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RESEARCH ON SYNTHETIC DYES. LII. CONDENSATION OF N-ARYLQUINALDINE SALTS WITH ACETANILINOMETHYLENEETHYLRHODANINE AND ETHOXYMETHYLENEPHENYLRHODANINE

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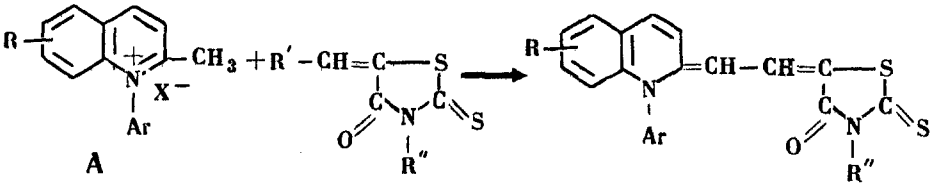
Fifteen merocyanine dyes are prepared by condensing N-arylquinaldine salts with ethoxymethylenephenylrhodanine and acetanilomethyleneethylrhodanine. These have not previously been described in the literature and are characterized. The absorption spectra of the dyes in the visible region are observed.

In continuation of research on N-arylquinaldine salts and their derivatives, certain N-arylquinaldine salts have been condensed with acetanilinomethyleneethylrhodanine and ethoxymethylenephenylrhodanine in order to produce merocyanine dyes. The merocyanines were formed according to the equation:



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Dye	R	Ar	X	R′	R″
I	H	C_6H_5	ClO_4	C_2H_5O	C_6H_5
II	5,6-benzo	C_6H_5	I		
III	6-CH_3	p-$CH_3C_6H_4$	ClO_4		
IV	5,6-benzo	p-$CH_3C_6H_4$	I		
V	5,6-benzo	p-$CH_3OC_6H_4$	ClO_4		
VI	5,6-benzo	p-$CH_3OC_6H_4$	I		
VII	H	α-$C_{10}H_7$	I		
VIII	H	C_6H_5	ClO_4	CH_3CO > N < H_5C_6	C_2H_5
IX	5,6-benzo	C_6H_5	I		
X	6-CH_3	p-$CH_3C_6H_4$	ClO_4		
XI	5,6-benzo	p-$CH_3C_6H_4$	I		
XII	5,6-benzo	p-ClC_6H_4	ClO_4		
XIII	5,6-benzo	p-$CH_3OC_6H_4$	I		
XIV	H	α-$C_{10}H_7$	I		
XV	5,6-benzo	β-$C_{10}H_7$	I		

Amounts of starting substances, product yields, properties, and analytical data for the merocyanines obtained are given in Tables 1 and 2. From the tables it can be seen that the merocyanines, which differ in respect of the presence of diethylamino and phenyl groups at the hetero-atom of the rhodanine group, have practically identical absorption maxima. The bathochromic shift, in comparison with the merocyanines that are rhodanines unsubstituted at the hetero-atom [1], is negligible.

Merocyanines that are derivatives of 5,6-benzoquinaldine and rhodanine unsubstituted at the nitrogen atom have one well-defined maximum. At 592 mμ there is only an inflection. Ethyl- and phenylrhodanine derivatives already exhibit two well-defined maxima. Thus all the merocyanines synthesized have two maxima, the shortwave one being the more intense, save in the case of dye III, where both maxima have the same intensity.

EXPERIMENTAL

Typical methods of synthesizing the dyes are described below.

I-VII. A mixture comprising approximately equimolecular amounts of quaternary salt A, and ethoxymethylenephenylrhodanine [2], 4-8 drops anhydrous alcohol, and a few drops of triethylamine is gently refluxed for 20-30 min on a steam bath. The crystals which separate on cooling are filtered off and washed with alcohol and ether. Dyes IV-VII are washed first with acetic acid, then with alcohol, and finally with ether.

TABLE 1

Synthesis and properties of merocyanines prepared from N-arylquinaldine salts and ethoxymethylenephenylrhodanine

Dye	Reacted: Quaternary salt, g (mmole)	Reacted: Ethoxymethylenephenylrhodanine, g (mmole)	Reacted: Absolute alcohol ml	Heating time, min	Mp, °C (decomp.)	Recrystallizing solvent	Appearance	λmax, mμ	Formula	N, % Found	N, % Calc.	Yield, %
I	0.12 (0.38)	0.1 (0.38)	6	20	289—291	Acetic acid	Pale green glistening crystals	545 580	$C_{26}H_{18}N_2OS_2$	6.45 6.39	6.38	72.7
II	0.32 (0.81)	0.22 (0.83)	8	30	209—211	Acetic acid	Glistening green crystals	564 595	$C_{30}H_{20}N_2OS_2$	5.57 5.72	5.73	87.5
III	0.35 (1.01)	0.27 (1.02)	8	25	285—287	Acetic acid	Glistening green crystals	548 583	$C_{28}H_{22}N_2OS_2$	5.79 5.82	6.00	63.8
IV	0.4 (0.97)	0.26 (0.99)	8	20	295—297	Acetic acid	Gray crystals	564 595	$C_{31}C_{22}N_2OS_2$	5.35 5.66	5.57	81.6
V	0.4 (0.99)	0.27 (1.02)	6	20	298—299	Pyridine alcohol	Gray crystals	564 595	$C_{30}H_{19}N_2OS_2Cl$	5.49 5.56	5.36	66.7
VI	0.4 (0.94)	0.25 (0.95)	7	30	298—299	Pyridine alcohol	Gray crystals with a green reflex	564 595	$C_{31}H_{22}N_2O_2S_2$	5.66 5.70	5.40	86.4
VII	0.4 (1.01)	0.27 (1.02)	4	30	320—322	Dioxane alcohol	Minute brown crystals	546 580	$C_{30}H_{20}N_2OS_2$	5.98 5.70	5.73	70.0

TABLE 2

Synthesis and properties of merocyanines from N-arylquinaldines and acetanilinomethyleneethylrhodanine

Dye	Reacted: Quaternary salt, g (mmole)	Reacted: Acetanilino-methylene-ethylrhodanine, g (mmole)	Reacted: Pyridine, ml	Heating time, min	Mp, °C (decomp)	Recrystallizing solvent	Appearance	λmax, mμ	Formula	N, %: Found	N, %: Calc.	Yield, %
VIII	0.32 (1.00)	0.31 (1.01)	1.5	60	252—253	Acetic acid	Glistening dark blue crystals	544 578	$C_{22}H_{18}N_2OS_2$	6.82 7.01	7.07	59.0
IX	0.40 (1.01)	0.31 (1.01)	2.0	60	268—269	Acetic acid	Grayish-green glistening crystals	564 595	$C_{26}H_{20}N_2OS_2$	6.57 6.41	6.36	53.5
X	0.35 (1.01)	0.31 (1.01)	1.5	40	250—251	Acetic acid	Bluish-green glistening crystals	550 584	$C_{24}H_{22}N_2OS_2$	6.61 6.58	6.69	60.0
XI	0.41 (1.00)	0.31 (1.01)	1.5	40	258—259	Acetic acid	Dark-green glistening crystals	564 595	$C_{27}H_{22}N_2OS_2$	5.90 5.87	6.16	64.4
XII	0.40 (0.99)	0.31 (1.01)	2.0	40	254—255	Acetic acid	Dark-green glistening crystals	565 596	$C_{26}H_{19}N_2OS_2Cl$	5.79 6.13	5.90	30.0
XIII	0.43 (1.01)	0.31 (1.01)	2.0	30	263—265	Acetic acid	Green crystals	565 596	$C_{27}H_{22}N_2O_2S_2$	6.14 6.08	5.95	60.0
XIV	0.40 (1.01)	0.31 (1.01)	1.5	30	260—261	Acetic acid	Brown crystals with bronze reflex	546 583	$C_{26}H_{20}N_2OS_2$	6.08 6.15	6.36	41.5
XV	0.45 (1.01)	0.31 (1.01)	2.0	40	175—177	Acetic acid	Dark green glistening crystals	564 595	$C_{30}H_{22}N_2OS_2$	5.77 5.95	5.71	35.0

VIII-XV. A mixture of approximately equimolecular quantities of salt A and acetanilinomethyleneethylrhodanine [3, 4], 0.14 ml triethylamine, and 1-2 ml pyridine, is gently refluxed by heating in a paraffin bath. The crystals formed are filtered off and washed with alcohol and ether. In the case of dye VIII the crystals are precipitated by adding 45 ml alcohol to the reaction products. Dyes XI, XII, XV are similarly precipitated, but with water.

All the merocyanine dyes prepared are quite soluble in pyridine, dioxane, acetone; some are less soluble in acetic acid and chloroform, and only slightly soluble in ethanol and methanol.

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