CONDENSATION OF 1,3-THIAZAN-2,4-DITHIONE

II.* MEROCYANINS FROM 1,3-THIAZAN-2,4-DITHIONE AND ITS DERIVATIVES

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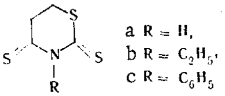
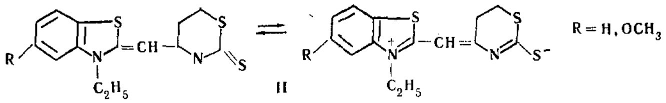
Thiopropiorhodanine condenses at the 4-thioketo group with quaternary salts of 2-methyl- and 2-methyl-5-methoxybenzothiazole to form merocyanins. N-Ethyl- and N-phenyl derivatives do not undergo this reaction.

The thioketo group in the 4-position of 1,3-thiazan-2,4-dithione



Ia-c

(thiopropiorhodanine) (Ia) displays activity with respect to nucleophilic agents [2-4]. We have attempted to use this fact for the condensation of I with quaternary salts of 2-methylbenzothiazole and 2-methyl-5-methoxybenzothiazole, which contain an active methylene group and are the starting compounds in the synthesis of cyanin dyes. It turned out that only unsubstituted thiazandithione reacts with these salts to form products which behave like typical intraionoid dyes – merocyanins: they are insoluble in water but soluble in benzene and similar solvents and manifest solvatochromic and halochromic properties. All of this, together with the analytical data, made it possible to assign formula II to them:



II

Thus, the behavior of unsubstituted thiopropiorhodanine in this reaction differs from that of 3-substituted thiopropiorhodanines Ib and Ic. This is also manifested in the condensation of thiopropiorhodanines I with aniline, where condensation proceeds only with Ia.† On the basis of the data presented, it can be assumed that thiopropiorhodanine participates in reactions in the mercapto form.

EXPERIMENTAL

1,3-Thiazan-2-thion-4-one was obtained in accordance with [5] with replacement of β-chloropropionic acid by β-bromopropionic acid. The yield was 44% (based on β-bromopropionic acid). Thiopropiorhodanine was obtained in accordance with [6].

3-Ethyl-2-[(1,3-thiazan-2-thion-4-yl)methylene]benzothiazoline (II, R = H). 2-Methyl-3-ethylbenzothiazolium p-toluenesulfonate [0.35 g (0.001 mole)] and 0.163 g (0.001 mole) of thiopropiorhodanine were dissolved in 3 ml of absolute alcohol, 0.1 g (0.001 mole of triethylamine was added, and the mixture was refluxed for 3 min. After cooling, the precipitate was filtered and washed with alcohol to give 0.19 g (63%)

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[*] See [1] for communication I.

[†] The condensation product was obtained in accordance with the method in [3].

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of a product with mp 195 deg (from alcohol) and λ$_{max}$ 475 nm. Found %: S 29.6; N 8.4. $C_{14}H_{14}N_2S_3 \cdot H_2O$. Calc. %: S 29.6; N 8.6.

This dye was also obtained from 2-methyl-3-ethylbenzothiazolium iodide.

3-Ethyl-2-[(1,3-thiazan-2-thion-4-yl)methylene]-5-methoxybenzothiazoline (II, R = OCH_3). A mixture of 0.19 g (0.0005 mole) of 2-methyl-3-ethyl-5-methoxybenzothiazolium p-toluenesulfonate, 0.81 g (0.0005 mole) of thiopropiorhodanine, 3 ml of absolute alcohol, and 0.1 g (0.001 mole) of triethylamine was refluxed for 1 min; and the resulting orange precipitate was filtered to give 0.095 g (51%) of a product with mp 221 deg [from alcohol–nitromethane (1:2)] and λ$_{max}$ 489 nm. Found %: S 28.8. $C_{15}H_{16}N_2OS_3$. Calc. %: S 28.6.

LITERATURE CITED

1. E. D. Sych and I. V. Fesenko, Khim. Geterotsikl. Soedin., No. 3 (1971, in press).
2. A. P. Grishchuk and G. I. Roslaya, Khim. Geterotsikl. Soedin., 537 (1966).
3. N. M. Turkevich and E. V. Vladzimirskaya, Dokl. Akad. Nauk Ukr. SSR, 376 (1966).
4. G. I. Roslaya, Khim. Geterotsikl. Soedin., 438 (1968).
5. A. P. Grishchuk and I. R. Barilyak, Zh. Obshch. Khim., 33, 3972 (1963).
6. E. V. Vladzimirskaya, USSR Author's Certificate No. 170,060; Byull. Izobr., No. 8, 20 (1965); A. P. Grishchuk, T. E. Gorizdra, I. D. Komaritsa, and S. N. Baranov, USSR Author's Certificate No. 172,808; Byull. Izobr., No. 14, 28 (1965).