787. *Polymethin Dyes from 4 : 5-Disubstituted Thiazoles.*

By Edward B. Knott

It is shown that α-aryloxy- and α-*p*-tolylthio-acetophenones may be α-brominated and condensed with thioacetamide, to give 4-aryl-5-aryloxy-2-methylthiazoles and 4-aryl-2-methyl-5-*p*-tolylthiothiazoles respectively.* These bases as well as a number of 4 : 5-diaryl-2-methylthiazoles have been quaternized and converted into cyanines, carbocyanines, and dimethin*mero*cyanines.

In view of the generally strong photographic desensitizing properties of optical sensitizers derived from 4-phenylthiazole it was interesting to note that the red-sensitive layers of certain German colour-photographic products were sensitized by trinuclear dyes containing the 4 : 5-diphenylthiazole nucleus (B.I.O.S. Final Report No. 1355, Item No. 22; U.S. Office, Bureau of Information, Microfilm P.B. 74,175).

Fig. 1.

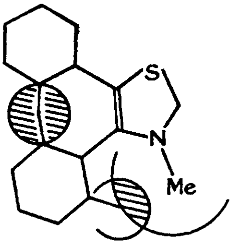


Fig. 2.

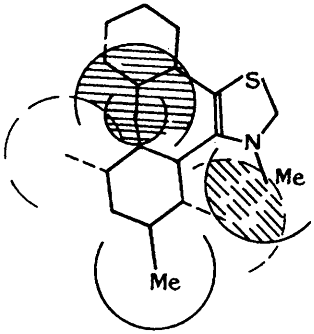
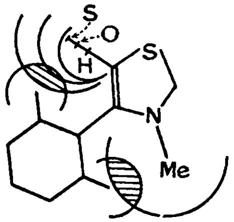


Fig. 3.



A number of cyanines and *mero*cyanines required as intermediates for related complex dyes have now been made from the latter nucleus and the work has been extended to other 4-aryl-5-phenylthiazoles. The requisite intermediates, *i.e.*, 4-aryl-2-methyl-5-phenylthiazoles, were obtained by the normal Hantzsch condensation of substituted α-bromo-α-phenylacetophenones with thioacetamide (cf. Hubacher, *Annalen*, 1890, **259**, 288, for 2-methyl-4 : 5-diphenylthiazole).

Many of these dyes are good photographic sensitizers but their most interesting property is their much higher solubility in organic solvents compared with closely related dyes from 4-arylthiazoles, benzothiazoles, and naphthothiazoles. This property, in view of the higher molecular weight of the diarylthiazole dyes, is noteworthy and is believed to be due to the fact (see Fig. 1) that the aryl groups are non-planar. The weakening of the cohesive forces in the crystal resulting from a looser packing in order to accommodate the non-planar groups would then be expected to increase the solubility. This is also reflected in the lower melting points of the 4 : 5-disubstituted bases and dyes. To test this theory 2-methyl-5-phenyl-4-*p*-xylylthiazole was synthesised and converted into dyes. As Fig. 2 shows the loss of planarity of the xylyl group must be very great and this is reflected in the high solubilities and low melting points of the dyes. The broken lines in Fig. 2 indicate the alternative position of the xylyl group.

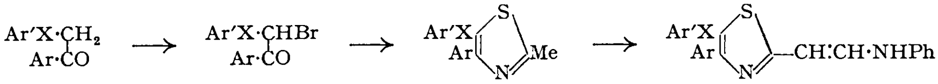
It was then considered that dyes of similarly high solubility might result by replacing one of the aryl groups by other units capable of preventing coplanarity of the remaining aryl group and the rest of the molecule. To this end aryloxy- and arylthio-groups were introduced into the 5-position (Fig. 3). Although the overcrowding here between the 5-substituent and the 2′-hydrogen atom of the 4-phenyl group is much less than in Fig. 1 it

---

* Since this paper was written, U.S.P. 2,500,142 by Wiesehahn, describing similar condensations, has been brought to my attention.

is sufficient to prevent the 4-phenyl group from bending upwards in order to relieve the overcrowding between the *N*-alkyl group and the 6′-hydrogen of the 4-phenyl group.

Aryloxyacetophenones (I; X = O) and arylthioacetophenones (I; X = S) (*e.g.*,



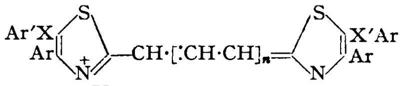
(I) (II) (III) (IV)

Möhlau, *Ber.*, 1882, **15**, 2497; Delisle, *ibid.*, 1889, **22**, 306; Kunckell, *Zentr.*, 1913, II, 153) were brominated smoothly to give well-defined crystalline α-bromo-derivatives (II) which were, for the most part, stable except for the simpler members which decomposed slowly to red solids. They all condensed readily with thioacetamide to give the required 4-aryl-5-aryloxy (or 5-arylthio)-2-methylthiazole (III; X = O or S). This behaviour may be contrasted with that of α-bromo-α-tolylsulphonylacetophenone (II; X = SO_2; Tröger and Müller, *Arch. Pharm.*, 1914, **252**, 51) in which the bromine is not labile to aqueous silver nitrate and which does not give the required thiazole with thioacetamide.

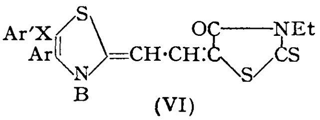
These new thiazoles were quaternized by alkyl toluenesulphonates or sulphates, and the resultant salts condensed with ethyl *iso*formanilide (cf. Knott, *J.*, 1946, 120) to give the required 2-2′-anilinovinyl derivatives (IV). These after acetylation were used to make many of the required dyes. Again the *mero*cyanines were designed as suitable intermediates for complex dyes.

As in the case of the dyes from 4 : 5-diarylthiazole these new dyes were soluble in organic solvents.

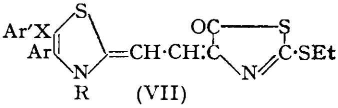
In this paper the formation of cyanines (V; $n = 0$), carbocyanines (V; $n = 1$), and dimethin*mero*cyanines (VI and VII) and a few unsymmetrical cyanines is described.



(V)

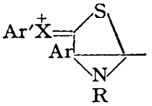


(VI)

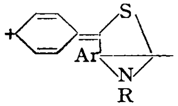


(VII)

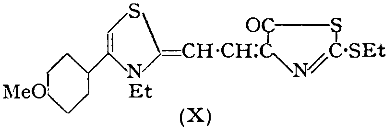
It is of interest that the introduction of substituents into the 4-aryl groups or the replacement of the 4-phenyl by the 4-β-naphthyl group causes little or no effect on the position of the absorption peak (see Experimental section) of any of these dyes. This indicates that the contribution to the dye hybrid by structures in which the positive charge has passed into this group is small. On the other hand the replacement of the 5-phenyl group by the aryloxy- or *p*-tolylthio-group causes a definite hypsochromic shift of 5—10 mμ in both series. In the carbocyanine series the 5-phenoxy-group causes a greater shift (10 mμ) than the 5-*p*-tolylthio-group (5 mμ). The direction of this shift is not unexpected in that, although increased contributions by structures such as (VIII) in which the positive charge passes



(VIII)



(IX)



(X)

beyond the auxochromes would be expected to function bathochromically, the absence of the phenyl groups and such contributing structures as (IX), etc., directly conjugated with $C_{(4)}$—$C_{(5)}$ bond of the thiazole rirg will function hypsochromically. The relatively strong bathochromic effect of the presence of this 5-phenyl group is shown by the fact that the removal of this group to give (X) shifts $\lambda_{max.}$ from 548 to 527 mμ, and from the corresponding 3-ethyl-2-thio-5-thiazolid-4-one dye from 548 to 540 mμ.

EXPERIMENTAL

Analyses are by Drs. Weiler and Strauss, Oxford.

α-Bromo-2 : 5-dimethyl-α-phenylacetophenone.—2 : 5-Dimethyl-α-phenylacetophenone (Wege, *Ber.*, 1891, **24**, 3540; b. p. 153°; 112 g., 0·5 mol.) was dissolved in chloroform (400 c.c.) in a 3-necked 1-l. flask fitted with stirrer, dropping funnel, and condenser, leading to an alkali-trap. A solution of bromine (26 c.c., 0·5 mol.) in chloroform (100 c.c.) was dropped in at room temperature. After completed addition the solvent was removed in an air-stream, and the residual *ketone* which soon solidified was obtained as heavy tablets, m. p. 47°, from light petroleum (b. p. 40—60°) in 79% yield (Found: Br, 26·3. $C_{16}H_{15}OBr$ required Br, 26·4%).

4-p-*Methoxyphenyl-2-methyl-5-phenylthiazole.*—α-Bromo-*p*-methoxy-α-phenylacetophenone (30·1 g., 0·1 mol.) (Meisenheimer and Jochelson, *Annalen*, 1907, **355**, 292), thioacetamide (7·5 g. 0·1 mol.), and methanol (100 c.c.) were warmed on the steam-bath until reaction occurred (*ca.* 1 minute). The methanol boiled, the heating was stopped, and the flask and contents allowed to cool. The required *hydrobromide* (Found: Br, 21·9. $C_{17}H_{16}ONBrS$ requires Br, 22·1%) was precipitated with ether and formed soft needles, m. p. 214° (27·5 g., 77%), from ethanol.

The *base* released with aqueous sodium carbonate formed a thick oil which slowly crystallized. A sample formed thick glassy prisms, m. p. 45°, from light petroleum (b. p. 40—60°) (Found: N, 5·1; S, 11·2. $C_{17}H_{15}ONS$ requires N, 5·0; S, 11·4%).

4-(3 : 4-*Dimethoxyphenyl*)-*2-methyl-5-phenylthiazole.*—α-Bromo-3 : 4-dimethoxy-α-phenylacetophenone (67 g., 0·2 mol.) (Kaufmann and Muller, *Ber.*, 1918, **51**, 129), thioacetamide (15 g., 0·2 mol.), anhydrous sodium carbonate (21·2 g., 0·2 mol.), and ethanol (150 c.c.) were refluxed for 15 minutes. Water (250 c.c.) was added to precipitate the *base* as an oil which rapidly crystallised (47 g., 76%). It formed glassy crystals, m. p. 98°, from methanol (Found: N, 4·6; S, 10·2. $C_{18}H_{17}O_2NS$ requires N, 4·5: S, 10·3%). In one experiment as above, on a 0·01-molar scale, the oil did not crystallize at once. In boiling light petroleum it crystallized and then formed hard aggregates, m. p. 153°, from alcohol (Found: N, 4·4; S, 9·95%).

*2-Methyl-4-phenyl-4-*p-*xylylthiazole.*—α-Bromo-2 : 5-dimethyl-α-phenylacetophenone (111 g.), thioacetamide (33·3 g.), and ethanol (110 c.c.) were brought to the b. p. and allowed to cool. Ether (1 l.) was added, to give 88 g. (66·5%) of the hydrobromide. The *base* (66 g.) formed needles, m. p. 72·5°, from light petroleum (Found: N, 5·2; S, 11·9. $C_{18}H_{17}NS$ requires N, 5·0; S, 11·5%).

α-Aryloxyacetophenones (I; X = O).—Potassium hydroxide (1 mole.) was dissolved in boiling alcohol (750 c.c.). The required phenol (1 mole) was then added and the solution cooled to 30°. The addition of the phenacyl bromide (1 mole) with shaking caused a temperature increase to *ca.* 40—45° and separation of potassium bromide. During 1 hour at room temperature, followed by chilling, the required α-aryloxyacetophenone separated. It was collected, washed with ice-cold alcohol (100 c.c.), then much water to remove potassium bromide. The product was often pure enough for the next step. Otherwise it was recrystallized from ethanol. The *products* are reported in Table 1.

TABLE 1. *α-Aryloxyacetophenones* (I; X = O).

Ar	Ar′	Yield, %	M. p.	Appearance	Formula	Found, %	Req., %
Ph	*p*-C_6H_4Y[a]	50	76°	Flat needles	$C_{22}H_{28}O_2$	C, 81·75 H, 8·7	81·5 8·65
p-MeO·C_6H_4	,,	90	102	Waxy plates	$C_{23}H_{30}O_3$	C, 78·1 H, 8·65	78·0 8·5
Ph	*p*-C_6H_4Ph	65	94	Flakes	$C_{20}H_{16}O_2$	C, 83·5 H, 5·25	83·4 5·55
p-C_6H_4Cl	*p*-C_6H_4Cl	52	132—133	Glossy needles	$C_{14}H_{10}O_2Cl_2$	Cl, 25·3	25·25
p-C_6H_4Br	*p*-C_6H_4Br	63	133—135	Laths	$C_{14}H_{10}O_2Br_2$	Br, 43·15	43·2
3 : 4 : 1-$(MeO)_2C_6H_3$	*p*-EtO·C_6H_4	70	103	Threads	$C_{18}H_{20}O_5$	C, 68·5 H, 5·55	68·3 5·35
Ph	α-$C_{10}H_7$	79	59	Laths	$C_{18}H_{14}O_2$	C, 82·25 H, 5·35	82·5 5·35

[a] Y = ·CMe_2·CH_2·CMe_3.

α-p-*Tolylthioacetophenones* (I; Ar′X = *p*-C_6H_4Me·S)—These *compounds* (see Table 2) were made in the same manner as (I; X = O) (cf. Delisle, *loc. cit.*). In general they separated rapidly as oils from the warm reaction solution and crystallized slowly. They were recrystallized from ethanol or methanol.

TABLE 2. p-*Tolylthioacetophenones* (I; Ar′X = *p*-$C_6H_4Me{\cdot}S$).

Ar	Yield, %	M. p.	Appearance	Formula	Found, %	Required, %
Ph	98·5	40°	Needles	$C_{15}H_{14}OS$	C, 74·3; H, 5·8 S, 13·55	C, 74·45; H, 5·8 S, 13·25
2 : 4 : 1-$C_6H_3Me_2$...	88	56	Flakes	$C_{17}H_{17}OS$	S, 12·2	S, 12·3
β-$C_{10}H_7$	93	63	Flakes	$C_{19}H_{16}OS$	S, 10·95	S, 10·95

α-Bromo-α-aryloxy- (II; X = O) *and α-Bromo-α-*p-*tolylthio-acetophenones*.—The ketone (I; X = O or S) (1 mole) in carbon disulphide or chloroform (1 l.) was treated at 5—60° with bromine (1 mole) in the same solvent (250 c.c.). The bromo-ketone was isolated by the removal of the solvent in an air-stream or by washing with dilute aqueous sodium carbonate, then water, drying, and removing the solvent under reduced pressure. The resultant solids or oils were often unstable and were used directly for thiazole formation. The *products* are listed in Table 3.

TABLE 3.

Ar	Ar′	Reaction temp.	Yield	M. p.	Appearance	Formula	Found, % Br	Req., % Br
a-Bromo-a-aryloxyacetophenones (II; X = O).								
Ph	Ph	5—10°	67·5	72°	Needles [c]	$C_{14}H_{11}O_2Br$	27·3	27·45
Ph	*p*-C_6H_4Y [a]	20	95	—	Oil [d]	$C_{22}H_{27}O_2Br$	18·5	19·85
p-$MeO{\cdot}C_6H_4$	Ph	5	87	80—81	Needles [e]	$C_{15}H_{13}O_3Br$	24·8	24·9
,,	*p*-C_6H_4Y	5	93	—	Oil [d]	$C_{23}H_{29}O_2Br$	18·1	18·45
Ph	*p*-C_6H_4Ph	20	81	indef.	Powder	$C_{20}H_{15}O_2Br$	21·9	22·5
Ver [b]	*p*-$EtO{\cdot}C_6H_4$	35	85	—	Oil	—	—	—
p-C_6H_4Cl ...	*p*-C_6H_4Cl	60	92·5	158	Plates [f, g]	$C_{14}H_9O_2Cl_2Br$	41·45	42·0
p-C_6H_4Br	*p*-C_6H_4Br	55	64	157	Needles [f, g]	$C_{14}H_9O_2Br_3$	53·7	53·5
*a-Bromo-a-*p-*tolylthioacetophenones* (II; X = S).								
Ph	—	10	94	79—81	Needles [f]	$C_{15}H_{13}OBrS$	24·65	24·9
p-Xylyl ...	—	30	73	110	Prisms [c, g]	$C_{17}H_{17}OBrS$	22·7	22·9
β-$C_{10}H_7$ ...	—	5	80	119—121	Flakes [c, g]	$C_{19}H_{15}OBrS$	21·75	21·55 [h]

[a] Y = $\cdot CMe_2{\cdot}CH_2{\cdot}CMe_3$. [b] 3 : 4 : 1-$(MeO)_2C_6H_3$. [c] From light petroleum (b. p. 60—80°). [d] Crude. [e] From light petroleum (b. p. 60—80°). [f] From ethanol. [g] Stable. [h] Found: S, 8·95. Reqd.: S, 8·65%.

4-*Aryl*-5-*aryloxy*-2-*methylthiazoles* (III; X = O).—The bromo-ketone (II; X = O) (1 mole) was dissolved or suspended in ethanol (500 c.c.), and thioacetamide (1·1 mole) added at 30°. There was usually a temperature rise and the mixture was heated, if necessary, to 70°, then allowed to cool. In some cases the required hydrobromide crystallized. In all cases anhydrous ether (2 l.) was added to precipitate all of the hydrobromide. This was collected, made into a slurry in acetone, collected, and washed with acetone. The *base* (see Table 4) was obtained by adding aqueous sodium carbonate to the salt in ethanol. It was usually obtained as a slowly crystallising oil and was then recrystallized from ethanol.

TABLE 4. 4-*Aryl*-5-*aryloxy*-2-*methylthiazoles* (III; X = O).

Ar	Ar′	Yield, %	M. p.	Apearance	Formula	Found, %	Required, %
Ph	Ph	59	63°	Aggreg. [c]	$C_{16}H_{13}ONS$	C, 71·6 H, 4·9 N, 5·5 S, 12·15	C, 71·9 H, 4·85 N, 5·25 S, 12·0
p-$MeO{\cdot}C_6H_4$	Ph	64	90	Needles [c]	$C_{17}H_{15}O_2NS$	N, 5·0 S, 10·6	N, 4·7 S, 10·45
Ph	*p*-C_6H_4Y	87	—	Oil [d]	—	—	—
p-$MeO{\cdot}C_6H_4$	,, (hydrobromide)	34	186—188	Plates	$C_{25}H_{31}O_2NS,HBr$	Br, 16·5	Br, 16·3
,,	*p*-C_6H_4Y [b]	30	65—72	Needles	$C_{25}H_{31}O_2NS$	N, 3·3 S, 7·45	N, 3·4 S, 7·85
Ph	*p*-C_6H_4Ph	25	102—105	Plates	$C_{22}H_{17}ONS$	C, 81·5 H, 4·9 N, 4·35	C, 82·0 H, 5·25 N, 4·35
Ver [a]	*p*-$EtO{\cdot}C_6H_4$	26	71—72	Needles	$C_{20}H_{22}O_4NS$	C, 64·2 H, 5·95 S, 8·5	C, 64·5 H, 5·9 S, 8·6
p-C_6H_4Cl ...	*p*-C_6H_4Cl	33	100—101	Rhombs	$C_{16}H_{11}ONCl_2S$	S, 9·9 Cl, 21·15	S, 9·55 Cl, 21·15

[a] 3 : 4 : 1-$(MeO)_2C_6H_3$. [b] Y = $\cdot CMe_2{\cdot}CH_2{\cdot}CMe_3$. [c] From light petroleum (b. p. 60—80°). [d] Crude.

4-*Aryl*-2-*methyl*-5-p-*tolylthiothiazoles* (III, Ar′X = *p*-$C_6H_4Me{\cdot}S$).—The *compounds* (see Table 5) were obtained as for the above thiazoles except that the reaction was carried out with 1 hour's refluxing before precipitation of the hydrobromides. The bases were recrystallized from light petroleum (b. p. 60—80°).

TABLE 5. 4-*Aryl*-2-*methyl*-5-p-*tolylthiothiazoles* (III; Ar′X = *p*-$C_6H_4Me{\cdot}S$).

Ar	Yield, %	M. p.	Appearance	Formula	Found, % N	Found, % S	Required, % N	Required, % S
Ph	82·5	41—42° (b. p. 200°/ 6 mm.)	Prisms	$C_{17}H_{15}NS_2$	6·65	21·85	4·7	21·55
3 : 4 : 1-$(MeO)_2C_6H_3$ ...	58	59—60	Needles	$C_{19}H_{19}NS_2$	4·5	19·6	4·3	19·7
β-$C_{10}H_7$	57	93—94	Needles	$C_{21}H_{17}NS_2$	4·2	18·4	4·05	18·4

2-2′-*Anilinovinyl*-4 : 5-*diphenylthiazole Ethotoluene*-p-*sulphonate*.—2-Methyl-4 : 5-diphenylthiazole (12·5 g., 0·05 mol.) (Hubacher, *loc. cit.*) and ethyl toluene-*p*-sulphonate (10 g., 0·05 mol.) were fused at 170° for 4 hours. Ethyl*iso*formanilide (8 g., 0·53 mol.) was added and the whole fused for a further 15 minutes. The whole rapidly solidified with evolution of ethanol. It was ground under acetone, and the solid *salt* collected, washed with acetone, and obtained as a yellow powder (18·2 g., 66%). It formed yellow needles, m. p. 233°, from ethanol (Found : N, 5·0; S, 11·4. $C_{32}H_{30}O_3N_2S_2$ requires N, 5·05; S, 11·55%).

2-2′-*Anilinovinyl*-4-p-*methoxyphenyl*-5-*phenylthiazole ethotoluene*-p-*sulphonate*, obtained similarly from 4-*p*-methoxyphenyl-2-methyl-5-phenylthiazole in 84% yield, formed yellow-brown needles, m. p. 250°, from ethanol (Found : N, 5·0; S, 10·9. $C_{33}H_{32}O_4N_2S_2$ requires N, 4·8; S, 10·95%). The *methotoluene*-p-*sulphonate* formed fine, bright yellow needles, m. p. 246° from ethanol (Found : N, 4·85. $C_{32}H_{30}O_4N_2S_2$ requires N, 4·9%).

2-2′-*Anilinovinyl*-5-*phenyl*-4-p-*xylylthiazole Ethiodide*.—2-Methyl-5-phenyl-4-*p*-xylylthiazole (2·74 g., 0·01 mol.) and ethyl sulphate (1·4 c.c., 0·01 mol.) were fused at 150° for 30 minutes. Ethyl*iso*formanilide (1·7 c.c.) was added and fusion continued for a further 30 minutes. The melt was dissolved in ethanol (15 c.c.) and a solution of potassium iodide (2 g.) in water (2 c.c.) added. The *ethiodide* (3·25 g.) separated slowly. It formed violet crystals, m. p. 226°, from ethanol (Found: I, 23·6. $C_{27}H_{27}N_2IS$ requires I, 23·4%).

The *methiodide* (4·3 g.), obtained similarly from the base (2·74 g.) and methyl toluene-*p*-sulphonate (1·9 g.) (30 minutes at 150°), formed light yellow needles, m. p. 247°, from ethanol (Found : I, 24·75. $C_{26}H_{25}N_2IS$ requires I, 24·25%).

2-2′-*Anilinovinyl*-4-(3 : 4-*dimethoxyphenyl*)-5-*phenylthiazole Ethotoluene*-p-*sulphonate*.—Obtained similarly in 83% yield, this *salt* formed fine yellow needles, m. p. 161°, from ethanol (Found : N, 4·6; S, 10·5. $C_{34}H_{34}O_5N_2S_2$ requires N, 4·65; S, 10·6%).

2-2′-*Anilinopropenyl*-4-p-*methoxyphenyl*-5-*phenylthiazole Ethiodide*.—4-*p*-Methoxyphenyl-2-methyl-5-phenylthiazole etho-*p*-toluenesulphonate (19·0 g.) and ethyl*iso*thioacetanilide (8·0 g.) were fused at 175° for 1 hour, by which time the evolution of ethanethiol had ceased. Ethanol (75 c.c.) was added to the red melt, the whole was heated to dissolution, and an excess of saturated aqueous potassium iodide added. The required *iodide* crystallized on the slow addition of ether. It (16·0 g., 68%) formed garnet-red crystals, m. p. 233°, from ethanol (Found : I, 22·9. $C_{27}H_{25}ON_2SI$ requires I, 22·95%).

2-2′-*Anilinovinyl*-4-*aryl*-5-*aryloxy*(*or arylthio*)*thiazolium Salts* (IV).—The above bases (1 mol.) and alkyl ester (1 mol.) were fused at 150—170° until the maximum water solubility of the product was obtained. Ethyl sulphate and methyl toluene-*p*-sulphonate required 90—120 minutes, and ethyl toluene-*p*-sulphonate 5—6 hours. When fusion was completed, ethyl*iso*formanilide (1·1 mols.), was added and the fusion continued at 150° until evolution of ethanol was complete (10—60 minutes). In some cases the melt had then solidified. If not, it was dissolved in ethanol and a solution of potassium iodide (2 mol.) in water added to give the *iodide* which was then crystallized from ethanol. The *salts* prepared are listed in Table 6; all are yellow; most of them form needles.

Unsymmetrical Cyanines.—[3-*Methyl*-2-*benzothiazole*][3-*ethyl*-4-p-*methoxyphenyl*-4-*phenyl*-2-*thiazole*]*methincyanine iodide*. 4-*p*-Methoxyphenyl-2-methyl-5-phenylthiazole ethotoluene-*p*-sulphonate (0·9 g.), 2-methylthiobenzothiazole methotoluene-*p*-sulphonate (0·7 g.), ethanol (5 c.c.), and triethylamine (0·3 c.c.) were refluxed for 30 minutes. Saturated aqueous potassium iodide (0·5 c.c.) was added and the dye *iodide* (0·95 g.) obtained as greenish-yellow needles, m. p. 304°, from methanol (Found : S, 10·9; I, 21·2. $C_{27}H_{25}ON_2IS_2$ requires S, 10·95; I, 21·75%). $\lambda_{max.}$ 425 mμ in methanol.

TABLE 6.

Ar	Ar′	RY	Yield, %	M. p.	Formula	Found, %	Required, %
2-2′-Anilinovinyl-4-aryl-5-aryloxythiazolium salts (IV; X = O).							
Ph	Ph	EtI	32	196°	$C_{25}H_{23}ON_2IS$ [d]	C, 56·0; H, 4·2	C, 57·0; H, 4·35
p-MeO·C_6H_4	,,	,,	38	196	$C_{26}H_{25}O_2N_2IS$	N, 4·9; I, 22·4	N, 5·05; I, 22·85
,,	,,	MeTs [c]	83	202	$C_{32}H_{30}O_5N_2S_2$	N, 4·7; S, 10·7	N, 4·8; S, 10·9
Ph	*p*-C_6H_4Y [b]	EtI	25	176	$C_{33}H_{39}ON_2IS$	I, 19·7	I, 19·9
p-MeO·C_6H_4	,,	MeTs [c]	42	236	$C_{42}H_{45}O_5N_2S_2$	N, 4·05; S, 8·9	N, 3·9; S, 8·9
Ph	*p*-C_6H_4Ph	MeI	72	266	$C_{29}H_{26}ON_2IS$	I, 21·75	I, 22·0
p-C_6H_4Cl	*p*-C_6H_4Cl	EtI	46	247	$C_{25}H_{21}ON_2Cl_2IS$	Hal, 33·5	Hal, 33·3
Ver [a]	*p*-EtO·C_6H_4	EtI	48	185	$C_{29}H_{31}O_4N_2IS$	I, 20·5	I, 20·2
2-2′-Anilinovinyl-4-aryl-5-arylthiothiazolium salts (IV; X = S).							
Ph	*p*-C_6H_4Me	EtI	57	225	$C_{26}H_{25}N_2IS_2$	S, 11·4; I, 22·6	S, 11·5; I, 22·8
,,	,,	MeI	55	243	$C_{25}H_{23}N_2IS_2$	N, 5·2; I, 23·5	N, 5·15; I, 23·4
p-Xylyl	,,	EtI	47	168	$C_{28}H_{29}N_2IS_2$	I, 22·0	I, 21·75
,,	,,	MeI	45	230	$C_{29}H_{27}N_2IS_2$	I, 22·3	I, 22·3
β-$C_{10}H_7$	,,	EtI	54	234	$C_{30}H_{26}N_2IS_2$	S, 10·6	S, 10·6

[a] Veratryl. [b] X = ·CMe_2·CH_2·CMe_3. [c] Ts = *p*-C_6H_4Me·SO_2. [d] Found: N, 5·3; S, 6·0; I, 24·4. Reqd.: N, 5·3; S, 6·0; I, 24·15%.

[1-*Methyl*-2-*quinoline*][3-*ethyl*-4 : 5-*diphenyl*-2-*thiazole*]*methincyanine iodide*, obtained similarly from 2-methyl-4 : 5-diphenylthiazole etho(ethyl sulphate) (1·2 g.), 2-methylthioquinoline methotoluene-*p*-sulphonate (1·0 g.) ethanol (10 c.c.), and triethylamine (0·5 c.c.), formed orange needles, m. p. 271°, from ethanol (Found: N, 5·0; I, 23·1. $C_{28}H_{25}N_2IS$ requires N, 5·1; I, 23·2%). $\lambda_{max.}$ 490 mμ in methanol.

[1-*Methyl*-2-*quinoline*][3-*ethyl*-4-p-*methoxyphenyl*-5-*phenyl*-2-*thiazole*]*methincyanine iodide* formed orange needles, m. p. 267°, from ethanol (Found: S, 5·5; I, 22·1. $C_{29}H_{27}ON_2IS$ requires S, 5·55; I, 22·0%). $\lambda_{max.}$ 490 mμ in methanol.

[1-*Methyl*-2-*quinoline*][3-*ethyl*-5-*phenoxy*-4-*phenyl*-2-*thiazole*]*methincyanine iodide* formed fine, orange threads, m. p. 258°, from ethanol (Found: S, 5·7; I, 22·3. $C_{28}H_{25}ON_2IS$ requires S, 5·7; I, 22·5%). $\lambda_{max.}$ 480 mμ in methanol.

[1-*Methyl*-2-*quinoline*][3-*ethyl*-5-*phenyl*-4-(3 : 4-*dimethoxyphenyl*)-2-*thiazole*]*methincyanine iodide* was obtained as flat, rust-red needles, m. p. 258°, from methanol (Found: I, 20·4. $C_{30}H_{29}O_2N_2IS$ requires I, 20·45%). $\lambda_{max.}$ 490 mμ in methanol.

[1-*Ethyl*-2-*quinoline*][2-*methyl*-4-*phenyl*-5-p-*tolylthio*-2-*thiazole*]*methincyanine iodide* formed flat, glossy, red needles, m. p. 227—228°, from methanol (Found: S, 10·4; I, 20·6. $C_{30}H_{27}N_2IS_2$ requires S, 10·55; I, 20·95%). $\lambda_{max.}$ 485 mμ in methanol.

Carbocyanines.—In all cases these were obtained by acetylating the required 2-2′-anilinovinyl derivative in acetic anhydride (½ hour's reflux), removing the solvent, and treating the resultant oily 2-2′-acetanilidovinyl derivative (1 mol.) with the parent 2-methylthiazolium salt (1 mol.) in presence of alcoholic triethylamine.

Bis-(3-*ethyl*-4 : 5-*diphenyl*-2-*thiazole*)*trimethincyanine iodide* was obtained as matted gold threads, m. p. 180°, from ethanol (Found: S, 9·1; I, 18·1. $C_{37}H_{33}N_2IS_2$ requires S, 9·2; I, 18·25%). $\lambda_{max.}$ 588 mμ in methanol.

Bis-(3-*ethyl*-4-p-*methoxyphenyl*-5-*phenyl*-2-*thiazole*)*trimethincyanine iodide* formed purple threads, m. p. 181°, from methanol (Found: I, 17·1. $C_{39}H_{37}O_2N_2IS_2$ requires I, 16·8%). $\lambda_{max.}$ 590 mμ in methanol.

Bis-[3-*ethyl*-4-p-*methoxyphenyl*-5-*phenyl*-2-*thiazole*]-β-*methyltrimethincyanine iodide* formed green crystals, m. p. 249°, from ethanol (Found: I, 16·4. $C_{40}H_{39}O_2N_2IS_2$ requires I, 16·5%). $\lambda_{max.}$ 561 mμ in methanol.

Bis-(3-*ethyl*-4-(3 : 4-*dimethoxyphenyl*)-5-*phenyl*-2-*thiazole*)*trimethincyanine iodide* was obtained as brilliant green crystals, m. p. 179°, from methanol (Found: S, 7·6; I, 15·4. $C_{41}H_{41}O_4N_2IS_2$ requires S, 7·85; I, 15·6%). $\lambda_{max.}$ 590 mμ in methanol.

Bis-(3-*ethyl*-5-*phenyl*-4-p-*xylyl*-2-*thiazole*)*trimethincyanine perchlorate* formed a mauve crystalline powder, m. p. 225°, from ethanol (Found: N, 3·8; S, 8·7. $C_{41}H_{41}O_4N_2ClS_2$ requires N, 3·85; S, 8·85%). $\lambda_{max.}$ 592 mμ in methanol.

Bis-(4-p-*methoxyphenyl*-3-*methyl*-5-*phenoxy*-2-*thiazole*)*trimethincyanine perchlorate* formed a bronze crystalline powder, m. p. 240°, from methanol (Found: C, 60·5; H, 4·5; S, 8·7. $C_{37}H_{33}O_8N_2ClS_2$ requires C, 60·5; H, 4·5; S, 8·75). $\lambda_{max.}$ 580 mμ in methanol.

Bis-(3-*methyl*-4-*phenyl*-5-p-*tolylthio*-2-*thiazole*)*trimethincyanine iodide* was obtained as flat, bronze needles, m. p. 224°, from ethanol (Found : S, 17·05. $C_{37}H_{33}N_2IS_4$ requires S, 16·85%). $\lambda_{max.}$ 585 mμ in methanol.

Bis-(3-*ethyl*-4-β-*naphthyl*-5-p-*tolylthio*-2-*thiazole*)*trimethincyanine iodide* formed bronze crystals, m. p. 194°, from methanol (Found : S, 14·2; I, 14·3. $C_{47}H_{41}N_2IS_4$ requires S, 14·4; I, 14·3%). $\lambda_{max.}$ 585 mμ in methanol.

[3-*Ethyl*-2-*benzothiazole*][3-*ethyl*-4-β-*naphthyl*-5-p-*tolylthio*-2-*thiazole*]*trimethincyanine perchlorate* formed green prisms, m. p. 205°, from methanol (Found : S, 14·4. $C_{34}H_{31}O_4N_2ClS_3$ requires S, 14·5%) $\lambda_{max.}$ 565 mμ in methanol.

[3-*Ethyl*-2-*benzothiazole*][3-*ethyl*-4-*phenyl*-5-p-*tolylthio*-2-*thiazole*]*trimethincyanine iodide* formed soft, flat, bronze needles, m. p. 195°, from methanol (Found: S, 15·1; I, 19·7. $C_{30}H_{29}N_2IS_3$ requires S, 15·0; I, 19·85%). $\lambda_{max.}$ 560 mμ in methanol.

*Dimethin*mero*cyanines*.—These dyes are derived from 3-ethyl-2-thiothiazolid-4-one (3-ethylrhodanine) (VI) or 2-ethylthiothiazol-5-one (VII). They were obtained by standard procedures through the 2-2′-acetanilidovinyl derivative of the quaternized thiazole and ketomethylene compound or from the 2-methyl derivative of the quaternized thiazole and 4-ethoxymethylene-2-ethylthiothiazol-5-one (cf. Cook, Harris, and Shaw, *J.*, 1949, 1435; Aubert, Knott, and Williams, *J.*, 1951, 2185). Unless otherwise stated, the *dyes* were recrystallized from benzene or benzene–methanol, usually forming needles : see Tables 7 and 8.

TABLE 7. 3-*Ethyl*-5-(*G-thiazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-4-*ones* (VI).

			$\lambda_{max.}$ (mμ)		Found, %		Required, %	
Substituent G	Appearance	M. p.	(MeOH)	Formula	N	S	N	S
3-Ethyl-4 : 5-diphenyl-	Magenta	242°	550	$C_{24}H_{22}ON_2S_3$	6·2	21·2	6·25	21·35
4-*p*-Methoxyphenyl-3-methyl-5-phenyl-	Red	216	552	$C_{24}H_{22}O_2N_2S_3$	—	20·1	—	20·4
3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-	Red	197	548	$C_{25}H_{24}O_2N_2S_3$	—	19·6	—	19·85
4-(3 : 4-Dimethoxyphenyl)-3-ethyl-5-phenyl-	Green	199	554	$C_{26}H_{26}O_3N_2S_3$ [a]	5·5	18·5	5·5	18·8
3-Methyl-5-phenyl-4-*p*-xylyl-	Green	111	552	$C_{25}H_{24}ON_2S_3$	—	20·6	—	20·7
3-Ethyl-5-phenyl-4-*p*-xylyl-	Green-brown	190	554	$C_{26}H_{26}ON_2S_3$	—	20·15	—	20·1
3-Ethyl-5-phenoxy-4-phenyl-	Green	174	544	$C_{24}H_{22}O_2N_2S_3$	5·7	20·3	6·0	20·6
4-*p*-Methoxyphenyl-3-methyl-5-phenoxy-	Green	186	547	$C_{24}H_{22}O_3N_2S_3$	5·85	19·6	5·8	19·9
3-Ethyl-4-*p*-methoxyphenyl-5-phenoxy-	Purple	150	544	$C_{25}H_{24}O_3N_2S_3$	—	19·2	—	19·35
4-*p*-Methoxyphenyl-3-methyl-5-(1 : 1 : 3 : 3-tetramethylbutyl)phenoxy-	Dull red	161	546	$C_{32}H_{38}O_3N_2S_3$ [b]	—	16·3	—	16·15
3-Ethyl-4-phenyl-5-*p*-tolylthio-	Bronze	165	544	$C_{25}H_{24}ON_2S_4$	—	25·6	—	25·8
3-Ethyl-4-β-naphthyl-5-*p*-tolylthio-	Garnet	198	544	$C_{29}H_{26}ON_2S_4$	5·1	23·6	5·15	23·4
3-Ethyl-4-*p*-methoxyphenyl-	Red	225	540	$C_{19}H_{19}O_2N_2S_3$	6·9	23·6	6·95	23·8

[a] Found : C, 61·3; H, 5·05. Reqd. : C, 61·2; H, 5·1%. [b] Found : C, 64·2; H, 6·3. Reqd. : C, 64·7; H, 6·4%.

TABLE 8. 2-*Ethylthio*-4-(*G-thiazolin*-2-*ylidene-ethylidene*)*thiazol*-5-*ones* (VII).

			$\lambda_{max.}$ (mμ)		Found, %		Required, %	
Substituent G	Appearance	M. p.	(MeOH)	Formula	N	S	N	S
3-Ethyl-4 : 5-diphenyl-	Violet	208°	547	$C_{24}H_{22}ON_2S_3$	6·3	21·5	6·25	21·35
3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-	Purple	181	548	$C_{25}H_{24}O_2N_2S_3$	—	19·8	—	20·0
4-(3 : 4-Dimethoxyphenyl)-3-ethyl-5-phenyl-	Red	229	550	$C_{26}H_{26}O_3N_2S_3$	5·7	19·0	5·5	18·8
3-Methyl-5-phenyl-4-*p*-xylyl-	Steel grey-red	108	548	$C_{25}H_{24}ON_2S_3$	5·85	20·5	6·05	20·7
4-*p*-Methoxyphenyl-3-methyl-5-phenoxy-	Red, green reflex	168	543	$C_{24}H_{22}O_3N_2S_3$	5·6	20·1	5·8	19·9
3-Ethyl-4-*p*-methoxyphenyl-5-phenoxy-	Purple	164	542	$C_{25}H_{24}O_3N_2S_3$	5·35	19·3	5·65	19·35
3-Methyl-4-phenyl-5-*p*-tolylthio-	Blue-green	133	544	$C_{24}H_{22}ON_2S$	5·8	26·7	5·8	26·8
3-Methyl-4-β-naphthyl-5-*p*-tolylthio-	Violet	180	544	$C_{28}H_{24}ON_2S_4$	—	24·1	—	24·0
3-Ethyl-4-*p*-methoxyphenyl-(X)	Maroon	182	527	$C_{19}H_{19}O_2N_2S_3$	6·75	23·7	6·95	23·8

3-*Ethyl*-5-(3-*ethyl*-4-p-*methoxyphenyl*-5-*phenylthiazolin*-2-*ylidene*iso*propylidene*)-2-*thiothiazolid*-4-*one*.—2-2′-Anilinopropenyl-4-*p*-methoxyphenyl-5-phenylthiazole ethiodide (4 g.) and acetic anhydride (20 c.c.) were refluxed for 30 minutes and the solvents removed. 3-Ethylrhodanine (1·2 g.), ethanol (10 c.c.), and triethylamine (1·5 c.c.) were added and the whole refluxed for 10 minutes. The dye (1·65 g.) crystallized on chilling and formed violet needles, m. p. 168°, from benzene–light petroleum (Found: N, 5·65; S, 19·5. $C_{26}H_{26}O_2N_2S_3$ requires N, 5·65; S, 19·4%). $\lambda_{max.}$ 535 mμ in methanol.

4-(3-*Ethyl*-4-p-*methoxyphenyl*-5-*phenylthiazolin*-2-*ylidene*iso*propylidene*)-2-*ethylthiothiazol*-5-*one* formed violet needles, m. p. 236°, from benzene–methanol (Found: N, 5·4; S, 19·4. $C_{26}H_{26}O_2N_2S_3$ requires N, 5·65; S, 19·4%). $\lambda_{max.}$ 550 mμ in methanol.

The author thanks Miss M. E. Cole for the preparation of some of the intermediates and Mrs. M. Turner for absorption measurements.

RESEARCH LABORATORIES, KODAK LIMITED,
WEALDSTONE, MIDDX.

[*Received, May 30th*, 1952.]