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Production and modification of sulfurous dyes on the basis of picoline

Abstract

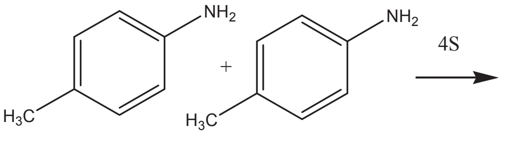
Interaction of γ – picoline with m-phenylenediamine and sulfur is studied. The obtained product sulfurous dye possesses dyeing abilities. The interaction of the obtained product with methylmethacrylate, butylacrylate and bromous butyl is investigated.

Keywords: modification, sulfurous dyes.

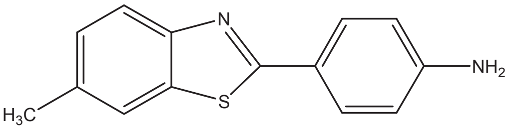
Introduction

Sulfurous dyes are received as a result of interaction of the sulfurate agent with the aromatic connections, such as nitrogen-containing substituting group. Sodium polysulfide mostly used as the sulfurate agent, usage of sodium hydroxide and sulfur mixture as the sulfurate agent is more efficient and profitable.

Sulfurous thiazole dyes receive as a result of curing of sulfur and aromatic compounds, containing methyl group or primary amine at the temperature as 200 – 250ºC. Usually are used amine, that have uncomplexed ortho – disposition to an amino group or containing simultaneously methyl and amino groups, for example:



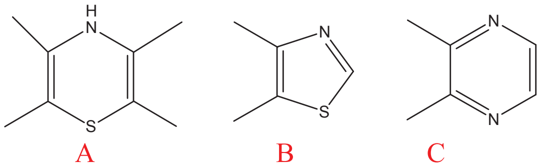
p-toluidine («dehydrate-p-toluidine»)



6-methyl-2-(aminophenyl)benzothiazole

Structure and properties of sulfurous dyes vary depending on conditions of their receiving: ratios of reagents, temperatures, depths of process, etc.

In molecules of sulfurous dyes sulfur included as a compound of heterocycles, and in the form of groups: sulfide – S-, mercapto- -SH, disulfide – S-S-, sulfoxide – SO-, polysulfide – S_n-. Molecules of black, dark blue and green sulfurous dyes contain thiazine (A) rings. Molecules of yellow, orange and some brown dyes – thiazole (B), and molecules of auburn, vinous and violet sulphurous-diazine (C):



So the nitrogen-containing heterocycle is the basic structural compound of sulfurous dyes.

For the purpose of swelling of amount cheap sulfurous we used dyes 4-(γ) picoline – 4 – methylpyridine with m- phenylenediamine and run its sulfuration by the mixture of sulfur and sodium hydroxide.

4-picoline cooperates with sulfur at 135 – 200ºC with cyclization of 1,2-bis-(4-pyridil) ethane (1) and a small amount 1,2,3-tris (4-pyridil) propane (2). As one of products of the reaction of 4-picoline with sulfur at 290 – 330ºC educed 2,3,4,5-tetra(4-pyridil) thiophene (3). In the presence of NaOH at 135 – 200ºC along with 1 and 2 it is received 1,2-bis-(4-pyridil) ethylene (4), with increase in time and process temperatures the production of thiophene (3) raises:

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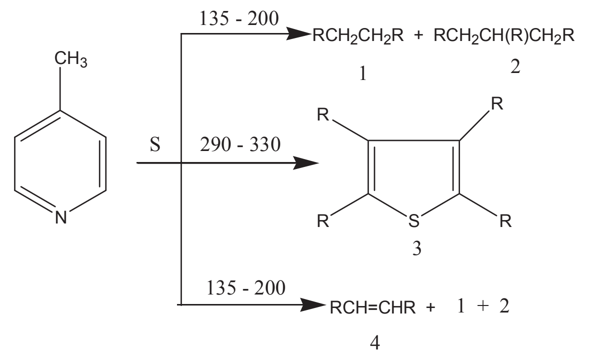
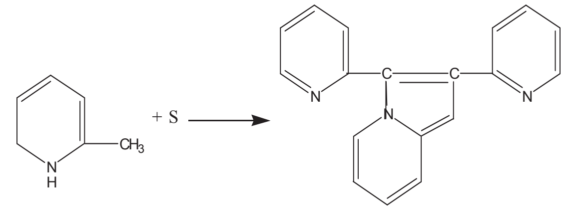


R = C_5H_4N

During long heating of 2-picoline with sulfur the disulfide of a difficult structure is allocated, addition of NaOH hasten the reaction:



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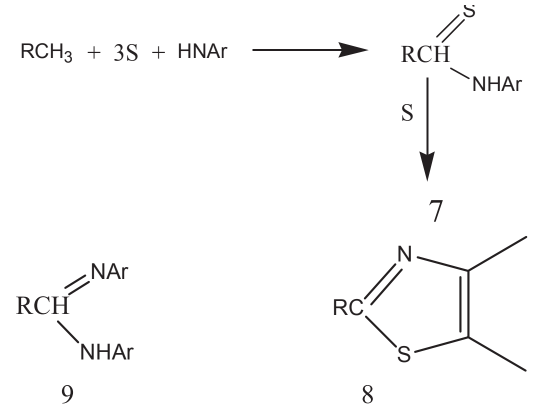
2-picoline during the heating with sulfur and some heterocyclic amine (aniline, o-the m-toluidine, p-anisidine, 2-aminopyridine) forms thioamide (7), and with others aromatic amine (o-anisidine, 1-naphthylamine) in the same cases – diplaced benzothiazole (8). In the process of reaction temperature increasing the production of benzothiazole increases, co-products are amidines (9):

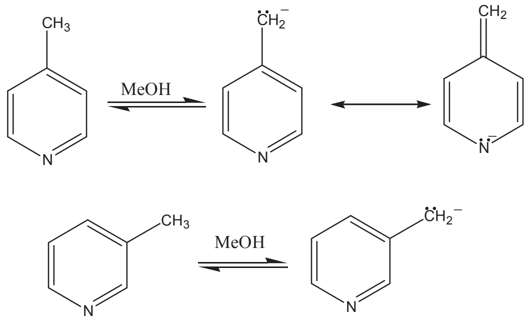


R=C_5H_4N; $CH_2C_5H_4N$, $CH_2CH_2C_5H_4N$

4-picoline, 4-n-propylpyridines react with sulfur and aromatic amine similarly as 2-picoline. At temperature of 160ºC are generally formed thioamides (1), and at 160 – 220ºC the main product of reaction – benzothiazole (8) [1].

As in this case we discussed interaction of picoline (alkylpyridine) with m-phenylenediamine it is considered that the methyl group is reactionary enabled pyridine ring.

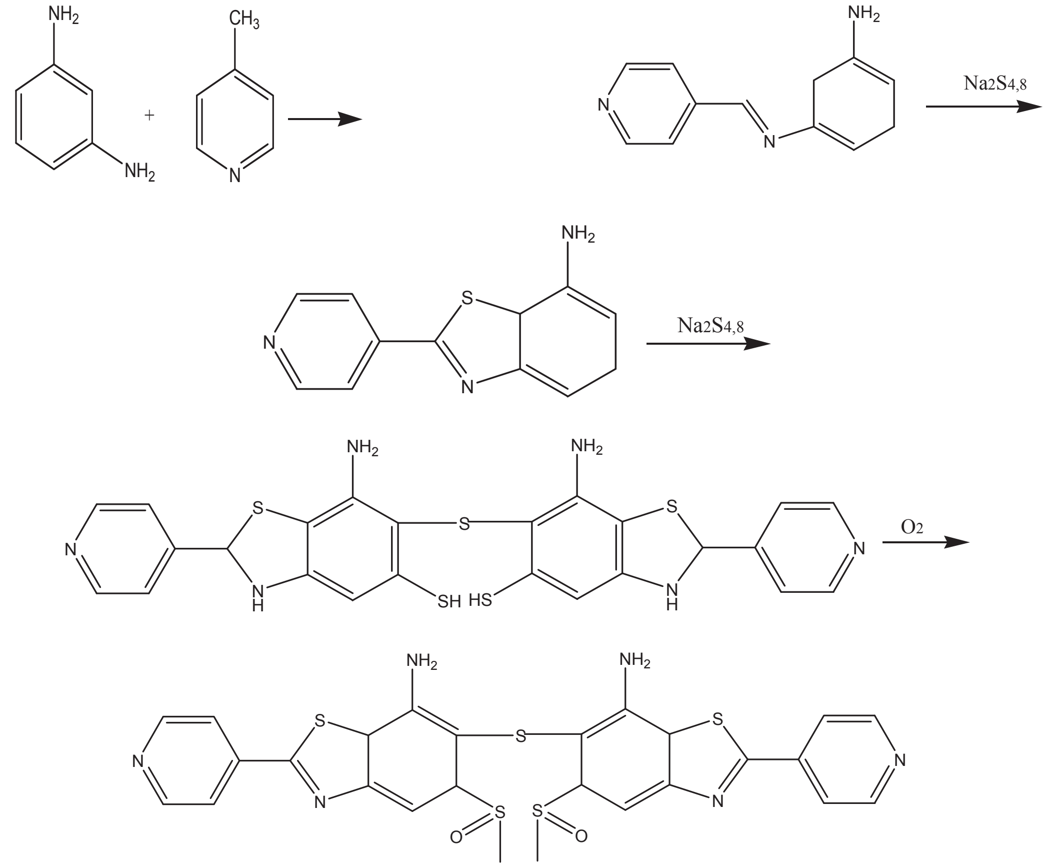
Alkylpyridin are capable to react by a deprotonation of the alkyl groups connected with ring atoms of carbon.



Preproduction studying of an exchange of H – D in the media of MeOD – MeO¯ showed that reactionary ability of isomers changes in the following order: 4->2->>3- in the ratio 1810:130:1. Higher activity in deprotonation reactions α and γ-isomeride explains stabilization of the negative charge, caused by mesomeric interaction with ring atom of nitrogen. Such interaction, is absent at β-isomerid; it can be stabilized only at the expense of inductive influence of an electron-deficient pyridinic ring. Being formed as a result of a deprotonation anions react as nucleophiles in various reactions; on the reactionary ability they are close to anions of enoles [2]. The produced dye has in structure a thiazole ring as the reaction run on methyl group of picoline.

Interaction of picoline with m-phenylene diamine and sulfur carry out by method of curing, at temperature 200 – 205ºC, more than 10 hours. Duration of time of this process was defined by control by a method of a paper chromatography before disappearance of reagents in a reactionary mix. Processing of a product carried out according to [3], boiling alkaline NaOH solution within 7 hours.

On the basis of above specified regularities of interaction aromatic amines and picoline expected structure of dye:



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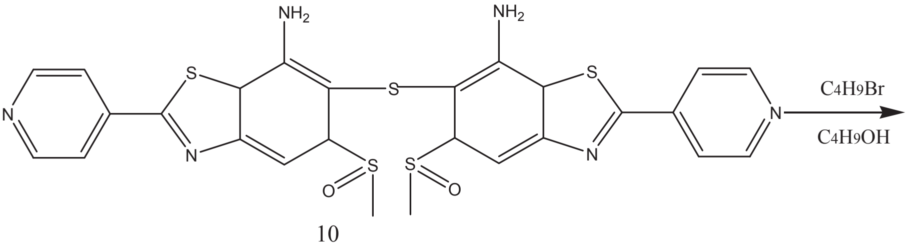
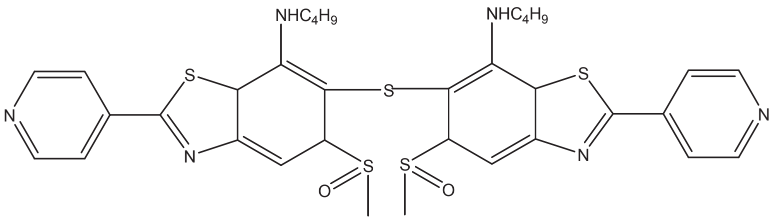
Expected structure of dye after an alkylation:





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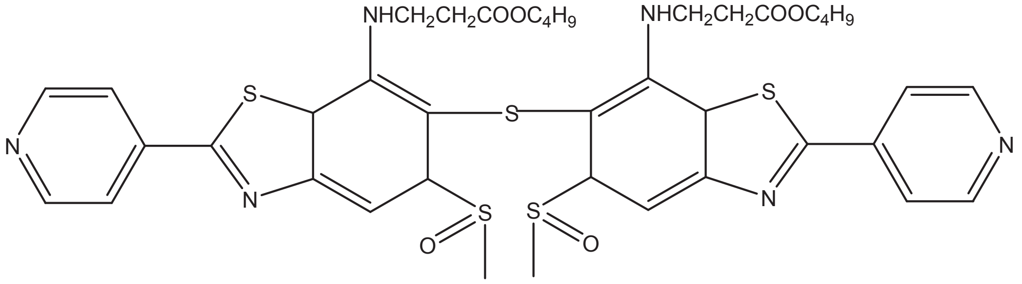
As alkylate reagent was used butyl bromide, thereby butanol was media for carrying out process of alkylation.

The reaction between butylacrylate and interaction products of picoline with m- phenylenediamine and sulfur

Reactions with C – electrophiles usually finished with formation of linking C – N. Reactions of N–alkylation and N – acidylation go more slowly in comparison with alkylamine because of reduction of basicity of atom of nitrogen [4]:

$$ArNH_2 + RR^1R^2C - X \rightarrow$$
$$[Ar - NH_2 + {-CRR^1R^2}]\ X^- \rightarrow$$
$$Ar - NH - CRR^1R^2 + HX$$
$$Ar - NH_2 + O{=}CRX \rightarrow Ar - NH - CRO + HX$$

Expected structure of dye after carrying out of the reaction:



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The reaction between methylmethacrylate and interaction products of picoline with m-phenylenediamine and sulfur

Interaction of the received dye with the methylmethacrylate carry out by long heating, as media is used hexane, the hydrochloric acid acts as the catalyst of this reaction.

Expected structure of dye after carrying out of the reaction:

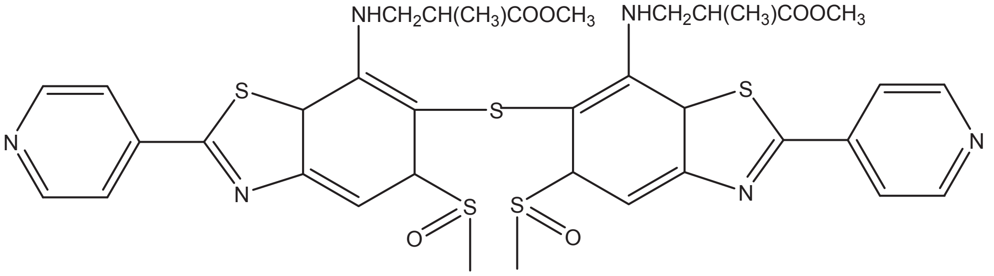

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Figure 1 – Electronic ranges of absorption of dyes in dioxane: 1–interaction of picoline with m-phenylenediamine and sulfur (10), 2 – an alkylated product of dye (11), 3 – a product of interaction of dye with butylacrylate, 4 – a product of interaction of dye with methylmethacrylate.

According to electronic ranges of absorption, the alkylated product of dye, unlike the akrylated products, shows bathochromic shift, i.e. absorption shift in more long-wave area, the certificate to that is deepening of color of the modified dye, and also emergence of fluctuations in the field of $2917\ cm^{-1}$ characterizing SN-, CH2-, CH3-groups, With – N of fluctuation.

Table 1 – Yields, spectral data, the elemental analysis of substances and the color of the dyed material

Compound		10	11	12	13
Yield, %		53.50	75.80	77.72	66.00
IR – spectrum, cm⁻¹	ν_{Ar}	1580 674	1505	1416	1578
	ν_{S-C}	739	629	868	665
	ν_{NH2}	3421	3432	3347	3353
	$\nu_{S=O}$	1131	1120	1230	1140
	ν_{NH}	-	1650	1550	1698
	ν_{CH3}	-	2928	2926	2891
UV –spectrum, λ_{max}, nm		268	269	267	267
The color of the dyed material		light brown	brown	light brown	khaki
Found %	S	42.23	24.03	14.23	14.37
Formula		$C_{24}H_{18}N_6O_2S_5$	$C_{32}H_{34}N_6O_2S_5$	$C_{38}H_{42}N_6O_6S_5$	$C_{34}H_{34}N_6O_6S_5$
Calculated %	S	27.49	23.05	19.09	25.07

Experimental

The course of the reaction was controlled the method of paper chromatography, in the systems: acetone: water (1:1), UF – spectrum was registered on the spectrophotometer – 26, IR – spectrum in KBr tablets was registered on NICOLET 5700. The yields of reaction products, data of elemental and spectral analyses of the compounds are given in Table 1, electron spectra of absorption are given in Fig. 1.

2.1. Interaction of picoline with m-phenylenediamine and sulfur (10). In a porcelain mortar 22.8 g (0.712 mol) of sulfur, 8.4 ml (0.086 mol) of picoline and 9.2 g (0.088 mol) of m-phenylenediamine are ground to a homogeneous mix. The mass is smelted at the temperature 200 – 205ºC for 10 hours.

20 ml of 40 % of NaOH solution is added to the obtained mass of 26.995 g and the mixture is boiled for 7 hours with stirring , then 50 ml of water is added the and air is purged at 50ºC. The dye is filtered and dried at 80 – 90ºC. 10.6 g (53.5 %) of dye is obtained. The electron spectrum of dioxane is λ_{max} = 268 nanometers [3].

2.2. Alkylation of the interaction products of picoline with m-phenylenediamine and sulfur (11). Bromous butyl in the amount of 0.735 ml (0.7 mol) with the dye in the mass of 4 g (0.007 mol) is mixed at temperature 100-105ºC for 8 hours,10 ml (0.12 mol) of butanol is used as the medium. 3.035 g (75.8 %) of powder of black color is obtained. The electron spectrum of dioxane is λ_{max} = 269 nanometers.

The content of sulfur was determined according to the technique [2.5]

2.3. The reaction of butylacrylate with interaction products of picoline with m-phenylenediamine and sulfur (12). Butylacrylate in the amount of 2.56 g (0.02 mol) and the dye in the mass of 6.06 g (0.01 mol) were heated at the temperature 58-65 ºC for 9 hours, then 3-4 ml of hydrochloric acid is added 40 ml of hexane is used as the medium. 4.710 g (77.7 %) of powder of gray – brown color is obtained. The electron spectrum of dioxane is λ_{max} = 267 nanometers.

2.4. The reaction of methylmetacrylate with interaction products of picoline with m-phenylenediamine and sulfur (13). Methylmetacrylate in the amount of 0.992 g (0.01 mol) with the dye in the mass of 3.03 g (0.005 mol) is mixed, then 3-4 ml of hydrochloric acid is added 40 ml of hexane is used as the medium. Were heated at the temperature 58-65 ºC for 9 hours. 2.00 g (66.0 %) of powder of green – brown color is obtained. The electron spectrum of dioxane is λ_{max} = 267 nanometers.

2.5. Determination of sulfur by the method of sedimentation of $BaCl_2$ to $BaSO_4$. The substance (dye) being analyzed in a dry state or in the form of solution is placed into a glass with the capacity of 100 ml, 3 drops of 4 % of NaOH solution and 10 ml of 30 % of H_2O_2 are added and heated up under hour glass for 20 minutes. Then, another portion of 10 ml of H_2O_2 is added and heating is continued to complete decomposition of the substance (decolouration or complete dissolution). The glass and the walls of the glass are washed with water and the solution is evaporated to 5 ml, once again washed with water and again evaporated. The mixture is filtered from not reacted substances, $BaCl_2$ is added in the ratio 1: 1.5 (dye: $BaCl_2$ solution), up to formation of $BaSO_4$. The content of sulfur is determined by the formula [5]:

$\omega_S = mBaSO_4*32.06*100/233.4*m$ (hinge plate)

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