate (III; R = Me, R′ = Et, Z = $MeSO_4$) (2·37 g.) and triethylamine (0·7 c.c.) in ethanethiol (15 c.c.) were refluxed for 2 hr. After cooling of the solution, the *dye* was filtered off (0·8 g.) and recrystallized from ethyl acetate–light petroleum as maroon prisms, m. p. 142°, $\lambda_{max.}$ 464 mμ (Found : N, 6·5; S, 29·9. $C_{19}H_{24}ON_2S_4$ requires N, 6·6; S, 30·2%). The same dye crystallized when the mother-liquor of preparations of trinuclear *mero*cyanines containing benzothiazole, 3-methylthiazolid-5-one, and thiazolid-4-one nuclei (Knott and Jeffreys, *loc. cit.*) was concentrated and kept for several days, and was purified as before.

Reactions of 5-Oxothiazolinium mero*Cyanines with Primary Amines.*—(i) The product from 3-ethyl-4-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-2-thiothiazolid-5-one (1·2 g.) and methyl toluene-*p*-sulphonate (0·65 g.), with ethylamine (0·45 c.c. of 33% ethanolic solution) and triethylamine (0·5 c.c.) in ethanol (10 c.c.) were refluxed for 15 min. and then chilled. 1 : 3-Diethyl-5-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-2-thiohydantoin, which was filtered off, recrystallized from benzene–light petroleum as maroon leaflets, m. p. 197°. It was identical with dye 8, Table 1. When the mother-liquor was concentrated, *methyl α-(*N*-dithiomethoxycarbonyl-*N*-ethylamino)-γ-(3-ethylbenzothiazolin-2-ylidene)thiolcrotonate* (VI; R = Et, R′ = Me) crystallized, and was purified by repeated recrystallization from ligroin, as red prisms, m. p. 152°, $\lambda_{max.}$ 463 mμ (Found : N, 6·8; S, 31·1. $C_{18}H_{22}ON_2S_4$ requires N, 6·8; S, 31·3%).

(ii) 4-(3-Ethylbenzothiazolin-2-ylidene-ethylidene)-2-ethylthio-5-oxo-3-methylthiazolinium methosulphate (III; R = Me, R′ = Et, Z = $MeSO_4$) (4·74 g.), and *cyclo*hexylamine (1·0 g.) with triethylamine (1·4 c.c.) in ethanol (15 c.c.) were refluxed for 10 min. Addition of water to the solution precipitated a dye. This was extracted with ligroin. After several crystallizations from benzene–light petroleum, *ethyl γ-(3-ethylbenzothiazolin-2-ylidene)-α-(3-*cyclo*hexyl-1-methylthioureido)thiolcrotonate* (VII*b*; R = C_6H_{11}) crystallized as a bright yellow powder, m. p. 198°, $\lambda_{max.}$ 426 mμ (ε 5·6 × 10^4) (Found : N, 9·1; S, 21·0. $C_{23}H_{31}ON_3S_3$ requires N, 9·1; S, 20·8%).

(iii) 4-(3-Ethylbenzothiazolin-2-ylidene-ethylidene)-2-ethylthio-3-methyl-5-oxothiazolinium methosulphate (III; R = Me, R′ = Et, Z = $MeSO_4$) (4·74 g.), and methylamine (1·0 c.c. of 33% alcoholic solution), with triethylamine (1·4 c.c.) in ethanol (15 c.c.), were refluxed for 10 min., and then chilled. 1 : 3-Dimethyl-5-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-2-thiohydantoin (Table 1, dye 4) was filtered off and recrystallized from benzene–light petroleum, as blue flakes, m. p. 235° (Found : C, 58·2; H, 5·1; N, 12·6; S, 19·4. Calc. for $C_{16}H_{17}ON_3S_2$: C, 58·0; H, 5·1; N, 12·7; S, 19·3%). The filtrate after concentration, yielded *α-(*N*-dithioethoxycarbonyl-*N*-methylamino)-γ-(3-ethylbenzothiazolin-2-ylidene)-*N*-methylcrotonamide* (VII*a*; R = Me, R′ = Et), which recrystallized from ethyl acetate–light petroleum as orange-brown prisms, m. p. 184° (decomp.) (Found : N, 10·8; S, 24·4. $C_{18}H_{23}ON_3S_3$ requires N, 10·7; S, 24·4%). Immediately after dissolution in methanol, it had $\lambda_{max.}$ 462 mμ (ε 5·8 × 10^4). The solution remained stable in darkness, or if acidified with acetic acid. However, in sunlight, or in the presence of triethylamine, the dye cyclized in 24 hr. with evolution of ethanethiol, forming 5-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-1 : 3-dimethyl-2-thiohydantoin, identified by a mixed m. p. determination with an authentic sample.

2-*Anilo*-4-(3-*ethylbenzothiazolin*-2-*ylidene-ethylidene*)-3-*methylthiazolid*-5-*one* (VIII; R = Me, R′ = Ph).—4-(3-Ethylbenzothiazolin-2-ylidene-ethylidene)-2-ethylthio-3-methyl-5-oxothiazolinium methyl sulphate (III; R = Me, R′ = Et, Z = $MeSO_4$) (2·37 g.) with aniline (0·47 g.) and triethylamine (0·7 c.c.) in ethanol (10 c.c.) were refluxed for 20 min. Whilst the solution was still refluxing the *dye* crystallized. It recrystallized from benzene–light petroleum as steel-blue needles, m. p. 244°, $\lambda_{max.}$ 520 mμ (Found: C, 63·9; H, 4·7; N, 10·6; S, 16·3. $C_{21}H_{19}ON_3S_2$ requires C, 64·2; H, 4·8; N, 10·7; S, 16·3%).

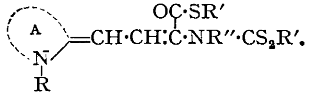
The dye (0·2 g.) in pyridine (10 c.c.) and 2N-sodium carbonate solution (5 c.c.) was heated for 1 hr. on the steam-bath. Adding water (30 c.c.) to the cooled solution precipitated a dye. This recrystallized from pyridine–methanol as maroon needles (0·15 g.), m. p. 275°, identical with 5-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-1-methyl-3-phenyl-2-thiohydantoin (Table 1, dye 2).

TABLE 2. 2-*Substituted* 5-(3-*ethyl*-A-2-*ylidene-ethylidene*)-3-*phenylthiazolid*-4-*ones* (I; *m* = 1, X = S, R′ = Ph).

No.	Heterocycle A	Appearance	M. p.	$\lambda_{max.}$ (mμ; MeOH)	Formula	Found (%) N	Reqd. (%) N
13	Benzoxazoline	Maroon leaflets [b]	259°	490	$C_{20}H_{16}O_2N_2S_2$	7·4	7·4
14	4 : 5-Diphenyloxazoline	Red prisms [a]	249	510	$C_{28}H_{22}O_2N_2S_2$	5·8	5·8
From 2-anilo-3-phenylthiazolid-4-one (IV; X = S, R′ = R″ = Ph)							
15	Benzoxazoline	Orange leaflets [a]	232 [c]	430	$C_{26}H_{21}O_2N_3S$	9·5	9·6
16	4 : 5-Diphenyloxazoline	Red [a]	268	470	$C_{34}H_{27}O_2N_3S$ [d]	7·7	7·8

[a] From benzene–light petroleum. [b] From pyridine–light petroleum. [c] Brooker *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 5326) give m. p. 236—239° (from ethanol). Dyes 15 and 16 were also prepared by quaternization of 13 and 14 with methyl sulphate, followed by treatment with aniline and triethylamine in ethanol. [d] Found: S, 5·9. Reqd.: S = 5·9.

TABLE 3. α-*Amino*(*thiolcrotonates*) *derived from* 5-*oxothiazolinium* mero*cyanines and primary amines*



No.	Heterocycle A	R′	R″	M. p.	$\lambda_{max.}$ (mμ; MeOH)	Formula	Found (%) N	Found (%) S	Required (%) N	Required (%) S
17 [a, c]	3-Ethylthiazolidin-2-ylidene	Me	Et	143°	420	$C_{14}H_{22}ON_2S_4$	—	34·8	—	35·4
18 [a, d]	3-Methylthiazolidin-2-ylidene	Me	*cyclo*-C_6H_{11}	198	412	$C_{17}H_{26}ON_2S_4$	6·9	31·6	7·0	31·8
19 [a, c]	3-Methylthiazolidin-2-ylidene	Et	Et	202	424	$C_{15}H_{24}ON_2S_4$	7·4	—	7·6	—
20 [a, c]	3-Ethylbenzothiazolin-2-ylidene	Me	Me	160	464	$C_{17}H_{20}ON_2S_4$	—	32·3	—	32·4
21 [b, e]	1-Ethyldihydroquinolin-4-ylidene	Me	Me	195	561	$C_{19}H_{22}ON_2S_3$	7·3	—	7·2	—

[a] From ethanol. [b] From benzene–light petroleum. [c] Yellow. [d] Orange prisms. [e] Copper-coloured plates.

TABLE 4. 2-*Thiohydantoin dyes derived from* 5-*oxothiazolinium* mero*cyanines and primary amines* (I; *m* = 1, X = NR″).

No.	Heterocycle A	R′	R″	Appearance	M. p.	$\lambda_{max.}$ (mμ, MeOH)
22	3-Methylthiazolidin-2-ylidene	*n*-C_7H_{15}	Me	Orange [a]	173°	Identical with Dye 5
23	3-Ethylbenzoxazolin-2-ylidene	*n*-C_7H_{15}	Me	Orange [a]	164	Identical with Dye 6
24 [c]	3-Ethylbenzoxazolin-2-ylidene	*n*-$C_{12}H_{25}$	Me	Yellow [a]	108	485
25 [d]	3-Ethylbenzoxazolin-2-ylidene	*n*-$C_{18}H_{37}$	Me	Yellow [a]	128	484
26	3-Ethylbenzothiazolin-2-ylidene	Et	Me	Magenta leaflets [b]	214	Identical with Dye 9
27	3-Ethylbenzothiazolin-2-ylidene	*n*-C_7H_{15}	Me	Red [a]	165	Identical with Dye 7

[a] From ethanol. [b] From benzene–light petroleum. [c] Found: N, 8·9. $C_{27}H_{39}O_2N_3S$ requires N, 9·0%. [d] Found: N, 7·5. $C_{33}H_{51}O_2N_3S$ requires N, 7·6%.

Ethylenebis-2-*imino*-4-(3-*ethylthiazolidin*-2-*ylidene*-*ethylidene*)-3-*methylthiazolid*-5-*one*.—The product obtained by fusing 4-(3-ethylthiazolidin-2-ylidene-ethylidene)-3-methyl-2-thiothiazolid-5-one (1·43 g.) and methyl toluene-*p*-sulphonate (0·93 g.) for ½ hr. at 130° was dissolved in ethanol (10 c.c.). Ethylenediamine (0·15 g.) and triethylamine (0·7 c.c.) were added. After 20 minutes' refluxing the solution was cooled, and the *dye* filtered off and washed with ethanol. It recrystallized from pyridine as orange-red needles, m. p. 244°, $\lambda_{\text{max.}}$ 488 mμ in pyridine (Found : S, 22·7. $C_{24}H_{32}O_2N_6S_4$ requires S, 22·7%). This dye (0·2 g.) in pyridine (20 c.c.) and 2N-sodium carbonate solution (10 c.c.) was heated for 1 hr. on the steam-bath. Water (40 c.c.) was added to the cooled solution, and the product was filtered off and recrystallized from nitrobenzene as orange-brown needles (0·15 g.), m. p. >360°. It was identical with dye 12, Table 1.

4-(3-*Ethylbenzothiazolin*-2-*ylidene-ethylidene*)-3-*methylthiazolid*-2 : 5-*dione* (XIV).—4-(3-Ethylbenzothiazolin-2-ylidene-ethylidene)-2-ethylthio-3-methyl-5-oxothiazolinium methyl sulphate (III; R = Me, R′ = Et, Z = $MeSO_4$) (2·37 g.) with triethylamine (0·7 c.c.) in ethanol (15 c.c.) were refluxed for 15 min., and the solution was chilled and filtered. The *dye*, in poor yield, recrystallized from methanol as blue prisms, m. p. 208°, $\lambda_{\text{max.}}$ 505 mμ (Found : N, 8·8; S, 20·2. $C_{15}H_{14}O_2N_2S_2$ requires N, 8·8; S, 20·1%).

Other Products.—Results of experiments similar to the above are recorded in Tables 3 and 4.

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MESSRS. KODAK LIMITED,
HARROW, MIDDLESEX.

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