A NEW GROUP OF MEROCYANINES CONTAINING SELENAZOLIDINE AND TETRAHYDROSELENAZINE RINGS

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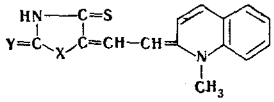
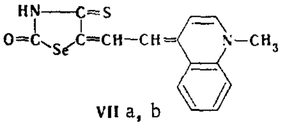
New merocyanine dyes containing selenazolidine and tetrahydroselenazine rings have been obtained. As compared with the analogous dyes of the isorhodanine series the long-wave maxima of their IR spectra have bathochromic shifts.

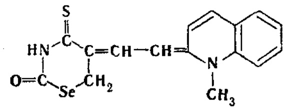
It is known [1, 2] that 3-alkylrhodanines readily condense with 3-alkylbenzothiazolium iodides forming merocarbocyanines. It has recently been shown that with alkyl halide derivatives of quinaldine and of lepidine isorhodanines give quinomerocyanines [3]. We have synthesized a new series of merocyanines containing selenazolidine and tetrahydroselenazine rings. In comparison with the analogous merocyanines derived from isorhodanine, the long-wave maxima of their selenium analogs have bathochromic shifts. The dyes obtained can possibly find use as sensitizers of silver bromide emulsions and in the ciné-photographic industry:



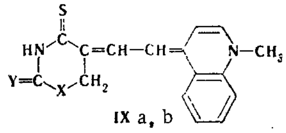
VI a, b'



VII a, b



VIII



IX a, b

VI a X=Se, Y=O; b X=S, Y=O; IX a X=Se, Y=O; b X=Se, Y=S

EXPERIMENTAL

5-Anilinomethylene-4-thioxoselenazolidine-2-thione (I). Separate solutions of 0.90 g (0.005 mole) of 4-thioxoselenazolidin-2-one [4] in 8 ml of freshly distilled dioxane and of 0.98 g (0.005 mole) of diphenylformamidine in 7 ml of dioxane were made. The solutions were mixed in a test tube which was then sealed. On the following day, the reaction mixture was filtered and the residue on the filter was washed with a small amount of dioxane. The addition of petroleum ether to the filtrate precipitated (I). Yield 1.95 g (68.8%), mp 222°C (from benzene). Found: N 9.9%. $C_{10}H_8N_2OSSe$. Calculated: N 9.9%.

4-Thioxotetrahydro-1,3-selenazin-2-one (II). To a solution of 3.56 g (0.02 mole) of tetrahydro-1.3-selenazine-2,4-dione [5] in 50 ml of m-xylene was added 5 g (0.022 mole) of P_2S_5, and the mixture was boiled for 2 h 30 min. Then it was filtered, the m-xylene was distilled off in vacuum, and hexane was added. The precipitate that deposited was crystallized from benzene. Yield 1.6 g (82.5%), mp 157°C (decomp.). Readily soluble in acetone, dichloroethane, and dimethylformamide and, on heating, in ethanol, benzene, and dioxane. The brief boiling of (II) with sodium bicarbonate led to partial hydrolysis with the formation of the initial tetrahydro-1,3-selenazine-2,4-dione. Found: N 7.5; Se 40.6%. C_4H_5NOSSe. Calculated: N 7.3; Se 40.7%.

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TABLE 1. Merocyanine Dyes (VI-IX)

Compound	X	Y	mp, °C (decomp.)	Empirical formula	N, %		λ_{max}, nm	Yield, %
					found	calc.		
VIa	Se	O	210	$C_{15}H_{12}N_2OSSe$	8,2	8,2	598	72
VIb	S	O	259—260	$C_{15}H_{12}N_2OS_2$	9,5	9,3	593	79
VII	Se	O	252	$C_{15}H_{12}N_2OSSe$	8,2	8,2	611	74
VIII	Se	O	227—228	$C_{16}H_{14}N_2OSSe$	7,7	7,8	604	61
IXa	Se	O	213	$C_{16}H_{14}N_2OSSe$	7,7	7,8	652	68
IXb	Se	S	218	$C_{16}H_{14}N_2S_2Se$	7,6	7,4	656	53

5-Anilinomethylene-4-thioxotetrahydroselenazin-2-one (III). This was obtained in a similar manner to (I) from (II) and diphenylformamidine. Yield 1.85 g (62.3%), mp 208°C (from benzene). Found: N 9.2%. $C_{11}H_{10}N_2OSSe$. Calculated: N 9.4%.

Tetrahydro-1,3-selenazine-2,4-dithione (IV). To a solution of 3.56 g (0.02 mole) of tetrahydro-1,3-selenazine-2,4-dione in 50 ml of dehydrated freshly distilled dioxane was added 5 g (0.022 mole) of P_2S_5 and the mixture was boiled for 2 h. Then it was filtered, the dioxane was distilled off in vacuum, and water was added. The precipitate that deposited was crystallized from benzene. Yield 1.75 g (83.4%), mp 153°C (decomp.). Readily soluble in acetone, dichloroethane, and dimethylformamide and, on heating, in ethanol, benzene, and dioxane. The brief heating of (IV) with sodium bicarbonate led to partial hydrolysis with the formation of the intial tetrahydro-1,3-selenazine-2,4-dione. Found: N 6.9; Se 37.5%. $C_4H_5NS_2Se$. Calculated: N 6.7; Se 37.6%.

5-Anilinomethyleneselenazin-2,4-dithione (V). This was obtained in a manner similar to I from IV and diphenylformamidine. Yield 2.1 g (65%), mp 212° (from benzene). Found: N 9.1%. $C_{11}H_{10}N_2S_2Se$. Calculated: N 9.0%.

Merocyanine Dyes (VI-IX). A mixture of 0.01 mole of a quaternary quinaldinium or lepidinium salt, 0.01 mole of (I), (III), or (V), 10 ml of butanol, and 0.2 ml of triethylamine was heated at the boil for 25-40 min. The crystals that deposited were filtered off and washed with ethanol and were then crystallized from ethanol.

LITERATURE CITED

1. F. C. Brown, Chem. Rev., 61, 463 (1961).
2. S. V. Lepikhova and G. T. Pilyugin, Zh. Obshch. Khim., 35, 647 (1965).
3. S. V. Lepikhova and G. T. Pilyugin, Zh. Obshch. Khim., 40, 863 (1970).
4. O. P. Shvaika, V. N. Artemov, V. E. Kononenko, and S. N. Baranov, Khim. Geterotsikl. Soedin., 930 (1973).
5. V. E. Kononenko, S. N. Baranov, and B. E. Zhitar', Zh. Organ. Khim., 9, 61 (1973).