THIAZOLOCYANINES

XVI.* N-HETARYLTHIAZOLIUM SALTS WITH ACTIVE METHYLTHIO GROUPS AND CYANINE DYES BASED ON THEM

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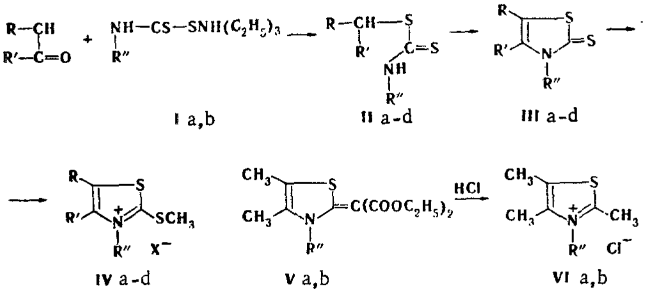
Quaternary thiazolium salts with active methylthio groups and 2-thiazolyl and 2-pyridyl residues attached to the nitrogen atom of the thiazole ring were obtained. 2-Methyl-3-(2-pyridyl)- and 2-methyl-3-(2-thiazolyl)thiazolium salts were synthesized by replacement of the methylthio group by a methyl group. Monomethylidynecyanines and nullmethylidyne- and dimethylidynemerocyanines were obtained from salts with active methyl and methylthio groups.

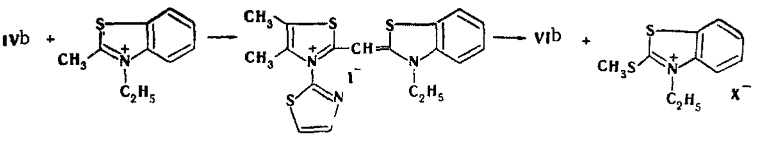
3-Heterylthiazolium salts (IV) with active methylthio groups were obtained from α-halo ketones or α-halo aldehydes and triethylammonium N-(2-hetaryl)dithiocarbamate (I).



II a,b $R=CH_3$, $R'=CH_3CO$; c, d $R=H$, $R'=HCO$; IIIa, b $R=R'=CH_3$; c, d $R=R'=H'$; IVa $R=R'=CH_3$, $X=I$; b $R=R'=CH_3$, $X=CH_3SO_4$; c $R=R'=H$, $X=I$; d $R=R'=H$, $X=I$; I–VI a, c R''=2-pyridyl; b, d R''=2-thiazolyl.

Replacement of the methylthio group in the quaternary salts by a methyl group via the method described for some other heterocyclic compounds [2] leads to thiazolium salts VI, which we previously obtained by another method [1]. This method for the preparation of salts VI for the most part gives better yields and purer products. The identical character of the dye 2-[(3-ethyl-2-benzothiazolyl)methylene]-4,5-dimethyl-3-(2-thiazolyl)thiazolium iodide (VII) obtained (method B) from salt IVb and from salt VIb (method A) confirms the structure of salts VI.

In addition, nullmethylidynemerocyanines (IX-XIII) and dimethylidynemerocyanines (XVI-XIX) substituted in the α position of the polymethine chain were obtained from salts IV, and dimethylidynemerocyanines without a substitutent in the chain (XIV-XV) (Table 1) were obtained from salts VI.



VII

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[*] See [1] for communication XV.

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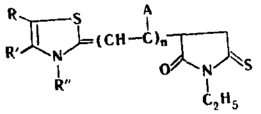
TABLE 1. Merocyanine



Compound	R	R′	R″*	*n*	A	mp, °C	Empirical formula	S, % found	S, % calc.	λ_{max}, nm in ethanol (log ε)	Yield, %
IX	CH_3	CH_3	t	0		229—230	$C_{13}H_{13}N_3OS_4$	35,8	36,0	437 (4,90)	85
X	CH_3	CH_3	p	0		228—229	$C_{15}H_{15}N_3OS_3$	27,6	27,5	437 (5,00)	50
XI	H	H	t	0		197—198	$C_{11}H_9N_3OS_4$	39,2	39,1	430 (4,82)	2
XII	H	H	p	0		175	$C_{13}H_{11}N_3OS_3$	29,9	29,9	430 (4,83)	50
XIII †	CH_3	CH_3	p	0		202—203	$C_{16}H_{15}N_3OS_3$	26,5	26,6	437 (5,07)	70
XIV ‡	CH_3	CH_3	C_2H_5	1	H	204	$C_{14}H_{18}N_2OS_3$	29,3	29,4	544 (5,26)	52
XV	CH_3	CH_3	t	1	H	230	$C_{15}H_{15}N_3OS_3$	33,6	33,6	537 (5,19)	18
XVI	CH_3	CH_3	t	1	CH_3	235	$C_{16}H_{17}N_3OS_4$	32,5	32,4	535 (5,39)	38
XVII	CH_3	CH_3	p	1	CH_3	211	$C_{18}H_{19}N_3OS_3$	24,8	24,7	540 (5,40)	30
XVIII	CH_3	CH_3	t	1	OC_2H_5	194—195	$C_{17}H_{19}N_3O_2S_4$	30,0	30,1	532 (5,16)	24
XIX	H	H	p	1	CH_3	178—179	$C_{16}H_{15}N_3OS_3$	26,3	26,5	537 (5,26)	10

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* t is 2-thiazolyl, and p is 2-pyridyl.

† Dye XIII has an allyl residue attached to the rhodanine nitrogen atom.

‡ This dye was obtained by E. K. Mikitenko.

Replacement of the ethyl group attached to the nitrogen atoms of the thiazole ring by a 2-hetaryl residue does not cause a bathochromic shift of the absorption maximum as in carbocyanines but rather a hypsochromic shift, i.e., the decisive factor in the change in the color of the dimethylidynemerocyanine is the decrease in the basicity of the thiazole ring bonded to the α position of the hetaryl residue, which increases the weight of the covalent structure and without that prevailing in merocyanines that are derivatives of rhodanine.

EXPERIMENTAL

The absorption spectra of the synthesized dyes in ethanol were measured with an SF-10 spectrophotometer.

α-Acetylethyl 3-(2-Pyridyl)dithiocarbamate (IIa). A 7.5-g (0.05 mole) sample of 3-bromo-2-butanone was added at room temperature to 13.5 g (0.05 mole) of triethylammonium 3-(2-pyridyl)dithiocarbamate (Ia) [3] in 100 ml of water. The reaction mixture became warm, and a colorless precipitate formed. The mixture was heated at 65° for 1 h, and the precipitate was removed by filtration and washed with water to give 10.3 g (90%) of a product with mp 141° (from alcohol). Found: S 26.7%. $C_{10}H_{12}N_2OS_2$. Calculated: S 26.7%.

3-(2-Pyridyl)-4,5-dimethylthiazoline-2-thione (IIIa). A mixture of 2.4 g (0.01 mole) of IIa and 6.5 ml of acetic anhydride was refluxed for 90 min, after which it was cooled and added with stirring to 50 ml of water to which 1.5 ml of acetic acid had been added. The viscous precipitate was separated and extracted with benzene. The benzene extract was dried with calcium chloride, the solvent was removed by vacuum distillation, and the residue was washed with ether to give 0.84 g (40%) of IIIa with mp 109° (from alcohol). Found: S 29.0%. $C_{10}H_{10}N_2S_2$. Calculated: S 28.8%.

3-(2-Pyridyl)-2-methylthio-4,5-dimethylthiazolium Iodide (IVa). A mixture of 3.2 g (14 mmole) of IIIa and 3.9 g (28 mmole) of methyl iodide was heated at 40° in 5 ml of benzene for 1.5 h to give 2.7 g (58%) of IVa with mp 150° (from isopropyl alcohol). Found: I 34.9%. $C_{11}H_{13}IN_2S_2$. Calculated: I 34.9%.

3-(2-Thiazolyl)-2-methylthio-4,5-dimethylthiazolium Methosulfate (IVb). A solution of 5.44 g (0.02 mole) of triethylammonium N-(2-thiazolyl)dithiocarbomate (Ib) [3] in 40 ml of 50% alcohol was heated to 65°, 3 g (0.02 mole) of 3-bromo-2-butanone was added, and the mixture was held at this temperature for 20 min. It was then evaporated to dryness on a water bath, and the residue was extracted several times with ether. The ether extract was dried, and the solvent was removed by distillation. The semisolid residue (4.6 g) of α-acetylethyl 3-(2-thiazolyl)dithiocarbamate (IIb) was heated with 13 ml of acetic anhydride at 100° for 30 min. The solution was cooled, and 2 ml of acetic acid in 30 ml of water was added. The resulting oil was extracted with benzene, the extract was dried with calcium chloride, and the benzene was evaporated to give 2.35 g of 4,5-dimethyl-3-(2-thiazolyl)thiazoline-2-thione (IIIa) as a viscous mass. It was heated with 1.5 g of dimethyl sulfate at 110-120° for 45 min. The resulting melt was triturated with anhydrous acetone, and the solid was removed by filtration and crystallized from anhydrous acetone (with the addition of alcohol) to give 2.7 g (76%) of a product with mp 164-165°. Found: S 36.0%. $C_{10}H_{14}N_2O_4S_4$. Calculated: S 36.1%.

Formylmethyl 3-(2-Pyridyl)dithiocarbamate (IIc). A 1.96-g (25 mmole) sample of freshly distilled chloroacetaldehyde (bp 85-90°) was added to 6.8 g (25 mmole) of Ia in 50 ml of water, and the mixture was heated at 100° for 1 h. An oil settled on the bottom of the flask and solidified on cooling to give 3.8 g (77%) of a product with mp 110-111° (from alcohol). Found: N 13.3%. $C_8H_8N_2OS_2$. Calculated: N 13.2%.

3-(2-Pyridyl)thiazoline-2-thione (IIIc). This compound was obtained from IIc by the method used to prepare IIIa. The yield of product with mp 89-90° (from alcohol) was 83%. Found: N 14.5%. $C_8H_6N_2S_2$. Calculated: N 14.4%.

2-Methylmercapto-3-(2-pyridyl)thiazolium Iodide (IVc). A 1.6-g (8 mmole) sample of IIIc was mixed with 2.3 g (16 mmole) of methyl iodide in 4 ml of benzene. The next day, the precipitate was removed by filtration and washed with acetone to give 2.4 g (88%) of a product with mp 145° (from alcohol). Found: I 38.1; S 18.7%. $C_9H_9IN_2S_2$. Calculated: I 37.8; S 19.0%.

The method used to prepare IIIc and IVc was used to obtain IIId and IVd as uncrystallizable viscous precipitates.

Replacement of the Methylthio Group by a Methyl Group in Thiazolium Salts

3-(2-Pyridyl)-2,4,5-trimethylthiazolium Chloride (VIa) and 3-(2-Thiazolyl)-2,4,5-trimethylthiazolium Chloride (VIb). A mixture of 5 mmole of salt VIa or IVb, 6 mmole of diethylmalonic ester, 6 mmole of triethylamine, and 3 ml of absolute alcohol was refluxed for 1.5 h, after which the solvent was evaporated, and the residue was chromatographed in chloroform solution on aluminum oxide. Compounds Va or Vb were isolated from the lower yellowish zone of the chromatography column as viscous syrups. These syrups were then refluxed with 40 ml of concentrated hydrochloric acid for 1 h, and the mixtures were then evaporated to dryness in vacuo to give VIa or VIb as uncrystallizable semisolid products, which were used for the subsequent syntheses without additional purification.

3-Ethyl-2-anilinovinyl-4,5-dimethylthiazolium Iodide (VIII). A 2-g sample of 2,4,5-trimethyl-3-ethylthiazolium iodide was heated with 1.22 g of ethyl isoformanilide at 160° for 20 min. The orange melt was triturated with acetone to give 2 g (91%) of a product with mp 211° (from alcohol). Found: S 14.8%. $C_{22}H_{26}N_2O_3S_2$. Calculated: S 14.9%.

The anilinovinyl derivatives were similarly obtained from salts VIa and VIb but under milder conditions (85° for 1 h).

Nullmethylidynemerocyanines

3-Ethyl-5-(3-hetaryl)-4,5-di(R-thiazolin-2-ylidene)thiazolidine-2-thion-4-ones (IX-XIII). A 1-mmole sample of 2-methylthio-3-(2-hetaryl)thiazolium salt (IVa-d) was refluxed with 1 mmole of 3-ethylrhodanine, 0.11 g of triethylamine, and 1 ml of absolute alcohol for 40 min. The dyes were purified by crystallization from alcohol and, where necessary, were first chromatographed.*

Dimethylidynemerocyanines (XIV-XIX)

3-Ethyl-5-(3-ethyl-4,5-dimethylthiazolin-2-ylideneethylidene)thiazolidine-2-thion-4-one (XIV). A 0.64-g (1.5 mmole) sample of VIII was heated with 1.5 mmole of 3-ethylrhodanine and 0.3 g of triethylamine in 2 ml of absolute alcohol at 80-85° for 1 h with a few drops of acetic anhydride. The products were purified by chromatography and crystallization from alcohol.

Dye XV (Table 1) was similarly obtained.

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* Here and elsewhere, chromatography was carried out on aluminum oxide with chloroform solutions of the compounds.

3-Ethyl-5-[(3-(2-thiazolyl)-4,5-dimethylthiazolin-2-ylidene)-α-methylethylidene-2]-thiazolidine-2-thion-4-one (XVI). A mixture of 0.35 g (1 mmole) of 2-methylthio-3-(2-thiazolyl)-4,5-dimethylthiazolium methosulfate,* 0.2 g (1 mmole) of 3-ethyl-5-isopropylidenerhodanine,† 0.11 g (10% excess) of triethylamine, and 1.5 g of absolute alcohol was refluxed for 45 min. The products were purified as indicated above for XIV.

Dyes XVII-XIX (Table 1) were similarly obtained.

3-(2-Thiazolyl)-2-(3-ethylbenzothiazolinylidene-2-methylene)-4,5-dimethylthiazolium Iodide (VII). A. A mixture of 0.27 g (0.9 mmole) of 2,4,5-trimethyl-3-(2-thiazolyl)thiazolium bromide, 0.32 g (0.9 mmole) of 2-methylthio-3-ethylbenzothiazolium tosylate, and 0.09 g of triethylamine was refluxed for 1 h in 4 ml of absolute alcohol, after which 0.5 ml of 20% potassium iodide solution was added, and the precipitate was removed by filtration to give 0.07 g (15%) of VII with mp 288° (from alcohol), λ_{max} 433 nm (log ε 4.7).

B. A mixture of 0.18 g (5 mmole) of 2-methylthio-4,5-dimethyl-3-(2-thiazolyl)thiazolium methosulfate, 0.15 g (5 mmole) of 2-methyl-3-ethylbenzothiazolium tosylate, and 0.06 g (10% excess) of triethylamine was refluxed in 2 ml of absolute alcohol for 45 min. The product was isolated and purified as indicated above to give 0.18 g (72%) of material with mp 288° (from alcohol). λ_{max} 433 nm (log ε 4.76). No melting-point depression was observed for a mixture of this product with the dye obtained by method A. Found: I 25.2; S 19.0%. $C_{18}H_{18}IN_3S_3$. Calculated: I 25.4; S 19.2%.

LITERATURE CITED

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3. E. B. Knott, J. Chem. Soc., 1944 (1956).

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*The iodide salts were used to obtain dyes XVII and XIX.

† 5-α-Ethoxyethylidene-3-ethylrhodanine was used for the synthesis of dye XVIII.