ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 7, pp. 1263−1267. © Pleiades Publishing, Ltd., 2009.
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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis and Modification of Sulfur Dyes

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Received August 18, 2008

Abstract—An integrated approach to sulfur utilization by synthesis of sulfur dyes derived from *m*- and *p*-phenylenediamine was suggested. The sulfur dyes obtained were modified by the reaction with butyl bromide. The possibility of dyeing cotton fabrics by the dyes prepared was examined, and the coloration fastness was evaluated.

DOI: 10.1134/S1070427209070192

An important line of scientific and technical progress is the development of new processes ensuring protection of the environment from pollution with industrial discharges and wastes. Of particular importance is utilization of sulfur from petroleum-extracting industry.

Vast world's resources of sulfur, need for sulfur utilization, and development of textile industry are decisive factors stimulating production of sulfur dyes. Sulfur dyes, which are the cheapest among synthetic organic dyes, give fairly fast coloration, but the majority of them have dull tints [1]. The assortment of sulfur dyes is restricted to black, blue, brown, olive green, violet, green, and yellow colors. Red and ruby colors are lacking. The dyeing power of sulfur dyes is poor, which leads to large dye expenditure [2]. On the other hand, with respect to resistance to various factors (except chlorine), sulfur dyes are among valuable products of dye chemistry [3]. They are used for dyeing cotton and viscose staple fiber, yarns, fabrics, and tricot. Despite the above-indicated drawbacks, interest in sulfur dyes in the world has not disappeared. Sulfur Black is the first black dye. Only the empirical formula of Sulfur Black is known: $C_{24}H_{16}N_6O_8S_7$ or $C_{24}H_{16}N_6O_8S_8$ [4]. It is also used in ball pen inks. Studies are made to reduce to a minimum the content of insoluble particles in aqueous inks, which tend to accumulate at the pen ball. To this end, Sulfur Black dye before use is either oxidized with hydrogen peroxide or treated with 6 M HCl.

Along with cotton dyeing, the possibility of Nylon-6,6 dyeing with various types of sulfur dyes using sugars was examined. In this case, deeper tints were obtained than in dyeing by traditional procedures [5, 6]. Silk dyeing with sulfur dyes using Na_2S for mordanting was examined. The resulting coloration on various substrates shows high lightfastness [7].

More than 90% efficiency of the process is attained in reduction of sulfur dyes with environmentally friendly agents: isomaltose, trehalulose, fructose, and sucrose, with the subsequent oxidation of the material [8].

A novel procedure was developed for dyeing with reduced sulfur dyes at 5–120°C, followed by oxidation in the presence of enzymes such as bilirubin oxidase, catechol oxidase, laccase, polyphenol oxidase, and ascorbate oxidase [9].

An ozone–air mixture is used for intensification of the dyeing process and improvement of the parameters of cotton fabric dyeing, with simultaneous treatment of wash waters [10].

A protective system for sulfur-containing textile dyes against oxidants, especially bleaching agents, has been developed. A dyed fabric is washed with a solution containing La^{3+}, Ce^{4+}, and Gd^{3+} ions or their combinations [11]. Recently an interest in the synthesis of styryl sulfur dyes has been observed [12, 13].

The phenothiazine moiety is the main structural unit of many sulfur dyes prepared from aromatic amines. Phenothazinyl-containing aromatic amines themselves found use as amorphous molecular materials for optoelectronics, exhibiting high heat resistance

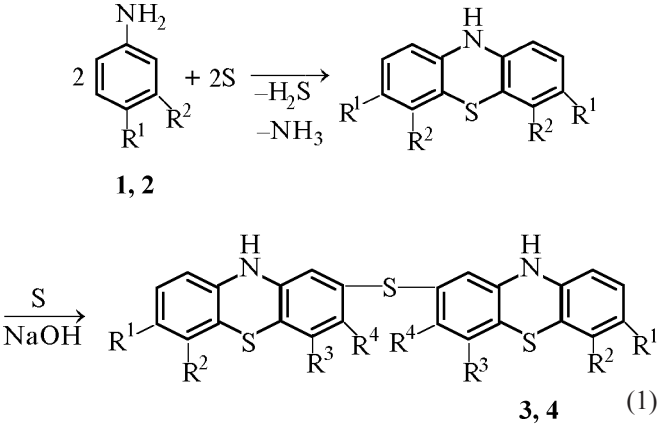
Table 1. Conditions of the synthesis of sulfur dyes derived from *m*- and *p*-phenylenediamine

Compound	*p*-Phenylenediamine : S : NaOH : H_2O	*T*, °C	τ, h	Yield, %	Color of dyed cotton fabric
3	1:2:5:12	115	10	59	Brown
	1:0.5:1:6	115	19	72.3	Light brown
	1:0.5:1:0	205–215	10	76	Dark violet
3a[a]	1:0.5:1:12	110	15.5	73	Violet
4b	1:0.5:1:0	196–205	6	77.3	Light brown

[a] (a) With addition of copper sulfate and (b) reaction with *m*-phenylenediamine.

[14]. Phenothiazine derivatives are biologically active substances. They are used as effective cardiovascular drugs exhibiting antiarrhythmic and spasmolytic action. They also exhibit neuroleptic and antihistamine action [15].

A sulfur dye derived from phenothiazine was prepared as far back as by Vidal. It gave very beautiful gray color of excellent fastness. The scheme of the reaction of phenylenediamines (PDAs) with sulfur is as follows:



1, 2 **3, 4**

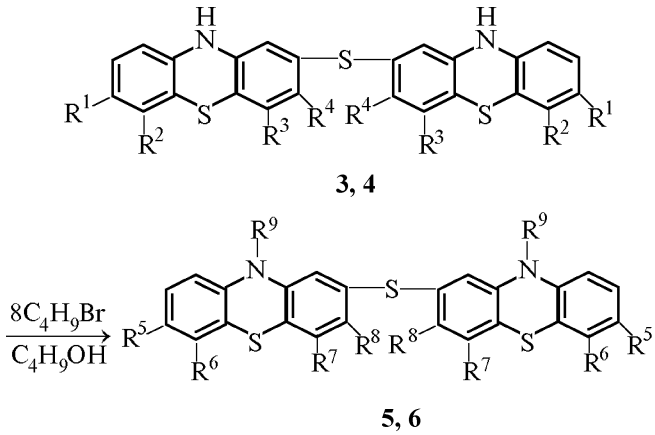
$R^1 = R^4 = NH_2$, $R^2 = H$, $R^3 = SNa$ (**3**), $R^1 = H$, $R^2 = R^3 = NH_2$, $R^4 = SNa$ (**4**).

In contrast to the Vidal procedure, the dye derived from *p*- and *m*-phenylenediamine was synthesized by high-temperature baking (190–220°C) and by low-temperature reaction in aqueous solution (110–120°C). Various ratios of *p*-phenylenediamine, sulfur, sodium hydroxide, and water were used (Table 1). The reaction progress was monitored by paper chromatography.

Table 1 shows that, with an increase in the NaOH amount by a factor of 4, the color intensity increases, and with an increase in temperature the color becomes deeper (violet). With *m*-phenylenediamine sulfur reacts faster than with *p*-phenylenediamine.

To purify the dye and improve its quality, an additional operation is performed: extraction from aqueous solution with ethyl acetate. The extract contains an individual substance, bis(2,8-diamino-1-sodiothiophenothiazinyl) sulfide (mp 114–117°C) (product **3**).

The sulfur dye extracts obtained were modified by exhaustive reaction with butyl bromide (Table 2) at 90–95°C for 9 h, according to the following scheme:



3, 4 **5, 6**

$R^1 = R^4 = NH_2$, $R^2 = H$, $R^3 = SNa$, $R^5 = R^8 = C_4H_9NH$, $R^9 = C_4H_9$, $R^6 = H$, $R^7 = C_4H_9S$ (**5**); $R^2 = R^3 = NH_2$, $R^1 = H$, $R^4 = SNa$, $R^6 = R^7 = C_4H_9NH$, $R^9 = C_4H_9$, $R^5 = H$, $R^8 = C_4H_9S$ (**6**).

The physicochemical constants of the synthesized dyes are given in Table 3.

The fastness of coloration of cotton fabrics with the dyes obtained was evaluated by generally accepted procedures. The fastness data are given in Table 4.

The synthesized dyes impart to the dyed fabric excellent fastness in pure water and soap solution, as well

as in seawater and distilled water. In 10% acid solution, the coloration is unstable.

EXPERIMENTAL

The IR spectra were recorded on a Nicolet Avatar device from KBr pellets. The UV spectra were taken with an SF-25 spectrophotometer from ethanol solutions. The concentration of the leuco form of the dye in ethanol was 10^{-4} M. The synthesis progress was monitored by paper chromatography, system ethanol : ammonia : water = 5 : 2 : 4 (EAW). The sulfur content was quantitatively determined by the procedure described in [16]. Fabric dyeing with the sulfur dyes prepared was performed according to [17].

Table 2. Modification of sulfur dyes derived from *m*- and *p*-phenylenediamine with butyl bromide. Dye : C_4H_9Br ratio 1 : 8; 95°C; 9 h

Compound	Yield, %	Color of dyed cotton fabric
5	70.5	Rose-brown
6	63	Dark brown

Bis(2,8-diamino-1-sodiothiophenothazinyl) sulfide **3** was prepared by three procedures: in aqueous solution (a), by fusion (b), and in the presence of a copper salt (c).

(a) A three-necked flask equipped with a stirrer, a reflux condenser, and a thermometer was charged with 10.8 g (0.1 mol) of *p*-phenylenediamine, 20.4 g (0.51 mol) of NaOH, 6.4 g (0.2 mol) of sulfur, and 22 ml (1.22 mol) of water. The flask contents were heated for 10 h at 115–117°C with continuous stirring. The precipitate that formed was filtered off on a Büchner funnel and dried. Yield of the solid product 25 g (60%). A 7.3-g portion of the product was dissolved in 100 ml of water. The insoluble residue (0.5 g) was filtered off. The filtrate was extracted with ethyl acetate (6 × 20 ml). The extract was dried over calcium chloride. After distilling off the solvent, 2.23 g of a solid product was obtained; mp 114–117°C, R_f 0.82. Found, %: S 26.7. $C_{24}H_{18}N_6S_5Na_2$. Calculated, %: S 26.84.

(b) A mixture of 33 g (0.305 mol) of *p*-phenylenediamine, 4.88 g (0.15 mol) of sulfur, and 12.21 g (0.3 mol) of NaOH was heated at 205–215°C for 10 h. A solid product (51.6 g) was obtained. A 20-g portion of the fusion cake was dissolved in 190 ml of water, and the insoluble residue (2.27 g) was filtered off. The filtrate was extracted with ethyl acetate (6 × 30 ml),

Table 3. Physicochemical constants of the dyes synthesized

Compd.	T_m, °C	R_f	Sulfur, %		Empirical formula	IR spectrum, cm^{-1}	UV spectrum, λ, nm	log ε
			found	calculated				
3	114–117	0.82	26.7	26.84	$C_{24}H_{18}N_6S_5Na_2$	3380, (ν_{NH}); 1265 (ν_{NH}), 1606, 1004, 870 (C–H)	218, 304	3.02, 2.51
3	115–118	0.83	26.67	26.84	$C_{24}H_{18}N_6S_5Na_2$	3369, (NH); 1598, 1265 (NH); 870 (C–H)	218, 308	3.02, 2.52
3	116–119	0.78	26.66	26.84	$C_{24}H_{18}N_6S_5Na_2$	3370, 3292 (NH); 1264 (NH); 3062 (C=H); 872 (C–H)	218, 300	3.04, 2.68
3a	114–116	0.72	28.02	28.35	$C_{24}H_{18}N_6S_6Na_2Cu$	3370, 3300 (NH); 1265 (NH); 3047 (C=H); 1602, 828 (C–H)	212, 292	3.21, 2.87
4	73–76	0.13	26.32	26.84	$C_{24}H_{18}N_6S_5Na_2$	3395, 3326 (NH); 1252 (NH); 3047 (C=H); 1602, 840 (C–H)	214, 295	3.24, 2.33
5	134–136	0.87	15.63	16.01	$C_{56}H_{84}N_6S_5$	3376, (NH); 1262 (NH); 1310, 1454 (C–H, C–CH_3); 2922 (C–H, –CH_2–); 3007 (C=H)	210, 252	2.94, 5.37
6	131–134	0.79	15.69	16.01	$C_{56}H_{84}N_6S_5$	3421, (NH); 1308, 860 (C–H); 2960 (C–H, C–CH_3)	206, 250	2.95, 2.44

Table 4. Fastness of sulfur dye colorations on cotton fabrics

Dye	Fastness parameter, points					
	laundering resistance		resistance to distilled water	resistance to 10% H_2SO_4	sweat resistance	resistance to "seawater"
	in pure water	in soap solution				
3	5/5/5	5/5/5	5/5/5	4/5/5	5/5/5	5/5/5
	5/4/5	5/5/5	5/5/5	3/5/5	5/5/5	5/5/5
3a	5/5/5	5/5/5	5/5/5	3/5/5	5/5/5	5/5/5
4	5/5/5	5/5/5	5/5/5	3/5/5	5/5/5	5/5/5
5	5/5/5	5/5/5	5/5/5	3/5/5	5/5/5	5/5/5
6	5/4/5	5/5/5	5/5/5	3/5/5	5/5/5	5/5/5

and the extract was dried over calcium chloride. After distilling off the solvent, 10.3 g of a solid product was obtained; mp 116–118°C, R_f 0.78. Found, %: S 26.66. $C_{24}H_{18}N_6S_5Na_2$. Calculated, %: S 26.84.

(c) A mixture of 24.5 g (0.226 mol) of *p*-phenylenediamine, 3.7 g (0.114 mol) of sulfur, 9 g (0.225 mol) of NaOH, and 7.2 g (0.023 mol) of $CuSO_4 \cdot 5H_2O$ dissolved in 40 ml of water was heated with continuous stirring for 15.5 h at 110°C. A solid product (28 g) was obtained. Its 26.2-g portion was dissolved in 160 ml of water. The insoluble residue (1.2 g) was filtered off. The filtrate was extracted with ethyl acetate (6 × 30 ml). The extract was dried over calcium chloride. After distilling off the solvent, 13.5 g of the product (**3a**) was obtained; mp 119–121°C, R_f 0.83. Found, %: S 28.02. $C_{24}H_{18}N_6S_6Na_2Cu$. Calculated, %: S 28.35.

Bis(1,9-diamino-2-sodiothiophenothiazinyl) sulfide 4. A mixture of 80 g (0.74 mol) of *m*-phenylenediamine, 11.9 g (0.37 mol) of sulfur, and 29 g (0.725 mol) of NaOH was heated at 196–205°C for 6 h. A solid product (100.5 g) was obtained. Its 20.5-g portion was dissolved in 120 ml of water. The insoluble residue (5.1 g) was filtered off. The filtrate was extracted with ethyl acetate (10 × 30 ml). The extract was dried over sodium chloride. After distilling off the solvent, 11 g of compound **4** was obtained; mp 73–76°C, R_f 0.13. Found, %: S 26.32. $C_{24}H_{18}N_6S_5Na_2$. Calculated, %: S 26.84.

Bis(2,8-bis(butylamino)-5-butyl-1-butylthiophenothiazinyl) sulfide 5. A three-necked flask equipped with a reflux condenser, a stirrer, and a dropping funnel was charged with 1.12 g (0.0025 mol) of the extract of **3**, dissolved in 50 ml of *n*-butanol, and a solution of 1.46 ml (0.02 mol) of C_4H_9Br in 10 ml of *n*-butanol was added dropwise over a period of 1 h. The mixture was heated with continuous stirring for 9 h at 95°C, 70 ml of 30% NaOH was added, and the organic layer was separated from the aqueous layer. The organic layer was distilled in a water-jet-pump vacuum. The residue was dissolved in 80 ml of acetone, and concentrated HCl was added to make the solution acidic to Congo Red. Hydrochloride of the leuco form of the dye was obtained; yield 1.32 g, mp 134–137°C, R_f 0.87. Found, %: S 15.63. $C_{56}H_{84}N_6S_5$. Calculated, %: S 16.01.

Bis(1,9-bis(butylamino)-5-butyl-2-butylthiophenothiazinyl) sulfide 6 was prepared similarly to **5** from 1.12 g (0.0025 mol) of the extract of **4**, dissolved in 50 ml of *n*-butanol, and a solution of 1.46 ml (0.02 mol) of C_4H_9Br in 10 ml of *n*-butanol. The mixture was heated with continuous stirring for 8–9 h at 90°C. After cooling and addition of 40 ml of 30% NaOH, the organic layer was separated from the aqueous layer. The organic layer was evaporated. The residue was dissolved in 30 ml of acetone, and 3–4 ml of concentrated HCl was added dropwise to make the solution acidic to Congo Red. Hydrochloride of **6** was obtained; yield 7.1 g (63%), mp 85–88°C, R_f 0.79. Found, %: S 15.69. $C_{56}H_{84}N_6S_5$. Calculated, %: S 16.01.

CONCLUSIONS

(1) Sulfur dyes bis(2,8-diamino-1-sodiothiophenothiazinyl) sulfide and bis(1,9-diamino-2-sodiothiophenothiazinyl) sulfide were synthesized from *p*- and *m*-phenylenediamine after extraction with ethyl acetate.

(2) Introduction of the butyl radical to the sulfur dyes prepared makes the color of the dyed fabrics deeper.

(3) The fabrics dyed with sulfur dyes are resistant to all kinds of actions except treatment with a sulfuric acid solution.

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