The Nucleophilic Reactivity of Alkylidene Derivatives of Cyclic Keto-methylene Compounds.

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3-Substituted rhodanines have been condensed with acetaldehyde, crotonaldehyde, acetone, diacetyl, and pyruvic acid, to give 4-alkylidene derivatives. These and the 1′-alkoxy- and 1′-alkylthio-ethylidene derivatives of a number of cyclic keto-methylene compounds have been condensed with electrophilic, cyclic quaternary ammonium salts to give simple and complex *mero*cyanines and oxamines. Some of the complex dyes have their main absorption band almost completely in the infra-red region, a phenomenon which is believed to be unique for non-ionic dyes.

THE nucleophilic reactivity of the methylene carbon atom in cyclic keto-methylene compounds is shown by the formation of condensation products with aldehydes (Nencki, *Ber.*, 1884, **17**, 2277), ketones (Knorr, *Annalen*, 1887, **238**, 180), and ortho-esters (preceding paper). It is also utilized in the preparation of *mero*cyanines (II) by treating the keto-methylene compound with derivatives of heterocyclic quaternary ammonium compounds (I) containing an electrophilic carbon atom. This method is usually employed in the preparation of *mero*cyanines and higher vinylogues (II; R′ = H). It is also used for dimethin*mero*cyanines carrying a chain substituent (II; R′ ≠ H) although the preparation of the intermediate (I; R′ ≠ H) usually involves a number of steps (cf. Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, and White, *J. Amer. Chem. Soc.*, 1951, **73**, 5326). In all cases the preparation of (I; $n > 0$) requires, as intermediate, the reactive methyl derivative of the quaternary salt (I; $n = 0$, G = Me) and in certain cases such derivatives are not readily accessible.

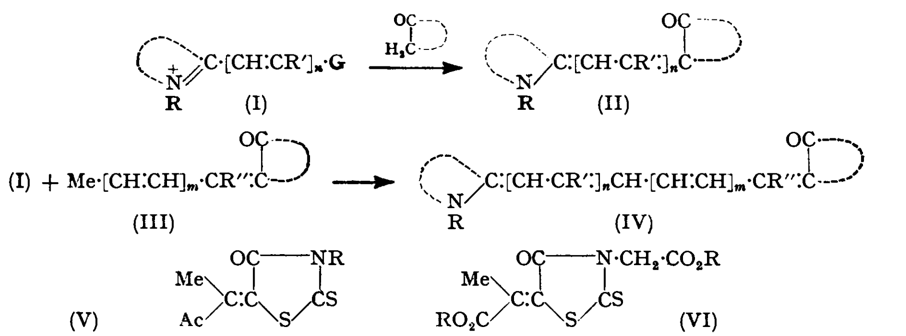
The discovery by Kendall and his co-workers, that the terminal methyl group of alkylidene derivatives (III; R″ = H, alkyl, or aryl) of pyrazolones, rhodanines, or 2-thiohydantoins (with Collins, B.P. 528,803/1939) or of 1′-alkoxyethylidene derivatives (III; $m = 0$, R″ = OEt) of pyrazolones (with Fry and Morgan, B.P. 672,291/1950) still showed the same nucleophilic reactivity associated with the original methylene carbon atom, established a novel method of preparing di- or tetra-methin*mero*cyanines (IV) with or without chain substituents.

Apart from the examples given in the above patents this reaction has not been exploited and the purpose of the present paper is to extend its scope and, in particular, to apply it to the synthesis of complex di- and tetra-methin*mero*cyanines not hitherto accessible.

5-*Alkylidenerhodanines.*—5-Ethylidene- and 5-but-2′-en-1′-ylidene-rhodanine have been prepared by heating rhodanine and paraldehyde or crotonaldehyde in acetic acid (Andreasch, *Monatsh.*, 1918, **39**, 423; Gränacher, Gerö, Ofner, Kloppenstein, and Schlatter, *Helv. Chim. Acta*, 1923, **6**, 458). It has now been found that acetaldehyde or crotonaldehyde readily condensed with 3-substituted rhodanines in acetic anhydride–sodium acetate, to give the ethylidene and butenylidene derivatives.

The condensation of acetone and pyrazolones occurs under reflux (Knorr, *loc. cit.*). On the other hand, rhodanine requires as catalyst either sodium acetate in acetic acid (Culvenor, Davies, Maclaren, Nelson, and Savige, *J.*, 1949, 2573) or ammonia and ammonium chloride (Brown, Bradshaw, McCallum, and Potter, *J. Org. Chem.*, 1950, **15**, 174; see also Allan, Maclean, and Newbold, *J.*, 1952, 5053). Cook and Cox (*J.*, 1949, 2343) used pyridine and morpholine for the condensation with 1 : 3-disubstituted 2-thiohydantoin. The 3-substituted rhodanines, it has now been found, condense best with acetone in the presence of zinc chloride.

Zinc chloride is also effective in the condensation of 3-substituted rhodanines with diacetyl, to give the 5-(3-oxobutan-2-ylidene) derivative (V; *i.e.*, III, $m = 0$, R″ = Ac), and with pyruvic acid to give 5-1′-alkoxycarbonylethylidene derivatives (VI), esterification accompanying condensation in alcohol. Both (V) and (VI) are strong photographic desensitizers. This was expected (cf. Kendall, Int. Congr. Photography, Paris, 1935) since both compounds contain the system of two $+M$ atoms connected by a conjugated chain of an even number of carbon atoms. Only one of the two possible geometrical isomers of each of these compounds was isolated and from steric considerations this is assumed to be the one with the configuration shown.



Simple mero*Cyanines and Vinylogues.*—All the above compounds contain a nucleophilic methyl group and can be condensed with suitable intermediates to give vinylogues of *mero*cyanines. The photographic desensitizing properties of (V) and (VI) are considerably enhanced in the dyes derived from them, possibly as a result of the stronger adsorption of the latter on the silver halide grains.

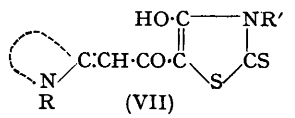
The 1′-alkoxy-, 1′-alkylthio-, and 1′-arylthio-ethylidene derivatives described in the previous paper may also be condensed with 2-alkylthio-derivatives of cyclic ammonium salts (I; $n = 0$, G = SR) (cf. Kendal, Fry, and Morgan, *loc. cit.*), to give dimethin*mero*cyanines containing a chain alkoxy- or alkyl(aryl)thio-group (IV; $n = m = 0$, $R'' =$ RO or RS). Other dyes of the type (IV; $n = m = 0$, $R'' =$ SR) have also been obtained by Edwards and Kendall (U.S.P. 2,531,913) by a different method. One of these dyes, 3-ethoxycarbonylmethyl-5-[1-ethylthio-2-(3-methylthiazolidin-2-ylidene)ethylidene]-2-thio-thiazolid-4-one was isolated in three crystalline forms, each of different melting point, but having the same absorption and photographic sensitization characteristics. The form first obtained consisted of well-defined crystals, m. p. 139—143°, which on further recrystallization separated into two forms, m. p. 152—154° and 131° respectively.

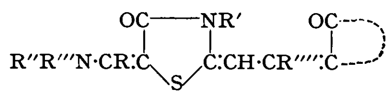
In general the replacement of $R' =$ H by $R' =$ OEt in (II) results in a hypsochromic absorption shift, whilst replacement by $R' =$ SR always gives a strong bathochromic shift.

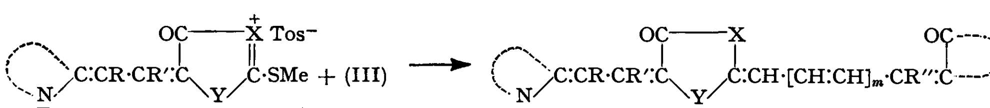
Dimethin*mero*cyanines substituted by alkoxyl in the chain, derived from rhodanines, are rapidly hydrolysed by strong alkali to the alkali-soluble ketones (VII).

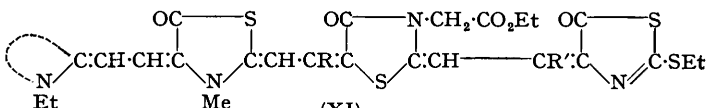
Condensation of (III; $m = 0$, $R'' =$ OR or SR) with 2-2′-acetanilidovinyl derivatives (I; $n = 1$, G = NAcPh) proceeds smoothly, to give higher vinylogues of the above dyes (IV; $R'' =$ OR, SR, $m = 0$, $n = 1$).

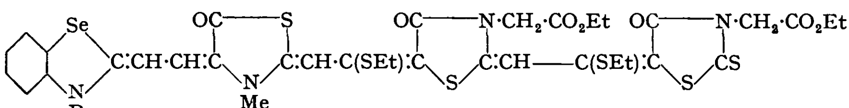
Complex mero*Cyanines*.—The formation of complex *mero*cyanines by reaction of a ketomethylene compound with a quaternized *mero*cyanine (VIII; $X \neq Y =$ NR or S) derived from a rhodanine or 3-alkyl-2-thiothiazolid-5-one is well known (Kendall, B.P. 487,051; Brooker, in Mees, "The Theory of the Photographic Process," Macmillan, New York, 1942, p. 1038; Knott and Jeffreys, *J.*, 1952, 4762). Such dyes are all characterized by ketonic nuclei attached directly to each other as in simple *mero*cyanines, *i.e.*, :CH·[CH:CH]$_m$·CR″: of (IX) is absent. In order to obtain higher vinylogues (IX; $R'' =$ H) Brooker (personal communication) first converted the SMe group of (VIII) into Me, and brought about the reaction of the product with diphenylformamidine, to give the

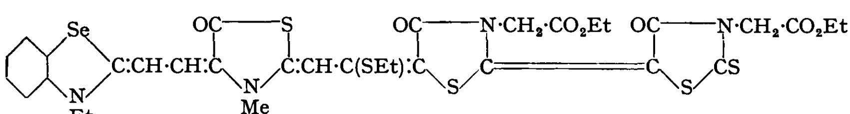

(VII)


(X)


(VIII) (IX)

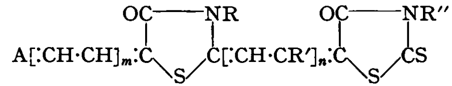

(XI)


(XII)


(XIII) (Tos⁻ = p-$C_6H_4Me{\cdot}SO_3^-$)

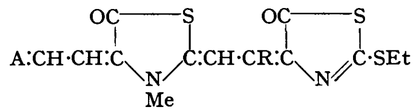
intermediate analogous to (I). Condensation of (VIII) with (III) which proceeds smoothly offers, however, a much more convenient method, in certain cases, of preparing (IX; $R'' =$ H) and allows the ready synthesis of chain-substituted analogues (IX; $R'' =$ Me, OR, SR, Ac, or CO_2R). Such dyes, in which $m = 0$ and $R'' =$ OR or SR, are of particular

TABLE 1.



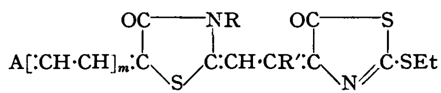
A	R	R′	R″	Yield (%)	Appearance	M. p.	$\lambda_{max.}$ (mμ) (pyridine)	Formula	Found (%) N	Found (%) S	Required (%) N	Required (%) S
3-R-2-[2-(3-R″-4-*Oxo-2-thiothiazolidin-5-ylidene*)-2-R′-*ethylidene*]-5-(A-2-*ylidene-ethylidene*)*thiazolid-4-one* ($m = n = 1$)												
3-Ethylbenzoxazolin	Et	H	$CH_2 \cdot CO_2Et$	16·5	Green needles	275°	610	$C_{25}H_{25}O_5N_3S_3$	7·6	17·7	7·75	17·7
,, ...	,,	OMe	,,	51	,,	244	605	$C_{26}H_{27}O_6N_3S_3$	7·35	—	7·35	—
,, ...	,,	OEt	,,	41	,,	223	600	$C_{27}H_{29}O_6N_3S_3$	6·8	16·4	7·15	16·35
,, ...	,,	SEt	,,	65	Green bronze	224	635	$C_{27}H_{29}O_5N_3S_4$	6·7	21·2	6·95	21·2
,, ...	,,	Ac	,,	50	threads							
3-Ethylbenzothiazolin	Allyl	H	Allyl	37	Green needles	237	622	$C_{27}H_{27}O_6N_3S_3$	7·0	—	6·95	—
,, ...	,,	OEt	,,	39	Bronze needles	236	616	$C_{25}H_{23}O_2N_3S_4$	7·95	—	8·0	—
3-Ethyl-4 : 5-diphenyl oxazolin	$CH_2 \cdot CO_2Et$	,,	$CH_2 \cdot CO_2Et$	38	Green needles	227	620	$C_{27}H_{27}O_3N_3S_4$	7·5	—	7·35	—
3-Ethyl-4 : 5-diphenylthiazolin	,,	,,	,,	37	Bronze-green	151	635	$C_{37}H_{37}O_8N_3S_3$	5·3	12·6	5·6	12·85
3-Ethylnaphtho(1′ : 2′-4 : 5)-					Green needles	192	645	$C_{37}H_{37}O_7N_3S_4$	5·5	16·7	5·5	16·8
thiazolin	Allyl	,,	Allyl	39	,,	209	670	$C_{33}H_{33}O_3N_3S_4$	6·3	17·0	6·5	17·15
3-Ethylbenzoselenazolin-	$CH_2 \cdot CO_2Et$	,,	$CH_2 \cdot CO_2Et$	37	,,	221	625	$C_{29}H_{31}O_7N_3S_3Se$	5·8	—	5·95	—
3-Methylthiazolidin-	,,	,,	,,	33	Brilliant green	211	590	$C_{24}H_{29}O_7N_3S_4$	6·8	21·2	7·0	21·4
1 : 3 : 3-Trimethylindolin	Et	,,	,,	33	Green flakes	212	600	$C_{29}H_{33}O_5N_3S_3$	6·7	16·0	7·0	16·0
1 : 3-Diethylbenzimidazolin ...	$CH_2 \cdot CO_2Et$	,,	,,	28	Brilliant green	212	650	$C_{31}H_{36}O_7N_4S_3$	8·3	14·1	8·35	14·3
1-Ethyl-1 : 2-dihydropyridin ...	,,	,,	,,	62	Green threads	179	665	$C_{27}H_{31}O_7N_3S_3$	6·85	15·7	6·95	15·85
1-Ethyl-1 : 4-dihydropyridin-4-	,,	,,	,,	33	Green flakes	213	685	,,	6·8	15·8	6·95	15·85
1-Ethyl-1 : 2-dihydroquinolin ...	,,	,,	,,	40	,,	216	660	$C_{31}H_{33}O_7N_3S_3$	6·35	14·5	6·4	14·65
1-Ethyl-1 : 4-dihydroquinolin-4-	,,	,,	,,	30	Green-gold needles	210	690	,,	6·5	14·3	,,	,,
3-R-2-[2-(3-*Allyl-4-oxo-2-thiothiazolid-5-ylidene*)*prop-1-ylidene*]-5-(A-2-*ylidene-ethylidene*)*thiazolid-4-one* ($m = n = 1$; R′ = Me; R″ = allyl)												
		R										
3-Ethylbenzoxazolin		Et		43	Green needles	264	611	$C_{25}H_{25}O_3N_3S_3$	8·3	18·9	8·2	18·8
3-Ethylbenzothiazolin		Allyl		33	,,	266	630	$C_{26}H_{25}O_2N_3S_4$	7·8	—	7·8	—
3-R-2-[4-(3-R″-4-*Oxo-2-thiothiazolidin-5-ylidene*)*but-2-en-1-ylidene*]-5-(A-2-*ylidene-ethylidene*)*thiazolid-4-one* ($m = 1$; $n = 2$; R′ = H)												
	R		R″									
3-Ethylbenzoxazolin	Et		Allyl	19	Gold-green needles	282	643	$C_{26}H_{25}O_3N_3S_3$	7·9	18·3	8·05	18·35
,, ...	,,		$CH_2 \cdot CO_2Et$	16	Grey	270	635	$C_{27}H_{27}O_5N_3S_3$	7·6	—	7·4	—
3-Ethylbenzothiazolin	Allyl		Allyl	33	Bronze needles	239	658	$C_{27}H_{25}O_2N_3S_4$	7·55	23·2	7·55	23·25
3-R-2-[2-(3-R″-4-*Oxo-2-thiothiazolidin-5-ylidene*)-2-R′-*ethylidene*]-5-A-*thiazolid-4-one* ($m = 0$; $n = 1$)												
	R	R′	R″									
3-Ethylbenzthiazolin-2-ylidene	Et	OEt	$CH_2 \cdot CO_2Et$	96	Mauve	250	595	$C_{33}H_{33}O_5N_3S_4$	6·05	18·7	6·3	18·85
Piperid-1′-ylmethylene	$CH_2 \cdot CO_2Et$	H	,,	33	Rust threads	196	529	$C_{22}H_{27}O_6N_3S_3$	7·7	18·3	8·0	18·3
,, ...	,,	OMe	,,	36	Red needles	129	528	$C_{23}H_{29}O_7N_3S_3$	7·5	—	7·65	—
Piperid-1′-ylmethylene	,,	SEt	,,	24	Magenta threads	168	561	$C_{24}H_{31}O_6N_3S_4$	7·5	21·7	7·2	21·9
n-Octylaminomethylene	Allyl	OEt	Allyl	29	Green plates	138—140	522	$C_{25}H_{35}O_3N_3S_3$	7·9	—	8·05	—
3-R-2-[2-(3-R″-4-*Oxo-2-thiothiazolidin-5-ylidene*)*prop-2-ylidene*)-5-A-*thiazolid-4-one* ($m = 0$; $n = 1$; R′ = Me)												
	R		R″									
n-Octylaminomethylene	Allyl		Allyl	32·5	Green-red threads	138	540	$C_{24}H_{33}O_2N_3S_3$	8·5	19·3	8·55	19·6
Piperid-1′-ylmethylene	$CH_2 \cdot CO_2Et$		$CH_2 \cdot CO_2Et$	31	Pink needles	200	529	$C_{23}H_{24}O_6N_3S_3$	7·75	—	7·85	—

TABLE 2.



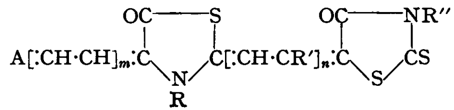
A	R	Yield (%)	Appearance	M. p.	$\lambda_{max.}$ (mμ) (pyridine)	Formula	Found (%) N	Found (%) S	Required (%) N	Required (%) S
			2-[2-R-2-(2-*Ethylthio-5-oxothiazolin-4-ylidene*)*ethylidene*]-4-(A-2-*ylidene-ethylidene*)-3-*methylthiazolid-5-one*							
3-Ethylbenzoxazolin	OEt	35	Green needles	229°	640	$C_{24}H_{25}O_4N_3S_3$	7·95	—	8·15	—
,, ...	SEt	34	,,	203	680	$C_{24}H_{25}O_3N_3S_4$	7·65	24·2	7·9	24·1
3-Ethylbenzothiazolin	OEt	19	,,	251	660	$C_{24}H_{25}O_3N_3S_4$	7·75	24·1	7·9	24·1
,, ...	SEt	33	Bronze threads	203	714	$C_{24}H_{25}O_2N_3S_5$	7·8	29·05	7·7	29·3

TABLE 3.



A	R	R′	Yield (%)	Appearance	M. p.	$\lambda_{max.}$ (mμ) (pyridine)	Formula	Found (%) N	Found (%) S	Required (%) N	Required (%) S
		3-R-2-[2-R′-2-(2-*Ethylthio-5-oxothiazolin-4-ylidene*)*ethylidene*]-5-(A-2-*ylidene-ethylidene*)*thiazolid-4-one* (m = 1)									
3-Ethylbenzoxazolin	Et	OEt	23	Green needles	209°	588	$C_{25}H_{27}O_4N_3S_3$	7·9	—	7·95	—
,, ...	,,	SEt	53	Brassy needles	194	635	$C_{25}H_{27}O_3N_3S_4$	7·6	23·3	7·7	23·5
3-Ethylbenzothiazolin	,,	OEt	33	Green needles	227	610	$C_{25}H_{27}O_3N_3S_4$	7·55	23·05	7·7	23·5
,, ...	,,	SEt	48	Brown needles	198	650	$C_{25}H_{27}O_2N_3S_5$	7·2	28·65	7·5	28·5
3-Ethyl-4 : 5-diphenylthiazolin	$CH_2·CO_2Et$	OEt	18	Coppery needles	240	630	$C_{35}H_{35}O_5N_3S_4$	5·85	18·05	5·95	18·15
,,	...	SEt	34	Bronze needles	205	675	$C_{35}H_{35}O_4N_3S_5$	5·7	22·0	5·85	22·2
		3-*Allyl*-2-[2-R′-2-(2-*ethylthio-5-oxothiazolin-4-ylidene*)*ethylidene*]-5-A-*thiazolid-4-one* (m = 0)									
Morpholin-3′-ylmethylene	—	OEt	34	Magenta threads	176	518	$C_{20}H_{25}O_4N_3S_3$	8·85	—	9·0	—
,, ...	—	SEt	19	Black flakes	146	567	$C_{20}H_{25}O_3N_3S_4$	8·4	26·3	8·7	26·5

TABLE 4.



A	R′	R″	Yield (%)	Appearance	M. p.	$\lambda_{max.}$ (mμ) (pyridine)	Formula	Found (%) N	Found (%) S	Required (%) N	Required (%) S
2-[2-(3-R″-4-*Oxo-2-thiothiazolidin-5-ylidene*)-2-R′-*ethylidene*]-4-(A-2-*ylidene-ethylidene*)-3-R-*thiazolid-4-one* ($m = n = 1$; R = Me)											
3-Ethylbenzoxazolin	H	$CH_2 \cdot CO_2Et$	32	Green needles	303°	644	$C_{24}H_{23}O_5N_3S_3$	7·7	17·9	7·95	18·2
,, ...	OMe	,,	18	,,	235	643	$C_{25}H_{25}O_6N_3S_3$	7·6	—	7·5	—
,, ...	OEt	,,	32	Brilliant green	231	650	$C_{26}H_{27}O_6N_3S_3$	7·05	16·5	7·35	16·75
,, *	,,	,,	46	Green needles	241	650	$C_{27}H_{29}O_6N_3S_3$	7·25	—	7·15	—
,, ...	SEt	,,	34	Green tablets	257	691	$C_{26}H_{27}O_5N_3S_4$	7·05	21·5	7·15	21·75
,, *	,,	,,	55	Gold-green	238	690	$C_{27}H_{29}O_5N_3S_4$	6·75	—	6·95	—
3-Ethylbenzothiazolin	OEt	,,	34	Dark green	241	676	$C_{26}H_{27}O_5N_3S_4$	7·15	21·6	7·15	21·75
,, *	,,	,,	43	Bronze	240	675	$C_{27}H_{29}O_5N_3S_4$	7·2	21·1	6·95	21·2
,, ...	OMe	,,	31	Green needles	215	676	$C_{25}H_{25}O_5N_3S_4$	7·3	22·3	7·3	22·3
,, ...	SEt	,,	35	Green–bronze threads	239	718	$C_{26}H_{27}O_4N_3S_5$	6·75	26·3	6·95	26·5
,, *	,,	,,	45	Brassy-green	233	720	$C_{27}H_{29}O_4N_3S_5$	—	25·7	—	25·85
,, ...	$S \cdot CH_2Ph$	,,	32	Green needles	240	718	$C_{31}H_{29}O_4N_3S_5$	6·35	—	6·3	—
3-Ethyl-4 : 5-diphenyloxazolin	H	Allyl	20	Green threads	237	660	$C_{31}H_{27}O_3N_3S_3$	7·0	—	7·2	—
,, ...	OEt	,,	29	Green needles	255	660	$C_{33}H_{31}O_4N_3S_3$	6·8	—	6·7	—
3-Ethyl-4 : 5-diphenylthiazolin	H	,,	40	,,	279	682	$C_{31}H_{27}O_2N_3S_4$	7·05	21·5	7·0	21·3
,, ...	OEt	,,	40	,,	252	710	$C_{33}H_{31}O_3N_3S_4$	6·55	19·6	6·5	19·85
,, ...	SEt	$CH_2 \cdot CO_2Et$	72	Golden threads	264	752	$C_{34}H_{33}O_4N_3S_5$	—	22·5	—	22·4
3-Ethylbenzoselenazolin	OEt	,,	37	Green needles	244	685	$C_{26}H_{27}O_5N_3S_3Se$	6·65	—	6·6	—
,, ...	SEt	,,	49	,,	236	726	$C_{26}H_{27}O_4N_3S_4Se$	6·55	—	6·45	—
3-Ethylthiazolidin	OEt	,,	45	,,	197	639	$C_{22}H_{27}O_5N_3S_4$	7·45	—	7·75	—
,, ...	SEt	,,	51	Green flakes	227	676	$C_{22}H_{27}O_4N_3S_5$	7·3	28·6	7·55	28·7
3-Ethylnaphtho(1′ : 2′-4 : 5)thiazolin	OEt	,,	38	Green needles	260	705	$C_{30}H_{29}O_5N_3S_4$	6·65	19·7	6·6	20·0
2-[2-(3-R″-4-*Oxo-2-thiothiazolidin-5-ylidene*)*prop*-1-*ylidene*]-4-(A-2-*ylidene-ethylidene*)-3-*methylthiazolid-5-one* ($m = n = 1$; R′ = Me)											
		R″									
3-Ethylbenzoxazolin-		$CH_2 \cdot CO_2Et$	37	Green needles	264	665	$C_{25}H_{23}O_5N_3S_3$	7·6	—	7·75	—
3-Ethyl-4 : 5-diphenyloxazolin		$CH_2 \cdot CH{:}CH_2$	38	,,	275	671	$C_{32}H_{29}O_3N_3S_3$	7·05	—	7·05	—
3-Ethyl-4 : 5-diphenylthiazolin		,,	54	Green-bronze needles	277	730	$C_{32}H_{29}O_2N_3S_4$	6·95	20·7	6·85	20·8
2-[4-(3-*Ethoxycarbonylmethyl*-4-*oxo*-2-*thiothiazolidin*-5-*ylidene*)*but*-2-*en*-1-*ylidene*]-4-(A-2-*ylidene-ethylidene*)-3-*methylthiazolid*-5-*one* ($m = 1$; $n = 2$; R′ = H, R″ = $CH_2 \cdot CO_2Et$)											
3-Ethylbenzoxazolin			14	Green needles	275	725	$C_{26}H_{25}O_5N_3S_3$	7·55	17·25	7·55	17·3
3-Ethylbenzothiazolin			21	Green-gold	273	758	$C_{26}H_{25}O_4N_3S_4$	7·25	22·4	7·35	22·4
3-Ethyl-4 : 5-diphenyloxazolin			11·5	Bronze flakes	305	755	$C_{34}H_{31}O_5N_3S_3$	6·4	14·3	6·4	14·6
3-Ethyl-4 : 5-diphenylthiazolin			27	Green flakes	298	780	$C_{34}H_{31}O_4N_3S_4$	6·1	19·1	6·25	19·0

* R = Et.

interest because these chain groups considerably increase the solubility of the dyes, which otherwise are difficultly soluble in common organic solvents. As with the simpler dyes, replacement of R″ = H by R″ = SEt in (IX) causes a strong bathochromic shift.

Similarly, quaternized oxamines (see preceding paper) condensed with (III; $m = 0$) to give complex dyes (X). These, like the lower vinylogues (preceding paper) are much lighter in colour than the related complex *mero*cyanines. The details of the complex dyes are given in Tables 1—4.

Even more complex tetranuclear dyes (XI—XIII) have also been synthesized from (IX; R″ = OEt or SEt; $m = 0$), where the end ketonic nucleus is 3-ethoxycarbonylmethyl-rhodanine, by a repetition of the procedure used in making the trinuclear dyes. Dyes (XI) and (XII) are remarkable in showing a lower m. p. than the parent trinuclear dyes, and are soluble in benzene or acetone. Their main absorption band lies almost completely in the infra-red region, a phenomenon which is believed to be unique amongst non-ionic dyes. The degraded blue colour of their solutions is a result of minor absorption bands which appear to be characteristic of these dyes.

EXPERIMENTAL

Determinations of $\lambda_{max.}$ refer to MeOH solution unless otherwise stated.

3-*Ethoxycarbonylmethyl-5-ethylidene-2-thiothiazolid-4-one.*—3-Ethoxycarbonylmethylrhodanine (2·2 g.), acetaldehyde (1 c.c.), acetic anhydride (10 c.c.), and anhydrous sodium acetate (1·2 g.) were refluxed for 1 hr. on the steam-bath, with the addition of acetaldehyde (1 c.c.) every 15 min. Acetic acid (5 c.c.) was added and the mixture poured into water, to give a yellow oil which soon solidified. The *product* (2·45 g., 100%) formed slender, pale yellow needles, m. p. 69°, from *iso*propanol (Found: C, 44·3; H, 4·9; S, 25·9. $C_9H_{11}O_3NS_2$ requires C, 44·05; H, 4·5; S, 26·15%).

3-*Allyl-5-ethylidene-2-thiothiazolid-4-one.*—3-Allylrhodanine (8·65 g.) anhydrous sodium acetate (6·0 g.), acetic anhydride (50 c.c.), and acetaldehyde (10 c.c.) were heated for 1 hr. in an autoclave in a steam-bath. The mixture was decomposed with dilute acetic acid, and the oil taken up in ether and distilled. The *product* (6·45 g., 65%) had b. p. 119—123°/3 mm., and formed yellow needles, m. p. 37°, from *iso*propanol (Found: S, 32·25. $C_8H_9ONS_2$ requires S, 32·2%).

5-*But-2′-en-1′-ylidene-3-ethoxycarbonylmethyl-2-thiothiazolid-4-one.*—3-Ethoxycarbonyl-methylrhodanine (11·0 g.), crotonaldehyde (9·0 c.c.), acetic anhydride (75 c.c.), and anhydrous sodium acetate (6·0 g.) were refluxed together for 10 min. Most of the solvent was removed under reduced pressure, and the residue was shaken with water (100 c.c.). The *product* soon solidified, forming orange needles, m. p. 104° (6·0 g., 44·5%), from *iso*propanol (Found: C, 48·85; H, 5·05; S, 23·4. $C_{11}H_{13}O_3NS_2$ requires C, 48·7; H, 4·8; S, 23·6%).

3-*Allyl-5-but-2′-en-1′-ylidene-2-thiothiazolid-4-one* was obtained similarly in 51·5% yield as orange-yellow needles, m. p. 92°, from *iso*propanol. The solutions in the latter solvent should be chilled rapidly to prevent a slight stickiness (Found: C, 53·1; H, 5·0; S, 28·05. $C_{10}H_{11}ONS_2$ requires C, 53·3; H, 4·9; S, 28·45%).

5-*But-2′-en-1′-ylidene-3-ethyl-2-thiothiazolid-4-one* formed brown flakes, m. p. 87—88°, from *iso*propanol (63% yield) (Found: C, 51·15; H, 5·5; S, 29·9. $C_9H_{11}ONS_2$ requires C, 51·25; H, 5·2; S, 30·3%).

3-*Ethoxycarbonylmethyl-5-prop-2′-ylidene-2-thiothiazolid-4-one.*—3-Ethoxycarbonylmethyl-rhodanine (22·0 g.), powdered anhydrous zinc chloride (30·0 g.), and dry acetone (250 c.c.) were heated for 4 hr. in an autoclave in a steam-bath. Water (1 l.) was added, to precipitate the *product* which solidified. It (16·6 g., 64%) formed soft, pale yellow needles, m. p. 75°, from *iso*propanol (Found: C, 46·1; H, 5·1; N, 5·35; S, 24·5. $C_{10}H_{13}O_3NS_2$ requires C, 46·3; H, 5·0; N, 5·4; S, 24·7%).

3-*Carboxymethyl-5-prop-2′-ylidene-2-thiothiazolid-4-one* was obtained similarly in 26% yield as pale yellow flakes, m. p. 162—168° from aqueous ethanol (Found: C, 41·6; H, 4·1; S, 27·5. $C_8H_9O_3NS_2$ requires C, 41·65; H, 3·9; S, 27·7%).

3-*Allyl-5-prop-2′-ylidene-2-thiothiazolid-4-one.*—3-Allylrhodanine (17·3 g.), zinc chloride (27 g.), and acetone (250 c.c.) were heated for 8 hr. in an autoclave in a steam-bath. The solid (18·5 g., 87%) obtained on precipitation with water formed pale, lemon-yellow needles, m. p. 53°, from *iso*-propanol (Found: C, 50·3; H, 5·15; S, 30·1. $C_9H_{11}ONS_2$ requires C, 50·7; H, 5·15; S, 30·05%).

3-*Ethoxycarbonylmethyl-5-(3-oxobut-2-ylidene)-2-thiothiazolid-4-one* (V; R = $CH_2{\cdot}CO_2Et$).—

3-Ethoxycarbonylmethylrhodanine (4·4 g.), diacetyl (1·8 c.c.), powdered zinc chloride (5·4 g.), and dioxan (10 c.c.) were heated for 5 hr. on a steam-bath. Addition of water (25 c.c.) to the deep yellow solution precipitated an oil which partly crystallized. The aqueous layer was decanted and the residue triturated with ethanol (15 c.c.). The solid (1·8 g., 31·5%), washed with ethanol formed long yellow needles, m. p. 111°, from ethanol (Found: C, 46·2; H, 4·3; N, 4·9; S, 21·9. $C_{11}H_{13}O_4NS_2$ requires C, 46·0; H, 4·55; N, 4·9; S, 22·3%).

3-*Carboxymethyl*-5-(3-*oxobut*-2-*ylidene*)-2-*thiothiazolid*-4-*one* (V; R = $CH_2 \cdot CO_2H$).—3-Carboxymethylrhodanine (7·65 g.), diacetyl (3·6 c.c.), zinc chloride (10·8 g.), and dioxan (20 c.c.) were heated for 5 hr. on a steam-bath. The addition of water precipitated yellow grains. The *product* (7·15 g., 77·5%) formed fine, yellow needles, m. p. 207°, from methanol (Found: C, 41·9; H, 3·5; S, 24·6. $C_9H_9O_4NS_2$ requires C, 41·7; H, 3·5; S, 24·7%).

When the reaction was carried out in *n*-butanol for 20 hr., the n-*butyl ester* (7·7 g.) was obtained and formed long yellow needles, m. p. 58—59°, from methanol (Found: C, 49·5; H, 5·4; N, 4·35; S, 20·4. $C_{13}H_{17}O_4NS_2$ requires C, 49·5; H, 5·4; N, 4·45; S, 20·35%).

5-1′-*Methoxycarbonylethylidene*-3-*methoxycarbonylmethyl*-2-*thiothiazolid*-4-*one* (VI; R = Me).—3-Carboxymethylrhodanine (9·5 g.), pyruvic acid (5 c.c.), methanol (35 c.c.), and zinc chloride (13·5 g.) were refluxed together for 17 hr. and treated with water. The solid (7·4 g., 59%) obtained on chilling formed flat, yellow needles, m. p. 87—88°, from *iso*propanol (Found: C, 42·1; H, 3·9; S, 21·9. $C_{10}H_{11}O_5NS_2$ requires C, 41·8; H, 3·8; S, 22·15%). Employing other alcohols as solvents gave the *diethyl*, yellow needles, m. p. 68° (from *iso*propanol; 49% yield) (Found: C, 45·2; H, 4·5; S, 20·15. $C_{12}H_{15}O_5NS_2$ requires C, 45·4; H, 4·7; S, 20·2%), and the *di*-n-*butyl ester* (52%), soft, yellow needles, m. p. 52° (from methanol) (Found: C, 51·3; H, 5·9; N, 3·9; S, 17·05. $C_{16}H_{23}O_5NS_2$ requires C, 51·5; H, 6·15; N, 3·75; S, 17·15%).

3-*Allyl*-5-[4-(3-*ethylbenzothiazolin*-2-*ylidene*)*but*-2-*en*-1-*ylidene*]-2-*thiothiazolid*-4-*one* (IV; R″ = H, n = 0, m = 1).—2-Ethylthiobenzothiazole ethotoluene-*p*-sulphonate (2·0 g.), 3-allyl-5-but-2′-en-1′-ylidenerhodanine (1·2 g.), pyridine (10 c.c.), and triethylamine (0·8 c.c.) were heated on the steam-bath for 30 min. Ethanol (20 c.c.) was added and the whole was chilled overnight. The *dye* (1·1 g., 57%) which separated formed blue needles, m. p. 220°, from benzene (Found: N, 7·2; S, 24·75. $C_{19}H_{18}ON_2S_3$ requires N, 7·25; S, 24·9%), $\lambda_{max.}$ 605 mμ.

3-*Allyl*-5-[6-(3-*ethylbenzothiazolin*-2-*ylidene*)*hexa*-2 : 4-*dien*-1-*ylidene*]-2-*thiothiazolid*-4-*one* (IV; R′ = R″ = H, $n = m$ = 1).—2-2′-Acetanilidovinylbenzothiazole ethiodide (2·25 g.), 3-allyl-5-but-2′-en-1′-ylidenerhodanine (1·15 g.), pyridine (10 c.c.), and triethylamine (0·8 c.c.) were heated for 30 min. on a steam-bath and then diluted with ethanol (20 c.c.). The *dye* separated rapidly, forming brilliant, green needles, m. p. 212° (1·0 g., 49·5%), from benzene (Found: N, 6·65; S, 23·25. $C_{21}H_{20}ON_2S_3$ requires N, 6·8; S, 23·3%), $\lambda_{max.}$ 630 mμ.

3-*Allyl*-5-{1-[3-*ethylnaphtho*(1′ : 2′-4 : 5)*thiazolin*-2-*ylidene*]*pent*-2-*en*-4-*ylidene*}-2-*thiothiazolid*-4-*one* (IV; n = 0, m = 1, R″ = Me).—2-2′-Acetanilidovinylnaphtho(1′ : 2′-4 : 5)thiazole ethiodide (2·5 g.), 3-allyl-5-prop-2′-ylidenerhodanine (1·1 g.), pyridine (10 c.c.), and triethylamine (0·8 c.c.) were heated on a steam-bath for 30 min. Ethanol (20 c.c.) was added to precipitate 1·4 g. (62·0%) of *dye*. It formed blue needles, m. p. 245°, from pyridine–ethanol (Found: N, 6·4; S, 21·2. $C_{24}H_{22}ON_2S_3$ requires N, 6·2; S, 21·35%), $\lambda_{max.}$ 610 mμ.

3-*Ethoxycarbonylmethyl*-5-[1-(3-*ethylbenzothiazolin*-2-*ylidene*)-5-*oxohex*-2-*en*-4-*ylidene*]-2-*thiothiazolid*-4-*one* (IV; n = 0, m = 1, R″ = Ac).—2-2′-Acetanilidovinylbenzothiazole ethotoluene-*p*-sulphonate (2·25 g.), 5-(3-oxobutan-2-ylidene)-3-ethoxycarbonylmethylrhodanine (1·45 g.), ethanol (10 c.c.), and triethylamine were refluxed together for 15 min. The dye was precipitated as a tar, on chilling of the mixture. Ethanol (10 c.c.) was added and the mixture was boiled until crystallization set in. The *dye* (1·0 g., 42%) formed a dark blue powder, m. p. 156°, from ethanol (Found: C, 55·6; H, 4·6; N, 5·65. $C_{22}H_{24}O_4N_2S_3$ requires C, 55·75; H, 4·65; N, 5·9%), $\lambda_{max.}$ 653 mμ.

3-*Ethoxycarbonylmethyl*-5-[1-(3-*ethylbenzothiazolin*-2-*ylidene*)-3-*oxobut*-2-*ylidene*]-2-*thiothiazolid*-4-*one* (IV; $m = n$ = 0, R″ = Ac).—2-Ethylthiobenzothiazole ethotoluene-*p*-sulphonate (2·0 g.), 3-ethoxycarbonylmethyl-5-(3-oxobutan-2-ylidene)rhodanine (1·4 g.), ethanol (10 c.c.), and triethylamine (0·8 c.c.) were refluxed together for 5 min. The *dye* separated from the hot solution. It (1·4 g., 62·5%) formed rosettes of blue needles, m. p. 195°, from benzene (Found: N, 6·2; S, 21·35. $C_{20}H_{20}O_4N_2S_3$ requires N, 6·25; S, 21·4%), $\lambda_{max.}$ 520 mμ.

3-*Methoxycarbonylmethyl*-5-[1-*methoxycarbonyl*-2-(3-*methylthiazolidin*-2-*ylidene*)*ethylidene*]-2-*thiothiazolid*-4-*one* (IV; $m = n$ = 0, R″ = CO_2Me).—2-Methylthiothiazoline methotoluene-*p*-sulphonate (1·6 g.), 3-methoxycarbonyl-5-1′-methoxycarbonylethylidenerhodanine (1·45 g.), ethanol (10 c.c.), and triethylamine (0·8 c.c.) were refluxed together for 10 min. The *dye* (1·0 g., 51·5%) separated as an oil and then crystallized slowly when chilled. It formed red needles or steel-blue prisms, m. p. 178°, from benzene–ethanol (Found: N, 7·05; S, 24·7. $C_{14}H_{16}O_5N_2S_3$ requires N, 7·2; S, 24·75%), $\lambda_{max.}$ 462 mμ.

4-[1-*Ethoxy*-2-(3-*ethylbenzothiazolin*-2-*ylidene*)*ethylidene*]-2-*phenyloxazol*-5-*one* (IV; $n = m = 0$, R″ = OEt).—2-Ethylthiobenzothiazole ethotoluene-*p*-sulphonate (2·0 g.), 4-1′-ethoxyethylidene-2-phenyloxazol-5-one (1·15 g.), *n*-propanol (5 c.c.), and triethylamine (0·8 c.c.) were refluxed together for 10 min., then chilled, and the containing vessel was scratched. The *dye* (0·8 g., 50%) formed orange threads, m. p. 198°, from ethanol (Found: C, 66·95; H, 5·05; N, 7·3; S, 8·3. $C_{22}H_{20}O_3N_2S$ requires C, 67·3; H, 5·1; N, 7·15; S, 8·15%), $\lambda_{max.}$ 480 mμ.

4-[1-*Ethoxy*-2-(1-*ethyl*-1 : 2-*dihydroquinolin*-2-*ylidene*)*ethylidene*]-2-*ethylthiothiazol*-5-*one*.—4-1′-Ethoxyethylidene-2-ethylthiothiazol-5-one (1·2 g.), 2-ethylthioquinoline ethotoluene-*p*-sulphonate (1·95 g.), pyridine (10 c.c.), and triethylamine (0·8 c.c.) were heated together for 15 min. on the steam-bath. Ethanol (20 c.c.) was added and the solution was chilled. The *dye* (1·05 g., 54·5%), after being washed with ethanol, formed golden-green crystals, m. p. 176°, from methanol (Found: C, 62·55; H, 5·8; N, 6·95; S, 16·4. $C_{20}H_{22}O_2N_2S_2$ requires C, 62·2; H, 5·7; N, 7·25; S, 16·6%). λ_{max} 545 mμ.

The following dyes are a selection of those obtained similarly.

2-[1-*Ethoxy*-2-(3-*ethylbenzothiazolin*-2-*ylidene*)*ethylidene*]*indane*-1 : 3-*dione* formed red needles (74% yield), m. p. 195—196°, from ethanol (Found: C, 69·8; H, 4·95. $C_{22}H_{19}O_3NS$ requires C, 70·0; H, 5·05%). $\lambda_{max.}$ 470 mμ.

4-[1-*Ethoxy*-2-(3-*ethylbenzothiazolin*-2-*ylidene*)*ethylidene*]-3-*phenyl*iso*oxazol*-5-*one* formed pink flakes with a blue reflex (47% yield), m. p. 185°, from ethanol (Found: N, 7·45; S, 8·2. $C_{22}H_{20}O_3N_2S$ requires N, 7·15; S, 8·15%), $\lambda_{max.}$ 448 mμ.

4-[1-*Ethoxy*-2-(3-*ethylbenzothiazolin*-2-*ylidene*)*ethylidene*]-3-*methyl*-1-*phenylpyrazol*-5-*one* was obtained in 74% yield as soft rosettes of orange-red needles, m. p. 172°, from ethanol (Found: N, 10·4. $C_{23}H_{23}O_2N_3S$ requires N, 10·35%), $\lambda_{max.}$ 548 mμ.

3-*Ethoxycarbonyl*-5-[1-*ethoxy*-2-(3-*ethylbenzothiazolin*-2-*ylidene*)*ethylidene*]-2-*thiothiazolid*-4-*one*, obtained in 52% yield, formed rosettes of magenta needles, m. p. 127°, from benzene–light petroleum (b. p. 60—80°) (Found: S, 21·1. $C_{20}H_{22}O_4N_2S_3$ requires S, 21·35%), $\lambda_{max.}$ 516 mμ.

4-[1-*Ethoxy*-4-(3-*ethylbenzoxazolin*-2-*ylidene*)*but*-2-*en*-1-*ylidene*]-2-*phenyloxazol*-5-*one* (IV; $n = 0$, $m = 1$, R″ = OEt).—2-2′-Acetanilidovinylbenzoxazole ethiodide (2·2 g.), 4-1′-ethoxyethylidene-2-phenyloxazol-5-one (1·2 g.), ethanol (10 c.c.), and triethylamine (0·8 c.c.) were refluxed together for 30 min. The whole solidified when chilled. The *dye* (1·2 g., 85%) formed magenta threads, m. p. 191°, from benzene–ethanol (Found: C, 71·55; H, 5·6; N, 7·1. $C_{24}H_{22}O_4N_2$ requires C, 71·7; H, 5·45; N, 6·95%), $\lambda_{max.}$ 545 mμ.

2-*Benzylthio*-4-[1-*ethoxy*-4-(3-*ethylbenzoxazolin*-2-*ylidene*)*but*-2-*en*-1-*ylidene*]*thiazol*-5-*one* was obtained in 35% yield as blue needles, m. p. 122°, from ethanol (Found: C, 64·5; H, 5·1; N, 6·25; S, 13·9. $C_{25}H_{24}O_3N_2S_2$ requires C, 64·7; H, 5·2; N, 6·05; S, 13·8%), $\lambda_{max.}$ 570 mμ.

3-*Ethoxycarbonylmethyl*-5-[1-*ethoxy*-4-(3-*ethylbenzothiazolin*-2-*ylidene*)*but*-2-*en*-1-*ylidene*]-2-*thiothiazolid*-4-*one*, obtained in 88% yield, formed soft, deep blue needles, m. p. 171°, from benzene–light petroleum (b. p. 60—80°) (Found: N, 5·7; S, 20·1. $C_{22}H_{24}O_4N_2S_3$ requires N, 5·9; S, 20·2%), $\lambda_{max.}$ 610 mμ.

3-*Ethoxycarbonylmethyl*-5-{4-[3-*ethylnaphtho*(1′ : 2′-4 : 5)*thiazolin*-2-*ylidene*]-1-*methoxybut*-2-*en*-1-*ylidene*}-2-*thiothiazolid*-4-*one* (IV; $n = 0$, $m = 1$, R″ = OMe) was obtained in 43% yield as green crystals, m. p. 184°, from benzene–ethanol (Found: N, 5·45; S, 18·7. $C_{25}H_{24}O_4N_2S_3$ requires N, 5·45; S, 18·75%), $\lambda_{max.}$ 642 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-5-[1-*ethoxy*-6-(3-*ethylbenzothiazolin*-2-*ylidene*)*hexa*-2:4-*dien*-1-*ylidene*]-2-*thiothiazolid*-4-*one* (IV; $n = m = 1$, R′ = H, R″ = OEt).—2-4′-Acetanilidobuta-2 : 4-dienylbenzothiazole ethiodide (2·4 g.), 3-ethoxycarbonylmethyl-5-1′-ethoxyethylidenerhodanine (1·5 g.), ethanol (20 c.c.), and triethylamine (0·8 c.c.) were refluxed together for 2 min. The mixture was chilled to give a tar. The liquor was decanted, and the tar was washed with ethanol and was then refluxed with ethanol (60 c.c.) until crystallization set in. The dye (1·1 g., 44%) was dissolved in benzene (25 c.c.) and filtered and an equal volume of ethanol was added. The whole was concentrated to 20 c.c. and chilled. The dye crystallized and the process was repeated. The *dye* formed small, bright green crystals, m. p. 187° (Found: C, 57·7; H, 5·25; N, 5·45. $C_{24}H_{26}O_4N_2S_3$ requires C, 57·4; H, 5·2; N, 5·55%), $\lambda_{max.}$ 620 mμ.

3-*Ethoxycarbonylmethyl*-5-[2-(3-*ethylbenzothiazolin*-2-*ylidene*)-1-*ethylthioethylidene*]-2-*thiothiazolid*-4-*one* (IV; $n = m = 0$, R″ = SEt).—2-Ethylthiobenzothiazole ethotoluene-*p*-sulphonate (1·3 g.), 3-ethoxycarbonylmethyl-5-1′-ethylthioethylidenerhodanine (1·0 g.), ethanol (10 c.c.), and triethylamine (0·5 c.c.) were refluxed together for 5 min. The dye (0·9 g., 58%) crystallized when the solution was chilled, and was obtained as flat, green needles, m. p. 157°, from ethanol

(Found : C, 51·7; H, 5·05; N, 6·25; S, 27·4. $C_{20}H_{22}O_3N_2S_4$ requires C, 51·5; H, 4·7; N, 6·0; S, 27·45%), $\lambda_{max.}$ 561 mμ.

3-*Ethoxycarbonylmethyl*-5-[1-*ethylthio*-2-(3-*methylthiazolidin*-2-*ylidene*)*ethylidene*]-2-*thiothiazolid*-4-*one*.—2-Methylthiothiazoline methotoluene-*p*-sulphonate (1·6 g.), 3-ethoxycarbonylmethyl-5-1′-ethylthioethylidenerhodanine (1·5 g.), pyridine (10 c.c.), and triethylamine (0·8 c.c.) were heated together on the steam-bath for 15 min. and diluted with water (25 c.c.). The *dye* was precipitated as an oil which crystallized rapidly. It (1·3 g., 64·5%) formed flat violet needles, m. p. 139—143°, after two crystallizations from ethanol (Found : C, 44·3; H, 4·75; N, 7·1; S, 31·55. $C_{15}H_{20}O_3N_2S_4$ requires C, 44·5; H, 4·95; N, 6·95; S, 31·7%), $\lambda_{max.}$ 515 mμ. A third crystallization from a more dilute alcoholic solution caused glossy, red flakes (0·9 g.; m. p. 147—149°) to separate, which had m. p. 152—154° after two more crystallizations from alcohol (Found : C, 44·75; H, 5·05; N, 7·25; S, 31·95%), $\lambda_{max.}$ 515 mμ.

The filtrate from the first crystallization gave, on concentration, soft red needles (0·15 g.), m. p. 131°, which on recrystallization from ethanol formed flat red needles, m. p. 131° (Found : C, 45·0; H, 5·3; N, 7·25; S, 32·0%), $\lambda_{max.}$ 515 mμ.

3-*Ethoxycarbonylmethyl*-5-[2-(3-*ethylbenzothiazolin*-2-*ylidene*)-1-p-*tolylthioethylidene*]-2-*thiothiazolid*-4-*one* (IV; $n = m = 0$, R″ = *p*-C_6H_4Me·S·), obtained similarly in 34% yield, formed flat, brassy needles, m. p. 237—239°, from benzene–ethanol (Found : N, 5·25; S, 24·5. $C_{25}H_{24}O_3N_2S_4$ requires N, 5·3; S, 24·25%), $\lambda_{max.}$ 566 mμ.

3-*Ethoxycarbonylmethyl*-5-[2-(3-*ethylbenzothiazolin*-2-*ylidene*)-1-n-*octylthioethylidene*]-2-*thiothiazolid*-4-*one* (IV; $n = m = 0$, R″ = *n*-C_8H_{17}·S·) obtained in 41% yield formed soft, dark green flakes, m. p. 103°, from ethanol (Found : N, 4·95; S, 23·3. $C_{26}H_{34}O_3N_2S_4$ requires N, 5·1; S, 23·3%), $\lambda_{max.}$ 570 mμ.

4-[2-(3-*Ethylbenzothiazolin*-2-*ylidene*)-1-*ethylthioethylidene*]-2-*ethylthiothiazol*-5-*one*.—2-Ethylthiobenzothiazole ethotoluene-*p*-sulphonate (2·0 g.), 2-ethylthio-4-1′-ethylthioethylidenethiazol-5-one (1·1 g.), ethanol (10 c.c.), and triethylamine (0·8 c.c.) were refluxed together for 5 min. The *dye* (1·1 g., 54%) which separated on chilling formed large, golden-green aggregates, m. p. 113°, from ethanol (Found : C, 52·75; H, 4·6; N, 7·0; S, 31·3. $C_{18}H_{20}ON_2S_4$ requires C, 52·95; H, 4·9; N, 6·85; S, 31·4%), $\lambda_{max.}$ 557 mμ.

3-*Ethoxycarbonylmethyl*-5-[4-(3-*ethylbenzoxazolin*-2-*ylidene*)-1-*ethylthiobut*-2-*en*-1-*ylidene*]-2-*thiothiazolid*-4-*one* (IV; $n = 0$, $m = 1$, R″ = EtS).—2-2′-Acetanilidovinylbenzoxazole ethiodide (1·45 g.), 3-ethoxycarbonylmethyl-5-1′-ethylthioethylidenerhodanine (1·0 g.), ethanol (10 c.c.), and triethylamine (0·5 c.c.) were refluxed for 5 min. The dye (0·7 g., 44%) which separated on chilling formed blue-green threads, m. p. 172°, from ethanol (Found : C, 55·6; H, 5·05; N, 5·8; S, 19·9. $C_{22}H_{24}O_4N_2S_3$ requires C, 55·5; H, 5·05; N, 5·9; S, 20·2%), $\lambda_{max.}$ 608 mμ.

3-*Ethoxycarbonylmethyl*-5-[4-(3-*ethylbenzothiazolin*-2-*ylidene*]-1-*ethylthiobut*-2-*en*-1-*ylidene*]-2-*thiothiazolid*-4-*one* was obtained in 69% yield and formed flat, blue-green needles, m. p. 174°, from benzene–light petroleum (b. p. 60—80°) (Found : N, 5·85; S, 25·85. $C_{22}H_{24}O_3N_2S_4$ requires N, 5·7; S, 26·0%), $\lambda_{max.}$ 643 mμ.

4-[4-(3-*Ethylbenzothiazolin*-2-*ylidene*)-1-*ethylthiobut*-2-*en*-1-*ylidene*]-2-*ethylthiothiazol*-5-*one* was obtained in 39% yield as flat golden-green needles, m. p. 162°, from benzene–ethanol (Found : S, 30·75. $C_{20}H_{22}ON_2S_4$ requires S, 30·95%), $\lambda_{max.}$ 638 mμ.

Hydrolysis of (IV; $n = m = 0$, R″ = OEt).—3-*Carboxymethyl*-5-(3-*ethylbenzothiazolin*-2-*ylidene*)*acetyl*-4-*hydroxy*-2-*thiothiazoline* (VII). 3-Ethoxycarbonylmethyl-5-[1-ethoxy-2-(3-ethylbenzothiazolin-2-ylidene)ethylidene]-2-thiothiazolid-4-one (0·9 g.), ethanol (20 c.c.), and a solution of potassium hydroxide (0·45 g.) in water (10 c.c.) were refluxed together on a steam-bath for 75 min. The orange solution was acidified to give an orange solid *dye* (0·6 g., 76%). It formed fine, rust red needles, m. p. 222°, from ethanol. It gave a yellow solution in aqueous sodium carbonate (Found : C, 48·5; H, 3·7; N, 6·8; S, 24·55. $C_{16}H_{14}O_4N_2S_3$ requires C, 48·75; H, 3·55; N, 7·1; S, 24·4%), $\lambda_{max.}$ 440 mμ.

3-*Carboxymethyl*-5-(1-*ethyl*-1 : 2-*dihydroquinolin*-2-*ylidene*)*acetyl*-4-*hydroxy*-2-*thiothiazoline* was obtained similarly in 51% yield as violet needles, m. p. 237°, $\lambda_{max.}$ 488 mμ in methanolic triethylamine, by dissolving the dye in alcoholic triethylamine and acidifying the solution with acetic acid (Found : N, 7·25; S, 16·3. $C_{18}H_{16}O_4N_2S_2$ requires N, 7·2; S, 16·5%).

3-*Allyl*-5-(3-*ethylbenzothiazolin*-2-*ylidene*)*acetyl*-4-*hydroxy*-2-*thiothiazoline* was obtained in 64% yield as pink needles, m. p. 199°, from ethanol (Found : C, 54·15; H, 4·55; S, 25·5. $C_{17}H_{16}O_2N_2S_3$ requires C, 54·25; H, 4·25; S, 25·5%, $\lambda_{max.}$ 442 mμ in ethanolic triethylamine.

Complex mero*Cyanines*.—The general procedure for these dyes (IX—XIII) consisted of fusing (IV) (0·01 mol.) with methyl toluene-*p*-sulphonate (0·01—0·015 mol.) at 120—140° for 30—120 min., adding (III) (0·01 mol.), pyridine (20 c.c.), and triethylamine (0·011 mol.) to the homogeneous melt or solid and heating the whole on the steam-bath for 10 min. The addition of ethanol (50 c.c.) then usually caused the dye to crystallize. It was collected, washed with ethanol, and recrystallized from benzene, or was dissolved in hot pyridine and treated with 2—3 times the volume of hot ethanol. In general 2—3 recrystallizations were necessary to obtain a pure specimen.

3-*Allyl*-2-[2-(3-*allyl*-4-*oxo*-2-*thiothiazolidin*-5-*ylidene*)*prop*-1-*ylidene*]-5-[1-(3-*ethylbenzothiazolin*-2-*ylidene*)*prop*-2-*ylidene*]*thiazolid*-4-*one* (IX; $m = 0$, R = H, R′ = R″ = Me, Y = S, X = $N{\cdot}C_3H_5$) was obtained in 19% yield and formed soft, dark green needles, m. p. 276°, from pyridine–ethanol (Found: N, 7·45; S, 23·2. $C_{27}H_{27}O_2N_3S_4$ requires N, 7·6; S, 23·5%), $\lambda_{max.}$ 648 mμ in pyridine.

3-*Allyl*-2-[2-(3-*allyl*-4-*oxo*-2-*thiothiazolidin*-5-*ylidene*)-2-*ethoxyethylidene*]-5-[1-(3-*ethylbenzothiazolin*-2-*ylidene*)*but*-2-*ylidene*]*thiazolid*-4-*one* (IX; $m = 0$, R = H, R′ = Et, R″ = OEt, Y = S, X = $N{\cdot}C_3H_5$) was obtained in 45% yield and formed soft, green needles, m. p. 209°, from pyridine–ethanol (Found: N, 6·9; S, 21·3. $C_{29}H_{31}O_3N_3S_4$ requires N, 7·05; S, 21·45%), $\lambda_{max.}$ 654 mμ in pyridine.

3-*Allyl*-2-[2-(3-*allyl*-4-*oxo*-2-*thiothiazolidin*-5-*ylidene*)-2-*ethoxyethylidene*]-5-[1-*ethoxy*-2-(3-*ethylbenzothiazolin*-2-*ylidene*)*ethylidene*]*thiazolid*-4-*one* (IX; $m = 0$, R = H, R′ = R″ = OEt, Y = S, X = $N{\cdot}C_3H_5$) was obtained in 12% yield as soft, green needles, m. p. 200°, from benzene–ethanol (Found: N, 6·85; S, 20·9. $C_{29}H_{31}O_4N_3S_4$ requires N, 6·85; S, 20·9%), $\lambda_{max.}$ 645 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-2-[2-(3-*ethoxycarbonylmethyl*-4-*oxo*-2-*thiothiazolidin*-5-*ylidene*)-2-*ethoxyethylidene*]-5-[2-(3-*methylthiazolidin*-2-*ylidene*)*prop*-1-*ylidene*]*thiazolid*-4-*one* (IX; $m = 0$, R = Me, R′ = H, R″ = OEt, X = $N{\cdot}CH_2{\cdot}CO_2Et$, Y = S). 3-Ethoxycarbonylmethyl-5-[2-(3-methylthiazolidin-2-ylidene)prop-1-ylidene]-2-thiothiazolid-4-one (1·8 g.) and methyl toluene-*p*-sulphonate (1·0 g.) were fused at 130° for 1 hr. To the viscous melt was added 3-ethoxycarbonylmethyl-5-1′-ethoxyethylidenerhodanine (1·45 g.), ethanol (10 c.c.), and triethylamine (0·8 c.c.), and the whole was refluxed for 10 min. on a steam-bath. The crystals (0·9 g., 30%) collected after chilling formed brilliant green crystals, m. p. 194—195°, from benzene–ethanol (Found: N, 6·5; S, 20·8. $C_{25}H_{31}O_7N_3S_4$ requires N, 6·85; S, 20·9%), $\lambda_{max.}$ 605 mμ in pyridine.

3-*Allyl*-5-[1-(3-*ethylbenzothiazolin*-2-*ylidene*)*but*-2-*ylidene*]-2-[2-*ethylthio*-2-(2-*ethylthio*-5-*oxothiazolin*-4-*ylidene*)*ethylidene*]*thiazolid*-4-*one* (IX; $m = 0$, R = H, R′ = Et, R″ = SEt, X = $N{\cdot}C_3H_5$, Y = S) was obtained in 50% yield as black needles (gold reflex), m. p. 147°, from benzene–ethanol (Found: N, 6·95; S, 26·4. $C_{28}H_{31}O_2N_3S_5$ requires N, 7·0; S, 26·6%), $\lambda_{max.}$ 684 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-5-[2-(3-*ethylbenzothiazolin*-2-*ylidene*)-1-*ethylthioethylidene*]-2-[2-*ethylthio*-2-(2-*ethylthio*-5-*oxothiazolin*-4-*ylidene*)*ethylidene*]*thiazolid*-4-*one* (IX; $m = 0$, R = H, R′ = R″ = SEt, X = $N{\cdot}CH_2{\cdot}CO_2Et$, Y = S), obtained in 29% yield, formed brassy needles, m. p. 186°, from benzene–ethanol (Found: N, 6·5; S, 28·15. $C_{29}H_{33}O_4N_3S_6$ requires N, 6·2; S, 28·3%), $\lambda_{max.}$ 684 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-2-[2-*ethoxy*-2-(2-*ethylthio*-5-*oxothiazolin*-4-*ylidene*)*ethylidene*]-5-{1-*ethoxy*-2-[4-(3-*ethyl*-4 : 5-*diphenylthiazolin*-2-*ylidene-ethylidene*)-5-*oxo*-3-*methylthiazolidin*-2-*ylidene*]*ethylidene*}*thiazolid*-4-*one* (XI; R = R′ = OEt). 2-[2-(3-Ethoxycarbonylmethyl-4-oxo-2-thiothiazolidin-5-ylidene)-2-ethoxyethylidene]-4-(3-ethyl-4 : 5-diphenylthiazolin-2-ylidene-ethylidene)-3-methylthiazolid-5-one (1·05 g.) and methyl toluene-*p*-sulphonate (0·5 g.) were fused at 130° in an oil-bath for ½ hr. The melt had then solidified. The cake was broken up, 4-1′-ethoxyethylidene-2-ethylthiothiazol-5-one (0·4 g.), ethanol (20 c.c.), and triethylamine (0·25 c.c.) were added and the whole was refluxed for 5 min. The *dye* separated as an oil from the cooled solution, then crystallized. It (0·75 g., 55·5%) was recrystallized from pyridine–ethanol (green needles, m. p. 244°), then twice from benzene–ethanol, and formed coppery red flakes, m. p. 247° (Found: C, 57·95; H, 4·8; N, 6·3; S, 17·95. $C_{43}H_{44}O_7N_4S_5$ requires C, 58·1; H, 5·0; N, 6·3; S, 18·05%), $\lambda_{max.}$ 772 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-5-{2-[4-(3-*ethyl*-4 : 5-*diphenylthiazolin*-2-*ylidene-ethylidene*)-5-*oxo*-3-*methylthiazolidin*-2-*ylidene*]-1-*ethylthioethylidene*}-2-[2-*ethylthio*-2-(2-*ethylthio*-5-*oxothiazolin*-4-*ylidene*)*ethylidene*]*thiazolid*-4-*one* (XI; R = R′ = SEt). 2-[2-(3-Ethoxycarbonylmethyl-4-oxo-2-thiothiazolidin-5-ylidene)-2-ethylthioethylidene]-4-(3-ethyl-4 : 5-diphenylthiazolin-2-ylidene)-3-methylthiazolid-5-one (1·4 g.) and methyl toluene-*p*-sulphonate (0·5 g.) were fused at 130° in an oil-bath for 1 hr. 2-Ethylthio-4-1′-ethylthioethylidenethiazol-5-one (0·6 g.), pyridine (15 c.c.), and triethylamine (0·4 c.c.) were added and the whole was heated for 5 min. on a steam-bath. Ethanol (20 c.c.) was added and heating continued for a further 10 min. After the addition of a similar quantity of ethanol the solution was chilled. The *dye* (1·3 g., 71·5%) which separated was washed with ethanol and acetone and obtained as soft bronze needles, m. p. 258°, after two recrystallizations from benzene (Found : C, 56·15; H, 4·8; N, 6·0; S, 24·2. $C_{43}H_{44}O_5N_4S_7$ requires C, 56·0; H, 4·8; N, 6·1; S, 24·4%), $\lambda_{max.}$ 865 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-5-{2-[4-(3-*ethylbenzoselenazolin*-2-*ylidene*-*ethylidene*)-5-*oxo*-3-*methylthiazolidin*-2-*ylidene*]-1-*ethylthioethylidene*}-2-[2-*ethylthio*-2-(2-*ethylthio*-5-*oxothiazolin*-4-*ylidene*)-*ethylidene*]*thiazolid*-4-*one* (XI; R = R′ = SEt) was obtained similarly in 62% yield and formed dark golden threads, m. p. 220°, after three recrystallizations from benzene (Found : C, 48·45; H, 4·5; N, 6·85. $C_{35}H_{38}O_5N_4S_6Se$ requires C, 48·6; H, 4·4; N, 6·45%), $\lambda_{max.}$ 822 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-2-(3-*ethoxycarbonylmethyl*-4-*oxo*-2-*thiothiazolidin*-5-*ylidene*)-5-{2-[4-(3-*ethylbenzoselenazolin*-2-*ylidene*-*ethylidene*)-5-*oxo*-3-*methylthiazolidin*-2-*ylidene*]-1-*ethylthioethylidene*}*thiazolid*-4-*one* (XIII) was obtained in 75% yield as brilliant golden flakes, m. p. 288°, from pyridine (Found : C, 47·2; H, 4·1; N, 6·65. $C_{33}H_{34}O_7N_4S_5Se$ requires C, 47·3; H, 4·05; N, 6·7), $\lambda_{max.}$ 765 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-2-[2-(3-*ethoxycarbonylmethyl*-4-*oxo*-2-*thiothiazolidin*-5-*ylidene*)-2-*ethylthioethylidene*]-5-{2-[4-(3-*ethylbenzoselenazolin*-2-*ylidene*-*ethylidene*)-5-*oxo*-3-*methylthiazolidin*-2-*ylidene*]-1-*ethylthioethylidene*}*thiazolid*-4-*one* (XII) was obtained in 73% yield and formed dark, bronze threads, m. p. 260°, from pyridine–ethanol (Found : C, 47·95; H, 4·35; N, 6·0; S, 20·5. $C_{37}H_{40}O_7N_4S_6Se$ requires C, 48·1; H, 4·35; N, 6·05; S, 20·8%), $\lambda_{max.}$ 832 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-5-{2-[4-(3-*ethylthiazolidin*-2-*ylidene*-*ethylidene*)-5-*oxo*-3-*methylthiazolidin*-2-*ylidene*]-1-*ethylthioethylidene*}-2-[2-*ethylthio*-2-(2-*ethylthio*-5-*oxothiazolin*-4-*ylidene*)*ethylidene*]*thiazolid*-4-*one* (XI; R = R′ = SEt) obtained in 62% yield formed flat, golden needles, m. p. 243°, from pyridine–ethanol (Found : N, 7·35; S, 29·05. $C_{31}H_{38}O_5N_4S_7$ requires N, 7·25; S, 29·1%), $\lambda_{max.}$ 782 mμ in pyridine.

3-*Ethoxycarbonylmethyl*-2-[2-*ethoxy*-2-(2-*ethylthio*-5-*oxothiazolin*-4-*ylidene*)*ethylidene*]-5-{2-4-(3-*ethylthiazolidin*-2-*ylidene*-*ethylidene*)-5-*oxo*-3-*methylthiazolidin*-2-*ylidene*]-1-*ethylthioethylidene*}-*thiazolid*-4-*one* (XI; R = SEt, R′ = OEt), obtained in 87·5% yield, formed tiny golden flakes, m. p. 228°, after recrystallization from benzene, then from pyridine–ethanol (Found : N, 7·3; S, 25·3. $C_{31}H_{38}O_6N_4S_6$ requires N, 7·45; S, 25·5%), $\lambda_{max.}$ 744 mμ in pyridine.

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