SULFUR- AND SELENIUM-CONTAINING MEROCYANINE DYES

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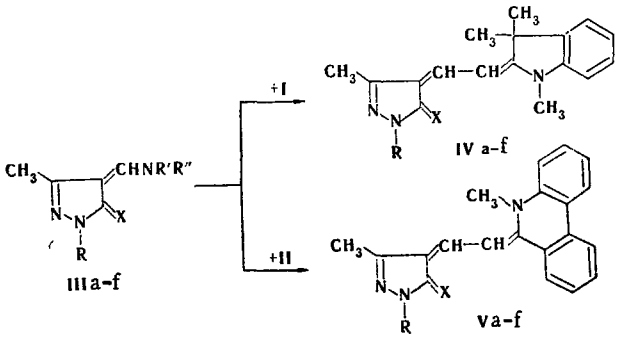
The corresponding merocyanine dyes were obtained by reaction of aminomethylene derivatives of 5-pyrazolone and 5-thio- and 5-selenopyrazolones with tetramethylindoleninium and phenanthridinium salts. Their UV spectra and the possibility of the formation of spiropyrans from them were studied.

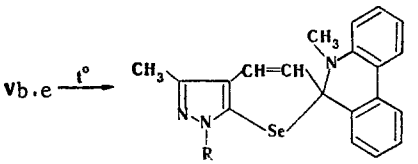
Merocyanine dyes that are not capable of intramolecular cyclization to give spiropyrans under the usual conditions are formed by the reaction of 1,2,3,3-tetramethylindoleninium salt I with alkylaminomethylene derivatives of 5-pyrazolone [1, 2] or with 1-phenyl-3-methyl-4-alkylthiomethylene-5-pyrazolone [3]. At the same time, merocyanines obtained from 5,6-dimethylphenanthridinium salt II and salicylaldehyde and its substituted derivatives [4] readily form the corresponding closed systems. Considering that the formation of the spiropyran ring depends on the magnitude of the positive charge on the carbon atom through which closing takes place [5] and on the nucleophilicity of the oxygen atom, the sulfur (IIId, e) and selenium (IIIc, f) analogs were subjected to reaction with salts I and II in place of the aminomethylene derivatives of 5-pyrazolone. Their reaction in the presence of piperidine gives deeply-colored merocyanine dyes (IV-V, Table 1).



III a R=CH_3, R'=CH_3, R"=H, X=O; b R=CH_3, R'=R"=CH_3, X=S; c R=CH_3, R'=C_6H_5, R"=H, X=Se; d R=C_6H_5, R'=R"=CH_3, X=O, e R=C_6H_5, R'=R"=CH_3, X=S; f R=R'=C_6H_5, R"=H, X=Se: IV a R=CH_3, X=O; b R=CH_3, X=S; c R=CH_3, X=Se; d R=C_6H_5, X=O; e R=C_6H_5, X=S; f R=C_6H_5, X=Se; V a R=CH_3, X=S; b R=CH_3, X=Se; c R=C_6H_5, X=O; d R=C_6H_5, X=S; e R=C_6H_5, X=Se

Substances of the same composition (VIa, b) but with less deep colors [λ_{max} (C_2H_5OH) 335 and 340 nm] were obtained only in the reaction of IIIc and IIIg with salt II along with the principal products (Vb and Ve). They can also be obtained by heating the appropriate merocyanines (Vb, e), and closed structure VI was assigned to them on the basis of their UV spectra:

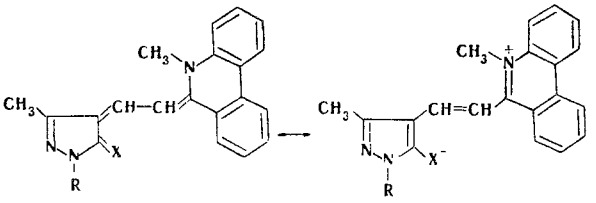
Lensovet Leningrad Technological Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 384-386, March, 1975. Original article submitted June 26, 1974.



VI a R = CH_3, b R = C_6H_5

The O → S → Se transition causes a bathochromic shift, which depending on the structure of the dyes and the nature of the solvent, reaches 180 nm in the UV spectra (Table 1) of merocyanines IV and V. Positive solvatochromism is observed in nonpolar solvents for oxygen-containing merocyanines, whereas negative solvatochromism is observed for sulfur- and selenium-containing merocyanines; this indicates the considerable contribution of dipolar structure B for the latter cases even in the ground state.

Replacement of the methyl group in the 1 position of the pyrazolone ring by a phenyl group causes a bathochromic shift (6-15 nm), which depends on heteroatom X and the solvent. The introduction of a phenanthridine residue in place of an indolenine residue also leads to a bathochromic shift. The effect of the nature of X and the polarity of the solvent is explained by predominance of dipolar structure B, which is probably maximal for X = Se.



A B

This also makes possible the formation of spiro derivatives on the basis of 5-selenopyrazolone when the carbon atom in the phenanthridine residue has the appropriate electrophilicity.

EXPERIMENTAL

The aminomethylene derivatives of 5-pyrazolone and 5-thio- and 5-selenopyrazolones were obtained by the methods in [2, 6, 7].

4-Ethylidene-5-oxo(thio, seleno)pyrazolideneindolines (IV). A mixture of 2 mmole of the appropriate pyrazole derivative III, 2 mmole of 1,2,3,3-tetramethylindoleninium iodide (I), and 3 mmole of piperidine was refluxed in 20 ml of isopropyl alcohol for 4 h. It was then cooled, and the resulting precipitate was removed by filtration, washed with a small amount of isopropyl alcohol, and dried (Table 1).

4'-Ethylidene-5'-oxo(thio, seleno)pyrazolidenephenanthridines (V). A mixture of 1 mmole of III, 1 mmole of 5,6-dimethylphenanthridinium methylsulfate (II), and 2 mmole of piperidine in 8 ml of isopropyl alcohol was refluxed for 4 h. It was then cooled, and the resulting precipitate was removed by filtration and dried. In the synthesis of Vc, the residue remaining after removal of the solvent by distillation was chromatographed twice with a column filled with Al_2O_3 with elution with chloroform.

Compounds VI were isolated by dilution of the filtrate after separation of Vb and Ve.

Compound VIa. This compound, with mp 138-140°, was obtained in 15% yield. UV spectrum, λ_{max}, nm (log ε), in ethanol: 248 (4.3), 335 (3.65), 380 shoulder; in benzene: 340 (3.79), 375 (3.73). Found: N 9.8%. $C_{23}H_{23}N_3Se$. Calculated: N 10.0%.

Compound VIb. This compound, with mp 114° (ethanol–water), was obtained in 35% yield. UV spectrum, λ_{max}, nm (log ε), in ethanol: 248 (4.45), 338 (3.7); in benzene; 344 (3.8). Found: N 9.2%. $C_{26}H_{21}N_3Se$. Calculated: N 9.2%.

TABLE 1. Merocyanines

Compound	mp, °C (crystallization solvent)	Empirical formula	N, % found	N, % calc.	λ_{max}, nm (lg ε) in ethanol	λ_{max}, nm (lg ε) in benzene	Yield, %
IVa	191—192 (water)	$C_{18}H_{21}N_3O$	14,4	14,2	273 (3,9), 400 (4,1), 477 (4,9)	408 (4,3), 464 (4,5)	72
IVb	231 (isopropyl alcohol)	$C_{18}H_{21}N_3S$*	13,7	13,5	264 (4,1), 406 (4,3), 525 (4,5)	434 (4,7), 570 (4,4)	82
IVc	251 (butyl alcohol)	$C_{18}H_{21}N_3Se$	11,7	11,7	263 (4,1), 414 (4,4), 537 (4,3)	443 (4,4), 605 (3,9)	92
IVd	212† (isopropyl alcohol)				250 (4,98), 475 (4,84)	245 (4,23), 300shoul. 444 (4,64)†	75
IVe	221‡ (isopropyl alcohol)				263 (4,18), 412 (4,4), 530 (4,56)	300 (4,14), 440 (4,44), 570 (4,2)	73
IVf	217 (isopropyl alcohol)	$C_{23}H_{23}N_3Se$	10,1	10,0	295 (4,2), 420 (4,22), 545 (4,56)	310 (4,09), 450 (4,63), 620 (4,15)	48
Va	241—242 (butyl alcohol)	$C_{21}H_{19}N_3S$**	12,3	12,1	322 (3,9), 412 (4,0), 545 (4,3)	310 (4,2), 462 (3,8), 625 (4,1)	80
Vb	232 (butyl alcohol)	$C_{21}H_{19}N_3Se$	10,8	10,7	324 (4,0), 415 (4,0), 550 (4,2)	313 (3,7), 472 (4,1), 655 (3,8)	81
Vc	92—93	$C_{26}H_{21}N_3O$	10,4	10,7	240 (4,62), 322 shoul. 530 (4,49)	328 (3,9), 514 (4,2)	30
Vf	201—203	$C_{26}H_{21}N_3S$	10,3	10,4	320 (3,66), 414 (3,7), 550 (3,95)	470 (3,56), 630 (3,45)	71
Ve	209 (methanol)	$C_{26}H_{21}N_3Se$	9,3	9,2	320 (3,8), 415 (4,17), 550 (3,90)	478 (4,34), 664 (3,93)	54

*Found: S 10.1%. Calculated: S 10.3%.
†In n-hexane.
††Found: S 9.2%. Calculated: S 9.3%.

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