675. *Oxazole Cyanine and* mero*Cyanine Dyes, and Intermediates. Part II.** *Intermediates Derived from Desylamines* (1 : 2-*Diaryl*-2-*oxoethylamines*).

By R. A. Jeffreys.

N-Alkyl- and *N*-aryl-desylamines (I) react with thiocarbonyl chloride, carbon disulphide, or acetyl chloride to give 4 : 5-diaryl-2-thio-oxazolines (II), 4 : 5-diaryl-2-thiothiazolines (VII), and 4 : 5-diaryl-2-methyloxazolium salts (V) respectively. These intermediates are used in the syntheses of mono- and tri-methincyanine dyes and *mero*cyanine dyes derived from oxazole and thiazole. Many of the dyes with short resonance paths are fluorescent and almost colourless.

Continuing the investigation of oxazole dyes and intermediates as photographically useful compounds, we wished to prepare a series of hitherto unknown monomethin oxazole cyanines (VI; $Y = Z = O$) and of *mero*cyanines (IV) with directly linked nuclei. The reaction between two equivalents of 2-methylazolium salt and pentyl nitrite in acetic anhydride, which provides symmetrical monomethincyanines in the benzoxazole series,[1] failed to give the required dyes in the oxazole series. An alternative synthesis was explored, involving the use of 2-alkylthio-oxazolium salts (III), which are intermediates common

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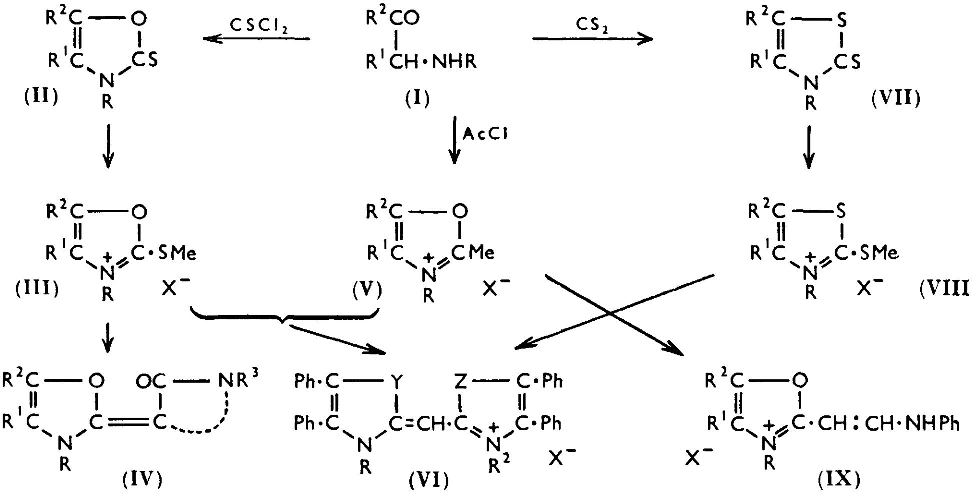
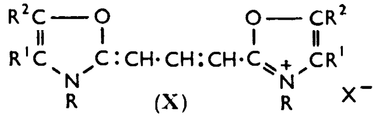
* Oxazole Cyanine and *mero*Cyanine Dyes, and Intermediates, *J.*, 1952, 4823, is regarded as Part I.

[1] Fisher and Hamer, *J.*, 1934, 962.

to the preparation of dyes (IV) and (VI). The starting materials for the preparation of 4 : 5-diaryloxazole dyes, the desylamines (1 : 2-diaryl-2-oxoethylamines) (I), are readily available by the condensation of benzoins with amines in the presence of acid catalysts.[2] McCombie and Parkes[3] showed that *N*-phenyldesylamine with carbonyl chloride gives 3 : 4 : 5-triphenyloxazol-2-one, and we now find that desylamines and thiocarbonyl chloride give 4 : 5-diaryl-2-thio-oxazolines (II) with alkyl or aryl groups in the 3-position. These thiones condense on fusion with alkyl esters to form water-soluble 2-alkylthio-oxazolium salts (III). The intermediates (II) and (III) have recently been described by Gompper,[4] who prepared the 2-thio-oxazolines from oxazol-2-ones and phosphorus pentasulphide. The salts (III) react with 2-methyloxazolium salts (V), to give di-(3 : 4 : 5-substituted 2-oxazole)methincyanines (VI; Y = Z = O), and with ketomethylene heterocyclic compounds to give *mero*cyanines (IV). Both of these groups of dyes absorb strongly in the near-ultraviolet region and are almost colourless. Some are strongly fluorescent, as solids and in solution, especially in ultraviolet light. Compared with analogous cyanines derived from benzoxazole, naphth(1′ : 2′-4 : 5)oxazole, and naphth(2′ : 1′-4 : 5)oxazole, which have absorption maxima in methanol at 370, 400, and 395 mμ respectively, the 4 : 5-diphenyloxazole cyanines absorb at about 385 mμ, sometimes with inflections on the longer-wavelength side, at about 395 mμ. The crude desylamine from 4-methoxybenzoin and ethylamine was converted into the isomers 3-ethyl-4(or 5)-*p*-methoxyphenyl-5(or 4)-phenyl-2-thio-oxazoline (II; R = Et, R^1 = *p*-$MeO{\cdot}C_6H_4$ or Ph, R^2 = Ph or *p*-$MeO{\cdot}C_6H_4$), which were separated by chromatography. These were converted into isomeric dyes.

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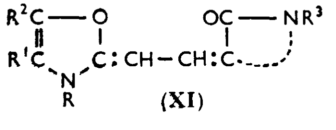
(XI)

Desylamines also react with carbon disulphide, the products being the analogous 2-thiothiazolines (VII). These are also converted into useful dye intermediates (VIII) by fusion with alkyl esters, thus providing a new route to thiazole analogues of dyes (IV) and (VI). Unsymmetrical cyanines with one oxazole and one thiazole nucleus can also be

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[2] Lutz, Freek, and Murphey, *J. Amer. Chem. Soc.*, 1948, **70**, 2015; Lutz and Murphey, *ibid.*, 1949, **71**, 478.

[3] McCombie and Parkes, *J.*, 1912, **101**, 1991.

[4] Gompper, *Chem. Ber.*, 1956, **89**, 1762.

obtained, with absorption maxima in methanol at *ca.* 415 mμ, *i.e.*, between those of the analogous oxazole and thiazole (440 mμ) cyanines. The thiazole dyes are also fluorescent.

Desylamines also condense with acetyl chloride in acetic anhydride to give 2-methyloxazolium salts (V) directly. Alternative methods [5] involve the isolation and subsequent quaternization of oxazole bases. The variety of desylamines available makes possible the synthesis of oxazolium salts and dyes possessing long-chain alkyl groups and aryl groups in the 3-position. Examples of 2-2′-anilinovinyl-4 : 5-diaryloxazolium salts (IX), symmetrical trimethincyanines (X), and dimethin*mero*cyanines (XI) have been prepared *via* 2-methyloxazolium salts (V) by previous procedures [5] or their modifications. 2-2′-Acetanilidovinyl derivatives of oxazoles are not readily prepared by refluxing anilinovinyl intermediates in acetic anhydride, and in dye syntheses that require acetanilidovinyl compounds this difficulty was overcome by using anilinovinyl compounds (1 mol.) with acetic anhydride (1 mol.) and triethylamine (1 mol. in excess of the usual quantity) in ethanol. Under these conditions, acetanilidovinyl derivatives could not be isolated, although good yields of dyes were obtained.

The vinylogous shifts of absorption maxima in methanol on passing from monomethin- to trimethin-oxazole and -thiazole dyes are 120 mμ and 140 mμ respectively, values in agreement with those found in other cyanine dye series (such as the benzazoles) in which the monomethin dyes have planar resonance systems: also, an increase in molecular extinction coefficient is observed on increasing the polymethin chain length.

Many of the dyes are strong sensitizers for photographic gelatino-silver halide emulsions, although dyes with long-chain alkyl substituents are less efficient sensitizers.

EXPERIMENTAL

Throughout the Tables the following solvent abbreviations are used: A = ethyl acetate, B = benzene, D = ether, E = ethanol, G = ligroin (b. p. 70—90°), L = light petroleum (b. p. 60—80°), M = methanol, N = nitrobenzene, P = pyridine, W = water.

Ethyl-(2-*oxo-*1 : 2-*diphenylethyl*)*amine Hydrochloride* (I,HCl; R = Et, $R^1 = R^2 =$ Ph).—Benzoin (21·2 g.), 70% aqueous ethylamine (30 c.c.), and ethylamine hydrochloride (1 g.) were refluxed for 4 hr. After 2 hr., more aqueous ethylamine (15 c.c.) was added. The cooled solution was then made alkaline with aqueous N-sodium carbonate and extracted with ether Hydrogen chloride was passed into the dried ether extract, and the precipitated *salt* was filtered off and recrystallized from ethanol–ether as a fluffy white powder, m. p. 236° (13·5 g., 49%) (Found: N, 5·1; Cl, 12·9. $C_{16}H_{18}ONCl$ requires N, 5·0; Cl, 12·8%).

Methyl-(2-*oxo-*1 : 2-*diphenylethyl*)*amine hydrochloride* (Table 1) and *ethyl-*[1(and 2)-p-*methoxyphenyl-*2-*oxo-*2(and 1)-*phenylethyl*]*amine hydrochloride* were prepared by the same method. Other desylamine hydrochlorides (Table 1) were prepared according to the method of Lutz *et al.*[2]

TABLE 1. *Desylamine* (1 : 2-*diaryl-*2-*oxoethylamine*) *hydrochlorides* (I,HCl).

R	$R^1 = R^2$	Form [e]	Yield (%)	M. p.
Me	Ph	Powder (E–D)	43	240° [a]
Bu	Ph	Powder (E–D)	33	229 [b]
n-$C_{18}H_{37}$	Ph [c]	Wax	90	—
Bu	p-MeO·C_6H_4	Needles (M–D)	68	204 [d]
n-$C_{12}H_{25}$	p-MeO·C_6H_4 [c]	Wax	64	—

[a] Goodson and Moffett, *J. Amer. Chem. Soc.*, 1949, **71**, 3219, report m. p. 216—220°. [b] Lutz, Freek, and Murphey, *J. Amer. Chem. Soc.*, 1948, **70**, 2015, report m. p. 184—186°. [c] Crude product used to prepare 2-methyloxazolium salt. [d] Found: N, 3·7; Cl, 9·8. $C_{20}H_{26}O_3NCl$ requires N, 3·8; Cl, 9·8%. [e] Solvent in parentheses.

4 : 5-*Diaryl-*2-*thio-oxazolines* (II) (Table 2).—A solution of the 1 : 2-diaryl-2-oxoethylamine hydrochloride (0·1 mol.) in water (125 c.c.) was made alkaline with sodium carbonate solution,

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[5] Jeffreys, *J.*, 1952, 4823.

TABLE 2. 4 : 5-*Diaryl-2-thio-oxazolines* (II).

R	R¹	R²	Form [c]	Yield (%)	M. p.	Formula	Found (%) N	Found (%) S	Reqd. (%) N	Reqd. (%) S
Et	Ph	Ph	Prisms (M)	53	163°	$C_{17}H_{15}ONS$	5·0	11·3	5·0	11·4
Bu	Ph	Ph	Needles (G)	20	145	$C_{19}H_{19}ONS$	4·3	10·2	4·5	10·4
n-C_8H_{17}	Ph	Ph	—	90		Oil; crude product used for dye preps.				
Ph	Ph	Ph	Prisms (N-E)	48	226 [a]	—	—	—	—	—
Et	*p*-MeO·C_6H_4	Ph	Needles (B-L)	32 [b]	180	$C_{18}H_{17}O_2NS$	4·5	10·5	4·5	10·3
Et	Ph	*p*-MeO·C_6H_4	Cubes		145	$C_{18}H_{17}O_2NS$	4·5	10·5	4·5	10·3

[a] Gompper, *Chem. Ber.*, 1956, **89**, 1762, reports m. p. 229°. [b] Total crude yield. The isomers were separated by chromatography on alumina with ligroin-benzene mixtures as eluants. [c] Solvent in parentheses.

TABLE 3. 4 : 5-*Diaryl-2-methyloxazolium salts* (V).

R	R¹ = R²	X	Form [b]	Yield (%)	M. p.	Formula	Found (%) N	Found (%) Hal	Reqd. (%) N	Reqd. (%) Hal
Me	Ph	ClO_4	Plates (E-D)	46	156°	$C_{17}H_{16}O_5NCl$	—	10·3	—	10·2
Et	Ph	ClO_4	Leaflets (M-D)	62	152	$C_{18}H_{18}O_5NCl$	3·8	10·0	3·9	9·8
Bu	Ph	I	Needles (E-D)	77	179	$C_{20}H_{22}ONI$	3·2	31·0	3·3	30·3
n-C_8H_{17}	Ph	I	Leaflets (M-D)	63	130	$C_{24}H_{30}ONI$	2·7	27·5	2·9	26·7
n-$C_{12}H_{25}$	Ph	ClO_4	Wax [a]	—	—	—	—	—	—	—
n-$C_{18}H_{37}$	Ph	ClO_4	Wax [a]	—	—	—	—	—	—	—
Ph	Ph	I	Needles (M-D)	60	266	$C_{22}H_{18}ONI$	3·2	29·3	3·2	28·9
Bu	*p*-MeO·C_6H_4	ClO_4	Needles (M-D)	83	181	$C_{22}H_{26}O_7NCl$	3·1	8·0	3·1	7·9
n-$C_{12}H_{25}$	*p*-MeO·C_6H_4	ClO_4	Wax (A-G)	85	120	$C_{30}H_{42}O_7NCl$	2·6	6·5	2·5	6·3

[a] Crude product used to prepare 2-2′-anilinovinyl derivative. [b] Solvent in parentheses.

TABLE 4. *Monomethincyanine dyes* (VI).

R	R²	X	Form [b]	Yield (%)	M. p.	$\lambda_{max.}$ (mμ, MeOH)	$10^{-4}\varepsilon$	Formula	Found (%) N	Found (%) Hal	Reqd. (%) N	Reqd. (%) Hal
(a) *Di*-(3-*R*-4 :5 -*diphenyl-2-oxazole*)*methincyanine salts* (VI; R = R², Y = Z = O).												
Et	Et	ClO_4	Primrose leaflets (PM-D)	15	281° [a]	381	3·7	$C_{35}H_{31}O_6N_2Cl$	4·5	5·9	4·6	5·8
n-C_8H_{17}	*n*-C_8H_{17}	ClO_4	Cream leaflets (M-D)	21	184	385 i 395	3·8	$C_{47}H_{55}O_6N_2Cl$	3·6	4·6	3·6	4·6
Ph	Ph	I	Lemon-yellow (P-D)	30	>330	383 i 392	3·5	$C_{43}H_{31}O_2N_2I$	3·8	17·1	3·8	17·3
(b) [3-*R*-4 : 5-*diphenyl-2-oxazole*][3-*R*²-4 : 5-*diphenyl-2-thiazole*]*methincyanine salts* (VI; Y = O, Z = S).												
Et	Et	I	Amber plates (E-D)	21	273	420	6·4	$C_{35}H_{31}ON_2IS$	— [c]	19·6	—	19·5
Et	Bu	ClO_4	Lemon-yellow leaflets (P-D)	24	254	412	5·9	$C_{37}H_{35}O_5N_2ClS$	4·3	5·3	4·3	5·4
(c) [3-*R*-4 : 5-*diphenyl-2-thiazole*][3-*R*²-4 : 5-*diphenyl-2-thiazole*]*methincyanine salts* (VI; Y = Z = S).												
Et	Bu	ClO_4	Yellow needles (P-M)	33	279 [a]	438	6·7	$C_{37}H_{35}O_4N_2ClS$	4·1	—	4·2	—

[a] Decomp. [b] Solvent in parentheses. [c] Found : S, 5·0. Reqd. : S, 4·9%.

TABLE 5. *Symmetrical trimethincyanine dyes* : *di*-[3-*R*-4 : 5-*diaryl-2-oxazole*]*trimethincyanine salts* (X).

R	R¹ = R²	X	Form [a]	Yield (%)	M. p.	$\lambda_{max.}$ (mμ, MeOH)	$10^{-4}\varepsilon$	Formula	Found (%) N	Found (%) Hal	Reqd. (%) N	Reqd. (%) Hal
Bu	*p*-MeO·C_6H_4	ClO_4	Orange leaflets (M-D)	67	203°	512 i 494	8·1	$C_{45}H_{49}O_{10}N_2Cl$	3·3	4·5	3·4	4·4
n-C_8H_{17}	Ph	I	Orange Sponge (M-D)	75	219	505 i 486	9·5	$C_{49}H_{57}O_2N_2I$	3·4	15·6	3·4	15·3
Ph	Ph	I	Brick-red (M-D)	50	301	511 i 492	9·3	$C_{45}H_{43}O_2N_2I$	3·7	16·7	3·7	16·7

[a] Solvent in parentheses.

TABLE 6. *2-2′-Anilinovinyl-4 : 5-diaryloxazolium salts* (IX). (*Prepared by the procedure used previously.*[5])

R	$R^1 = R^2$	X	Form [a]	Yield (%)	M. p.	Formula	Found (%) N	Found (%) Hal	Reqd. (%) N	Reqd. (%) Hal
n-C_8H_{17}	Ph	I	Yellow (M–D)	87	182°	$C_{31}H_{35}ON_2I$	4·7	22·8 [c]	4·8	22·0
n-$C_{12}H_{25}$	Ph	ClO_4	,, (A–L)	69	127	$C_{35}H_{43}O_5N_2Cl$	4·6	5·9	4·6	5·8
n-$C_{18}H_{37}$	Ph	ClO_4	,, (M–D)	62	131	$C_{41}H_{55}O_5N_2Cl$	4·0	5·3	4·1	5·1
Ph	Ph	I	Orange-red (M–D)	62	260	$C_{29}H_{23}ON_2I$	5·1	23·4	5·2	23·4
Bu	p-MeO·C_6H_4	ClO_4	Yellow (E–D)	88	224	$C_{29}H_{31}O_7N_2Cl$	5·0	6·6	5·1	6·4
n-$C_{12}H_{25}$	p-MeO·C_6H_4	ClO_4	Orange (M)	54	169	$C_{37}H_{47}O_7N_2Cl$	4·1	5·5	4·2	5·3

[a] Solvent in parentheses. [b] Prisms; others are leaflets. [c] Found: C, 64·2; H, 6·2. Reqd.: C, 64·4; H, 6·1%.

TABLE 7. mero*Cyanines: 3-Alkyl-5-(3-R-4 : 5-diaryloxazolin-2-ylidene)-2-thio-azolid-4-ones* (IV).

R	$R^1 = R^2$	R^3	Form [d]	Yield (%)	M. p.	$\lambda_{max.}$ (mμ, MeOH)	$10^{-4}\varepsilon$	Formula	Found (%) N	Found (%) S	Reqd. (%) N	Reqd. (%) S
From 3-R^3-2-*thiothiazolid*-4-*one*.												
Et	Ph	Et	(B–L)	64	179°	405 420	4·1 4·2	$C_{22}H_{20}O_2N_2S_2$	6·7	15·8	6·9	15·7
Et	Ph	CH_2·CO_2H	Needles (B–L)	30	257	404 417	3·6 3·5	$C_{22}H_{18}O_4N_2S_2$	6·7	14·9	6·4	14·6
Bu	Ph	CH_2·CO_2Et	Needles (B–L)	28	139	404 416	3·5 3·4	$C_{26}H_{26}O_4N_2S_2$	5·5	13·0	5·7	13·0
n-C_8H_{17}	Ph	Et	Powder (E)	49	106	408	4·4	$C_{28}H_{32}O_2N_2S_2$	5·7	13·0	5·7	13·0
Ph	Ph	CH_2·CO_2Et	Leaflets (P–M)	74	331	404 413	— —	$C_{28}H_{22}O_4N_2S_2$	5·5	12·6	5·5	12·5
Et	[b]	CH_2·CO_2H	Powder (P–L)	42	250 [a]	411	—	$C_{23}H_{20}O_5N_2S_2$	6·0	13·9	6·0	13·7
Et	[b]	Et	(B–L)	—	180	415	—	$C_{23}H_{22}O_3N_2S_2$	6·4	14·6	6·4	14·6
Et	[c]	Et	Prisms (B–L)	37	205	405 419	4·4 4·3					
From 3-*ethyl*-2-*thio-oxazolid*-4-*one*.												
Et	Ph	Et	Needles (B–L) [e]	31	177	381 395	3·9 3·3	$C_{22}H_{20}O_3N_2S$	7·0	8·1	7·1	8·2
From 1 : 3-*diethyl*-2-*thiohydantoin*.												
Et	Ph	Et	Needles (G)	14	182	393	3·8	$C_{24}H_{25}O_2N_3S$	9·9	8·8	10·0	7·6

[a] Decomp. [b] R^1 = Ph, R^2 = p-MeO·C_6H_4. [c] R^1 = p-MeO·C_6H_4; R^2 = Ph. [d] Solvent in parentheses. [e] Cream-coloured; others are yellow.

TABLE 8. *Dimethin*mero*cyanines: 3-alkyl-5-(3-R-4 : 5-diaryl-oxazolin-2-ylidene-ethylidene)-2-thio-azolid-4-ones* (XI).

R	$R^1 = R^2$	R^3	Form [a]	Yield (%)	M. p.	$\lambda_{max.}$ (mμ, MeOH)	$10^{-4}\varepsilon$	Formula	Found (%) N	Found (%) S	Reqd. (%) N	Reqd. (%) S
From 3-R^3-2-*thio-oxazolid*-4-*one*.												
Bu	p-MeO·C_6H_4	Et	Orange needles (B–L)	40	142°	495	7·5	$C_{28}H_{30}O_5N_2S$	5·2	6·2	5·5	6·3
Bu	Ph	Et	Red leaflets (B–L)	85	209	491	8·7	$C_{26}H_{26}O_3N_2S$	6·1	7·4	6·3	7·2
n-C_8H_{17}	Ph	Et	Orange needles (E–W)	68	103	491	8·8	$C_{30}H_{34}O_3N_2S$	5·5	6·7 [b]	5·6	6·4
Ph	Ph	Et	Red prisms (B–L)	56	250	491	8·7	$C_{28}H_{22}O_3N_2S$	6·0	—	6·0	—
From 1 : 3-*diethyl*-2-*thiohydantoin*.												
Bu	p-MeO·C_6H_4	Et	Red needles (B–L)	41	186	514	7·6	$C_{30}H_{35}O_4N_3S$	7·7	6·0	7·9	6·0
Ph	Ph	Et	Red powder (B–L)	73	247	511	8·6	$C_{30}H_{27}O_2N_3S$	8·5	6·8	8·5	6·5
n-C_8H_{17}	Ph	Et	Maroon needles (E–W)	87	140	513	9·5	$C_{32}H_{39}O_2N_3S$	7·6	[c]	7·9	—
From 3-R^3-2-*thiothiazolid*-4-*one*.												
Ph	Ph	CH_2·CO_2Et	Maroon leaflets (B–L)	35	244	512 i 492	9·6	$C_{30}H_{24}O_4N_2S_2$	5·2	12·0	5·2	11·9

[a] Solvent in parentheses. [b] Found: C, 71·5; H, 7·1. Reqd.: C, 71·7; H, 6·8.% [c] Found: C, 72·5; H, 7·5. Reqd.: C, 72·6; H, 7·4%.

and extracted with chloroform (600 c.c.). Thiocarbonyl chloride (0·1 mol.) was slowly added to the dried, stirred chloroform solution, cooled in ice-water. After 30 min. at room temperature the solution was washed thoroughly with sodium carbonate solution, and water. On removal of the chloroform from the dried solution, the product solidified, and was purified by recrystallization.

4 : 5-*Diaryl*-2-*methylthio-oxazolium Methyl Sulphates* (III; $X = MeSO_4$).—A 4 : 5-diaryl-2-thio-oxazoline (1 mol.) and methyl sulphate (1·5 mols.) were fused together on the steam-bath for ½—1 hr. The crude product, washed with ether, was used to prepare dyes.

3-*Ethyl*-4 : 5-*diphenyl*-2-*thiothiazoline* (VII; $R = Et$, $R^1 = R^2 = Ph$).—To a solution of ethyl-(2-oxo-1 : 2-diphenylethyl)amine hydrochloride (27·5 g., 0·1 mol.) and carbon disulphide (10 g., 0·13 mol.) in ethanol (100 c.c.) was added potassium hydroxide (11·2 g., 0·2 mol.) in water (12 c.c.), and the resulting solution was refluxed for 1 hr. The *product* was precipitated from the cooled solution with water, filtered off, and recrystallized from benzene–light petroleum as needles, m. p. 132° (17 g., 57%) (Found : S, 21·5. $C_{17}H_{15}NS_2$ requires S, 21·5%).

3-*Butyl*-4 : 5-*diphenyl*-2-*thiothiazoline* (VII; $R = Bu$, $R^1 = R^2 = Ph$) was prepared similarly, as glistening leaflets, m. p. 139° (from benzene–light petroleum), in 90% yield (Found : N, 4·2. $C_{19}H_{19}NS_2$ requires N, 4·3%).

3-*Alkyl*-2-*methylthio*-4 : 5-*diphenylthiazolium Toluene*-p-*sulphonates* (VIII; $R^1 = R^2 = Ph$, $X = p\text{-}Me{\cdot}C_6H_4{\cdot}SO_3$).—3-Alkyl-4 : 5-diphenyl-2-thiothiazoline (1 mol.) and methyl toluene-*p*-sulphonate (1·1 mols.) were fused together at 130° for 1 hr. The crude products, washed with ether, were used to prepare dyes.

4 : 5-*Diaryl*-2-*methyloxazolium Salts* (V) (Table 3).—A solution of the 1 : 2-diaryl-2-oxo-ethylamine hydrochloride (0·1 mol.) and acetyl chloride (0·1 mol.) in acetic anhydride (120 c.c.) was refluxed for 3 hr. Solvents were removed at the pump, and the residue was dissolved in a little ethanol. This solution was poured into aqueous sodium perchlorate or potassium iodide to precipitate the required salt, which was purified by recrystallization.

Monomethincyanine Dyes (VI) (Table 4).—4 : 5-Diaryl-2-methylthio-azolium salt (0·01 mol.), 4 : 5-diaryl-2-methylazolium salt (0·01 mol.), and triethylamine (0·01 mol.) in ethanol (20 c.c.) or pyridine (20 c.c.) were refluxed for 10 min. The cooled solution, if the dye did not crystallize, was poured into aqueous potassium iodide or sodium perchlorate to precipitate the *product*. The dye was recrystallized.

Symmetrical Oxazole Trimethincyanine Dyes (X) (Table 5).—4 : 5-Diaryl-2-methyloxazolium salt (0·01 mol.), 2-2′-anilinovinyl-4 : 5-diaryloxazolium salt (0·01 mol.) (see Table 6), acetic anhydride (0·01 mol.), triethylamine (0·02 mol.), and ethanol (20 c.c.) were refluxed together for ¼—½ hr., and the solution was chilled; the *product* was filtered off and recrystallized.

3-*Alkyl*-5-(3-*R*-4 : 5-*diaryloxazolin*-2-*ylidene*)-2-*thio-azolid*-4-*ones* (IV) (Table 7).—4 : 5-Diaryl-2-methylthio-oxazolium salt (0·01 mol.), 3-alkyl-azolid-4-one (thiazolidone, oxazolidone, or hydantoin) (0·01 mol.), and triethylamine (0·01 mol.) in ethanol (25 c.c.) were refluxed for ¼ hr. A few drops of water were added, and the solution was chilled. The *dye* was filtered off, washed, and recrystallized.

3-*Alkyl*-5-(3-*R*-4 : 5-*diaryloxazolin*-2-*ylidene-ethylidene*)-2-*thio-azolid*-4-*ones* (XI) (Table 8).—2-2′-Anilinovinyl-4 : 5-diaryloxazolium salt (0·01 mol.), 3-alkyl-2-thio-azolid-4-one (as above) (0·01 mol.), acetic anhydride (0·01 mol.), and triethylamine (0·02 mol.) in ethanol (25 c.c.) were refluxed for 10 min. A few drops of water were added, and the solution was chilled. The *dye* was filtered off, washed, and recrystallized.

5-(3-*Butyl*-4 : 5-*diphenylthiazolin*-2-*ylidene*)-3-*carboxymethyl*-2-*thiothiazolid*-4-*one* (IV; thiazole analogue, $R = Bu^n$, $R^1 = R^2 = Ph$, $R^3 = CH_2{\cdot}CO_2H$).—3-Butyl-2-methylthio-4 : 5-diphenylthiazolium toluene-*p*-sulphonate (2·6 g.), 3-carboxymethyl-2-thiothiazolid-4-one (1·0 g.) and triethylamine (0·5 g.) in ethanol (10 c.c.) were refluxed for 10 min. The chilled solution was filtered, and the *dye* recrystallized from pyridine–methanol as orange needles, m. p. 266° (decomp.) (0·9 g., 38%) (Found : S, 20·0. $C_{24}H_{22}O_3N_2S_3$ requires S, 19·9%), $\lambda_{max.}$ 423 mμ (ε 5·6 × 10^4 in MeOH).

[3-*Ethyl*-4-p-*methoxy*-5-*phenyl*-2-*oxazole*][3-*ethyl*-4 : 5-*diphenyl*-2-*oxazole*]*methincyanine Perchlorate* (Analogue of VI, $Y = Z = O$).—3-Ethyl-4-*p*-methoxyphenyl-2-methyl-5-phenyloxazolium toluene-*p*-sulphonate (4·65 g.), 3-ethyl-2-methylthio-4 : 5-diphenyloxazolium methyl sulphate (4·07 g.), and triethylamine (1·4 c.c.) in ethanol (20 c.c.) were refluxed for ¼ hr. Aqueous sodium perchlorate was added to the chilled solution, and the *dye* which precipitated was filtered off, washed with a little ethanol, and recrystallized from pyridine–water as cream leaflets, m. p.

277° (1·4 g., 22%) (Found: N, 4·3; Cl, 5·6. $C_{36}H_{33}O_7N_2Cl$ requires N, 4·4; Cl, 5·5%), $\lambda_{max.}$ 380 mμ (ε 3·9 × 10^4), infl. 394 mμ (cf. dyes in Table 4a).

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