

THIAZOLOCYANINES

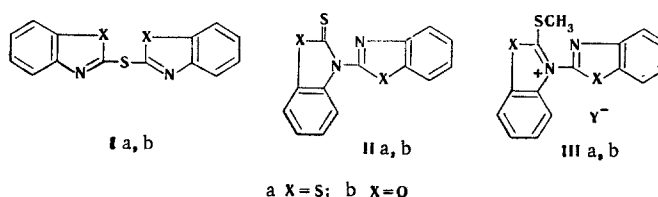
XVII.* SYNTHESIS AND SOME REACTIONS OF NITROGENOUS DIHETARYL SULFIDES AND THEIR USE IN THE SYNTHESIS OF CYANINE DYES

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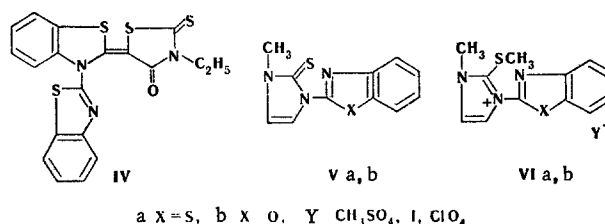
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The reaction of 2-chloro derivatives of benzothiazole and benzoxazole with 2-mercapto derivatives of benzothiazole, of 1-methylimidazole, and of 4,5-dimethylthiazole has given sulfides and thiones which have then been used for the synthesis of merocyanines.

It has been shown [2,3] that by heating 2-mercaptobenzothiazole with 2-chlorobenzothiazole, and also 2-mercaptobenzothiazole with 2-chlorobenzoxazole, it is possible to obtain sulfides (I) and from them, by heating to a higher temperature, thiones (II).



We have obtained (IIa) by this method [2] and have heated it with dimethyl sulfate. It was found that the thione sulfur was methylated with the formation of the salt (IIIa), as was shown by its conversion into the zeromethinemercyanine (IV). It appeared of interest to obtain merocyanines by a similar method. With this aim, 2-mercapto-4,5-dimethylthiazole and 2-mercapto-1-methylimidazole were brought into reaction with 2-chlorobenzothiazole and 2-chlorobenzoxazole. However, the thiones (V) and quaternary salts (VI) could be obtained only from the imidazole derivatives.



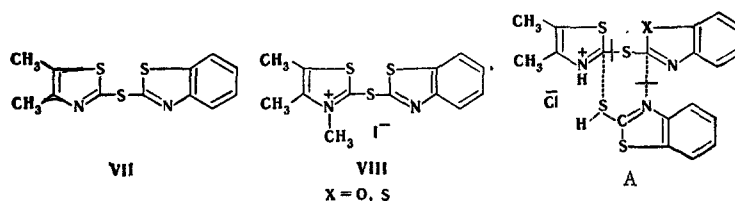
So far as concerns 2-mercapto-4,5-dimethylthiazole, the products of its reaction with 2-chlorobenzothiazole proved to be the sulfides (VII) (first stage of a process taking place normally) and (Ia). The formation of (Ia) can be explained by assuming the existence of the complex A in the transition state. Its formation is favored by the increase in the positive charge on the meso-carbon atom of the thiazole ring of (VII) because of the formation of the salt through the hydrogen chloride liberated during the reaction (see scheme on following page).

The existence of such a complex was assumed by Amico et al. [2] but with a difference in structure resulting from the fact that their complex had the nature of an anion, since the starting material was the

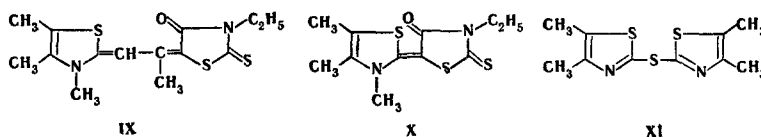
*For Communication XVI, see [1].

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sodium salt of 2-mercaptobenzothiazole. The decomposition of the complex A may yield 2-mercaptobenzothiazole, subsequently reacting with the 2-chlorobenzothiazole present in the reaction mixture to give (Ia). The methylation of (VII) gave the quaternary salt (VIII), in which the 2-benzothiazolylthio group is split off just as readily as a methylthio group in reactions with nucleophilic agents. Thus, the reaction of both salts with 3-ethyl-5-isopropylidenerhodanine and with 3-ethylrhodanine forms the same dyes (IX and X). This reaction served as a proof of the quaternization of (VII) at the nitrogen atom of the thiazole and not of the benzothiazole nucleus, as was to be expected in view of the greater basicity of the former. No bisquaternary salt is formed under these conditions.



The existence of the complex A explains the occurrence of a reaction of 2-mercapto-4,5-dimethylthiazole with 2-chlorobenzoxazole even better. In this case, (IIb) and (XI) were isolated as reaction products. With 2-chlorobenzoxazole, the 2-mercaptobenzoxazole liberated from the complex forms di(benzoxazol-2-yl) sulfide (Ib) which then rearranges into the thione (IIb) in agreement with the literature [4]. Compound (XI) was identified in the form of the monopycate by comparison with an authentic sample obtained by a different route [7].

It can be seen from all that has been said that the dihetaryl sulfides investigated are extremely labile compounds capable of forming very diverse products. It must be noted that — in contrast to compounds (Va, b), imidazolethione derivatives (Va, b), and their analogs (IIIa, b) — the benzothiazolethiones and, in particular, the benzoxazolethiones are extremely unstable compounds which cannot be isolated in the pure state. The quaternary salts (IIIb) decompose with the liberation of mercaptan both when an attempt is made to crystallize them and when they are converted into dyes. Compounds (Va) and (Vb) consist of white crystalline substances readily soluble in the usual organic solvents. Even in the cold, they are readily alkylated both by dimethyl sulfate and by methyl iodide. The merocyanines obtained from them differ in their stabilities. Only the zeromethinemerocyanines (XII and XIII) are stable; dimethinemerocyanines of type (IX) lose their color in ethanolic solution after a few minutes.

EXPERIMENTAL

3-(Benzothiazol-2-yl)-1-methylimidazoline-2-thione (Va). A mixture of 1.14 g (0.01 mole) of 2-mercapto-1-methylimidazole and 1.7 g (0.01 mole) of 2-chlorobenzothiazole [5] was fused at 195°C for 2 h. The melt was extracted with chloroform, the extract was evaporated to dryness, and the residue was crystallized from toluene and ethanol. mp 192°C, yield 32%. Found, %: N 17.0; S 26.3. $C_{11}H_9N_3S_2$. Calculated, %: N 17.0; S 25.9.

3-(Benzothiazol-2-yl)-1-methyl-2-(methylthio)imidazolium Perchlorate (VIa). A mixture of 0.25 g of (Va) (1 mmole) and 0.15 g (1.2 mmole) of dimethyl sulfate in 3 ml of dry toluene was heated at 120°C for 2 h. The toluene was poured off, and the viscous residue was washed with hot toluene and dissolved in ethanol, and compound (VIa) was precipitated by the addition of a 20% solution of sodium perchlorate. mp 177–178°C (from ethanol), yield 0.2 g (55%). Found, %: N 11.8; S 17.9. $C_{12}H_{12}ClN_3O_4S_2$. Calculated, %: N 11.6; S 17.7.

3-(Benzoxazol-2-yl)-1-methylimidazoline-2-thione (Vb). A mixture of 1.53 g (0.01 mole) of 2-chlorobenzoxazole [6] and 1.14 g (0.01 mole) of 2-mercapto-1-methylimidazole in 12 ml of dry xylene was boiled for 5 h. The hot solution was filtered, and the precipitate that deposited on cooling was washed with ethanol and water to give 1.1 g (47%) of (Vb), mp 158°C. Found, %: N 18.3; S 14.1. $C_{11}H_9N_3OS$. Calculated, %: N 18.2; S 13.9.

3-(Benzoxazol-2-yl)-1-methyl-2-(methylthio)imidazolium Iodide (VIb). At room temperature, 2 ml (30 mmoles) of methyl iodide was added to 1.16 g (5 mmoles) of (Vb). On the following day, the mixture was triturated with acetone, and the precipitate was filtered off and washed with acetone. This gave 1.75 g (94%) of (VIb). mp 153°C. Found, %: N 11.5. $C_{12}H_{12}IN_3OS$. Calculated, %: N 11.3.

3-(Benzothiazol-2-yl)-2-(methylthio)benzothiazolium Methosulfate (IIIa). A mixture of 2.67 g (9 mmoles) of (IIa) [2] and 1.4 g (11 mmoles) of dimethyl sulfate was boiled in 100 ml of dry toluene for 4 h. The toluene was poured off and the residue was triturated with toluene and rapidly filtered off. The precipitate was very hygroscopic, and it was stored over phosphorus pentoxide. The yield of (IIIa) was 3.5 g (90%); it was used without further purification.

Reaction of 2-Mercapto-4,5-dimethylthiazole with 2-Chlorobenzoxazole. A mixture of 1.16 g (8 mmoles) of 2-mercapto-4,5-dimethylthiazole and 1.23 g (8 mmoles) of 2-chlorobenzoxazole was boiled with 25 ml of xylene for 5 h. Crude 3-(benzoxazol-2-yl)benzoxazoline-2-thione (IIb) precipitated. It was washed with water and ethanol, to give 0.89 g (42%) of pure (IIb), mp 154°C (from ethanol) [4]. The xylene filtrate was evaporated. From part of the residue the picrate of bis(4,5-dimethylthiazol-2-yl) sulfide (XI) was obtained with mp 107°C (according to the literature [7], 111°C). Found, %: N 14.7. $C_{10}H_{12}N_2S_3 \cdot C_6H_3N_3O_7$. Calculated, %: N 14.4. The remainder was heated in dry toluene with dimethyl sulfate and a few drops of perchloric acid. The precipitate (0.46 g) – the methyl perchlorate derivative of (XI) – was recrystallized from ethanol, water, and isopropanol. mp 174–175°C. Found, %: Cl 9.9; S 26.0. $C_{11}H_{15}ClN_2O_4S_3$. Calculated, %: Cl 9.6; S 25.9.

2-(Benzothiazol-2-ylthio)-3,4,5-trimethylthiazolium Iodide (VIIIa). A mixture of 1.01 g (7 mmoles) of 2-mercapto-4,5-dimethylthiazole and 1.18 g (7 mmoles) of 2-chlorobenzothiazole in 3 ml of xylene was boiled for 5 h. The xylene solution was poured off and evaporated in vacuum, the oil was triturated with petroleum ether, the ether was poured off, the residue was treated with 5 ml of hot ethanol, and the crystalline residue of di(benzothiazol-2-yl) sulfide (Ia) was filtered off. mp 99–100°C (from ethanol) (according to [2], 101°C). The ethanolic filtrate was evaporated, and the residue was heated with 3 ml of toluene and 0.76 g (6 mmoles) of dimethyl sulfate at 100°C for 2 h. The toluene was poured off, the residue was dissolved in ethanol, and KI was added to give 0.63 g (30%) of (VIIIa). Needles with mp 185–186°C (from acetone and ethanol). Found, %: I 30.3. $C_{13}H_{13}IN_2S_7$. Calculated, %: I 30.2.

5-[3-(Benzothiazol-2-yl)-1-methylimidazolin-2-ylidene]-3-ethyl-2-thioxothiazolidin-4-one (XII). A mixture of 0.37 g (1 mmole) of (VIa) ($Y = CH_3SO_4$), 0.16 g (1 mmole) of 3-ethylrhodanine, 0.11 g (1.1 mmole) of triethylamine, and 1 ml of absolute ethanol was heated at 70°C for 1 h. The dye was filtered off, dissolved in chloroform, and chromatographed on alumina. This gave 0.1 g (30%) of product with mp 229°C (from ethanol), λ_{max} 427 nm, $\log \epsilon$ 41.11. Found, %: N 15.1; S 25.5. $C_{16}H_{14}N_4OS_3$. Calculated, %: N 15.0; S 25.7.

5-[3-(Benzoxazol-2-yl)-1-methylimidazolin-2-ylidene]-3-ethyl-2-thioxothiazolidin-4-one (XIII). With heating, 0.37 g (1 mmole) of (VIb) ($Y = I$) was dissolved in 10 ml of absolute ethanol, and then 0.16 g (1 mmole) of 3-ethylrhodanine and 0.11 g (1.1 mmole) of triethylamine were added and the mixture was left at room temperature for 20 h. Then the ethanol was evaporated off in vacuum. The yield of (XIII) with mp 209°C (from isopropanol) was 0.1 g (23%). λ_{max} 427 nm, $\log \epsilon$ 4.36. Found, %: N 15.6; S 17.6. $C_{16}H_{14}N_4O_2S_2$. Calculated, %: N 15.6; S 17.9.

5-[3-(Benzothiazol-2-yl)benzothiazolin-2-ylidene]-3-ethyl-2-thioxothiazolidin-4-one (XIV). A mixture of 0.46 g (1 mmole) of (IIIa), 0.16 g (1 mmole) of 3-ethylrhodanine, 0.11 g (1.1 mmole) of triethylamine, and 1 ml of ethanol was heated at 80°C for 1 h. The dye was chromatographed and recrystallized from nitromethane, giving 0.018 g (4.5%) of (XIV), mp 267–268°C. λ_{max} 429 nm, $\log \epsilon$ 4.93. Found, %: N 9.7. $C_{19}H_{13}N_3OS_4$. Calculated, %: N 9.8.

5-[β -[3-(Benzothiazol-2-yl)benzothiazolin-2-ylidene]- α -methylethylidene]-3-ethyl-2-thioxothiazolidin-4-one (XV). A mixture of 0.46 g (1 mmole) of (IIIa), 0.2 g (1 mmole) of 3-ethyl-5-isopropylidenerhodanine, 0.11 g (1.1 mmole) of triethylamine, and 1 ml of dimethylformamide was heated at 100°C for 30 min. The product was purified in the usual way. Yield 0.02 g (4%) of (XV), mp 236–237°C (from ethanol with nitromethane). λ_{max} 529 nm, $\log \epsilon$ 5.06. Found, %: N 8.6. $C_{22}H_{17}N_3OS_4$. Calculated, %: N 9.0.

3-Ethyl-5-[α -methyl- β -(3,4,5-trimethylthiazolin-2-ylidene)ethylidene]-2-thioxothiazolidin-4-one (IX). A mixture of 0.32 g (0.8 mmole) of (VIIIb), 0.16 g (0.8 mmole) of 3-ethyl-5-isopropylidenerhodanine, 0.1 g (1 mmole) of triethylamine, and 1.5 ml of dimethylformamide was heated at 100°C for 45 min. The dye was crystallized from a mixture of ethanol and nitromethane; mp 232°C; yield 0.09 g (35%). λ_{max} 539 nm, $\log \epsilon$ 5.02. Found, %: N 8.9; S 29.6. $C_{14}H_{18}N_2OS$. Calculated, %: N 8.9; S 29.5.

3-Ethyl-5-(3,4,5-trimethylthiazolin-2-ylidene)-2-thioxothiazolidin-4-one (X).* A. A mixture of 0.54 g (2.2 mmoles) of 3,4,5-trimethyl-2-(methylthio)thiazolium bromide, 0.32 g (2 mmoles) of 3-ethyl-rhodanine, 0.3 g (3 mmoles) of triethylamine, and 3 ml of absolute ethanol was boiled for 10 min. The yield of (X) was 0.4 g (66%), mp 252°C (from ethanol with nitromethane). λ_{\max} 418, 432 nm, log ϵ 4.62. Found, %: S 33.3. $C_{11}H_{14}N_2OS_3$. Calculated, %: S 33.6.

B. The substance was obtained in a similar manner to that described above starting from 2-(benzothiazol-2-ylthio)-3,4,5-trimethylthiazolium methosulfate (VIIIc), mp 250°C. Mixtures of the samples of the dye obtained by methods A and B gave no depression of the melting point.

The values of λ_{\max} and ϵ for compounds (IX, X, XII-XV) were measured for solutions in ethanol.

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* This dye was prepared by E. K. Mikitenko.