

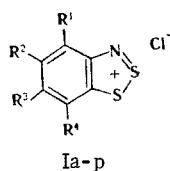
REACTION OF BENZO-1,2,3-DITHIAZOLIUM SALTS WITH AROMATIC AMINES

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UDC 547.794.1:543.422.25.4

The character of a displaceable group depends substantially on the rate of reaction of substituted 6-chloro and 6-methoxy derivatives of benzo-1,2,3-dithiazolium salts, which gives the corresponding 6-phenylaminobenzo-1,2,3-dithiazolium salts. In 4,6-disubstituted benzo-1,2,3-dithiazolium salts, an aniline residue displaces only the substituent in the 6 position.

The products of the Herz reaction — 6-chlorobenzo-1,2,3-dithiazolium salts (Ia,f,g,k) [1] — react rapidly at room temperature with aniline and its derivatives to give bright-violet substances, for which a 6-phenylamino derivative structure (Ib) has been proposed. Their hydrolysis [2] leads to the practically valuable 4-amino-3-mercaptopodiphenylamines.



I\* a R<sup>1</sup>=R<sup>2</sup>=H, R<sup>3</sup>=Cl; b R<sup>1</sup>=R<sup>2</sup>=H, R<sup>3</sup>=C<sub>6</sub>H<sub>5</sub>NH; c R<sup>1</sup>=R<sup>2</sup>=H, R<sup>3</sup>=CH<sub>3</sub>O; d R<sup>1</sup>=H, R<sup>2</sup>=R<sup>3</sup>=CH<sub>3</sub>O; e R<sup>1</sup>=H, R<sup>2</sup>=CH<sub>3</sub>O, R<sup>3</sup>=C<sub>6</sub>H<sub>5</sub>NH; f R<sup>1</sup>=H, R<sup>2</sup>=CH<sub>3</sub>O; R<sup>3</sup>=Cl; g R<sup>1</sup>=CH<sub>3</sub>O, R<sup>2</sup>=H, R<sup>3</sup>=Cl; h R<sup>1</sup>=CH<sub>3</sub>O, R<sup>2</sup>=H, R<sup>3</sup>=C<sub>6</sub>H<sub>5</sub>NH; i R<sup>1</sup>=Cl, R<sup>2</sup>=H, R<sup>3</sup>=CH<sub>3</sub>O; j R<sup>1</sup>=Cl, R<sup>2</sup>=H, R<sup>3</sup>=C<sub>6</sub>H<sub>5</sub>NH; k R<sup>1</sup>=R<sup>3</sup>=Cl, R<sup>2</sup>=H; l R<sup>1</sup>=R<sup>3</sup>=H, R<sup>2</sup>=CH<sub>3</sub>O; m R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H, R<sup>4</sup>=CH<sub>3</sub>O; n R<sup>1</sup>=CH<sub>3</sub>, R<sup>2</sup>=H, R<sup>3</sup>=C<sub>6</sub>H<sub>5</sub>NH; o R<sup>1</sup>=H, R<sup>2</sup>=CH<sub>3</sub>, R<sup>3</sup>=C<sub>6</sub>H<sub>5</sub>NH; p R<sup>1</sup>=H, R<sup>2</sup>=Cl, R<sup>3</sup>=C<sub>6</sub>H<sub>5</sub>NH

For the first time we have been able to obtain salts Ib,e,h,j in pure form; they are also readily obtained by the action of aniline on 6-methoxybenzo-1,2,3-dithiazolium salt Ic, although the reaction of aniline with Ic is slower (by a factor of almost eight) than the reaction with Ia.

In disubstituted derivatives of the benzodithiazolium salt only one substituent is displaced as a result of reaction with aniline. Thus the corresponding 6-phenylamino derivative (Ie) is obtained by the action of aniline on 5,6-dimethoxybenzo-1,2,3-dithiazolium chloride (Id). The structure of Ie was proved by alternative synthesis from aniline and 5-methoxy-6-chlorobenzo-1,2,3-dithiazolium chloride (If).

The 6-phenylamino derivative (Ih) is obtained by reaction of aniline with 4-methoxy-6-chlorobenzo-1,2,3-dithiazolium chloride (Ig). The isomeric II reacts with aniline to give Ij with displacement of a methoxy group. Structure Ij is confirmed by alternative synthesis from the 4,6-dichlorobenzo-1,2,3-dithiazolium salt (Ik).

These results constitute unambiguous evidence that in benzodithiazolium cations the energy of localization of the positive charge in the 6 position is lower than in the 4 position. It seemed of interest to study the possibility of nucleophilic reactions with benzodithiazolium derivatives containing only one substituent in the 5 and 7 positions.

For this, we obtained o-aminothiophenols, from which the corresponding benzodithiazolium salts II and Im are formed by treatment with thionyl chloride.

\*In all cases except Im, R<sup>4</sup> = H.

Leningrad Branch, All-Union Scientific-Research Institute of Synthetic Fibers. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 183-185, February, 1976. Original article submitted April 4, 1975.

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TABLE 1. Chlorozincates of 6-Phenylamino-benzo-1,2,3-di-thiazolium Chloride Derivatives

Compound	Empirical formula	Found, %			Calc., %			$\lambda_{max}$ , nm	log ε	Yield, %
		Cl	N	S	Cl	N	S			
Ib	C <sub>12</sub> H <sub>9</sub> Cl <sub>3</sub> N <sub>2</sub> S <sub>2</sub> Zn	7.0	15.2	25.4	7.0	15.4	21.5	530	4.3	71
Ie	C <sub>13</sub> H <sub>11</sub> Cl <sub>3</sub> N <sub>2</sub> S <sub>2</sub> Zn	6.4	14.2	23.7	6.3	14.4	23.8	505	4.4	76
Ih	C <sub>13</sub> H <sub>11</sub> Cl <sub>3</sub> N <sub>2</sub> S <sub>2</sub> Zn	6.4	14.2	23.7	6.3	14.4	23.8	525	4.2	48
Ij	C <sub>12</sub> H <sub>8</sub> Cl <sub>3</sub> N <sub>2</sub> S <sub>2</sub> Zn	6.4	14.4	31.0	6.2	14.2	31.1	538	4.4	57
In	C <sub>13</sub> H <sub>11</sub> Cl <sub>3</sub> N <sub>2</sub> S <sub>2</sub> Zn	6.6	14.7	24.5	6.5	14.9	24.6	527	4.2	52
Io	C <sub>13</sub> H <sub>11</sub> Cl <sub>3</sub> N <sub>2</sub> S <sub>2</sub> Zn	6.7	14.7	24.4	6.5	14.9	24.6	520	4.1	64
Ip	C <sub>12</sub> H <sub>8</sub> Cl <sub>4</sub> N <sub>2</sub> S <sub>2</sub> Zn	6.2	14.4	31.2	6.2	14.2	31.1	530	4.2	49

It was found that salts II and I<sub>m</sub> do not react with aniline. The increased capacity of benzodithiazolium salts for nucleophilic attack in the 6 position is in good agreement with the results of an analysis of the electronic and PMR spectra of these compounds [3-5].

## EXPERIMENTAL

The electronic spectra of acetic acid solutions of the compounds were recorded with an SF-4A spectrophotometer. The benzo-1,2,3-dithiazolium chloride derivatives (Ia,c,d,f,g,i,k) were obtained by the Herz reaction [3, 5].

3-Nitro-4-thiocyanatoanisole. A 45-g (0.27 mole) sample of 3-nitro-4-aminoanisole was dissolved in 420 ml of water and 250 g of concentrated H<sub>2</sub>SO<sub>4</sub>, and the solution was cooled to 0° and diazotized with a solution of 22.5 g (0.325 mole) of sodium nitrite in 50 ml of water, while maintaining the temperature at no higher than 5°. The resulting solution was added dropwise with vigorous stirring to a solution of 75 g of crystalline cobalt chloride and 87 g of potassium thiocyanate in 600 ml of water, after which the mixture was stirred at 0-10° for 3 h and allowed to stand overnight. It was then stirred at 50° for 16 h until nitrogen evolution had ceased. The precipitate was removed by filtration, washed with water, and dried at 80° to give 33.5 g (59%) of 3-nitro-4-thiocyanatoanisole with mp 97° (n-butyl alcohol). Found, %: N 13.4; S 15.2. C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>O<sub>3</sub>. Calculated, %: N 13.3; S 15.2.

3-Nitro-2-thiocyanatoanisole, with mp 117° (n-butyl alcohol), was similarly obtained in 48% yield. Found, %: N 13.5; S 15.3. C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>O<sub>3</sub>. Calculated, %: N 13.4; S 15.2.

2-Amino-4-methoxythiophenol Hydrochloride (IIa). A solution of 10 g (47 mmole) of 3-nitro-4-thiocyanatoanisole in benzene was added dropwise with stirring and cooling to a suspension of 15 g of technical-grade lithium aluminum hydride in 150 ml of absolute ether, after which the mixture was refluxed with stirring in a stream of dry argon for 8 h. The excess lithium aluminum hydride was decomposed (with cooling) with ice water, 100 ml of water was added, and the mixture was acidified to pH 6 with dilute HCl. It was then extracted with benzene, and the extract was dried with MgSO<sub>4</sub> and treated with HCl to give 6.3 g (70%) of hydrochloride IIa with mp 214°. Found, %: Cl 17.7; N 7.5; S 17.0. C<sub>8</sub>H<sub>9</sub>NOS•HCl. Calculated, %: Cl 17.5; N 7.3; S 16.7.

2-Amino-6-methoxythiophenol hydrochloride (IIb), with mp 234°, was similarly obtained in 61% yield. Found, %: Cl 17.7; N 7.5; S 16.8. C<sub>8</sub>H<sub>9</sub>NOS•HCl. Calculated, %: Cl 17.5; N 7.3; S 16.7.

5-Methoxybenzo-1,2,3-dithiazolium Chloride (II). A 2-g sample of hydrochloride IIa was added to 50 ml of refluxing thionyl chloride, after which the mixture was refluxed for 1 min. The hot mixture was then filtered through a layer of carbon in a glass filter into 150 ml of absolute benzene. The resulting yellow-orange needles were removed by filtration, washed successively with absolute benzene and ether, and vacuum dried to give 1.85 g (80%) of II. Found, %: Cl 16.3; N 6.2; S 30.3. C<sub>8</sub>H<sub>6</sub>ClNOS<sub>2</sub>. Calculated, %: Cl 16.1; N 6.4; S 30.4.

7-Methoxybenzo-1,2,3-dithiazolium chloride (Im), with mp 174-181° (decomp.), was similarly obtained in 68% yield.

Synthesis of 6-Phenylamino Derivatives of Benzo-1,2,3-dithiazolium Chloride (Ib,e,h,j,n,o,p). A cooled solution of 10 g of aniline in 20 ml of glacial CH<sub>3</sub>COOH was added to a suspension of 0.01 mole of benzo-1,2,3-dithiazolium chloride in 10 ml of glacial acetic acid, after which the mixture was stirred at room temperature for 24 h, and the resulting precipi-

ate was removed by filtration, washed with acetic acid and ether, and vacuum dried. A 10- to 20-ml sample of a 10% solution of  $ZnCl_2$  in  $CH_3COOH$  was added to a hot saturated solution of the chloride in acetic acid, and the mixture was cooled after a certain time to precipitate the corresponding chlorozincate, which was washed with acetic acid and ether and vacuum dried (Table 1).

Kinetics of the Reaction of 6-Methoxy- and 6-Chlorobenzo-1,2,3-dithiazolium Chlorides with Aniline. The kinetics were studied by spectrophotometry with an SF-4A spectrophotometer at 25°. An 0.5-ml sample of a  $2 \cdot 10^{-3}$  M solution of the salt in  $CH_3COOH$  was added to 19.5 ml of a 1 M solution of aniline in  $CH_3COOH$  (for the 6-methoxy derivative) or was injected into an acetic acid solution of aniline in the spectrophotometer cuvette (for the 6-chloro derivative). It was shown by preliminary experiments that the reaction goes to completion and that the concentration of the resulting 6-phenylamino derivative is equal to the concentration of the 6-chloro and 6-methoxy derivative used for the investigation. The rate constants calculated for the pseudomolecular reactions were  $(1.58 \pm 0.04) \cdot 10^{-2}$  liter $\cdot$ sec $^{-1}$  $\cdot$ mole $^{-1}$  and  $(1.24 \pm 0.03) \cdot 10^{-3}$  liter $\cdot$ sec $^{-1}$  $\cdot$ mole $^{-1}$  for the 6-chloro (Ia) and 6-methoxy (Ic) derivatives, respectively.

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#### SATURATED NITROGEN-CONTAINING HETEROCYCLES.

#### VIII.\* SYNTHESIS AND PROPERTIES OF SOME SUBSTITUTED PYRROLIDYLALKANOLS

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UDC 547.743.1:547.722:547.584:  
547.495.1

Phenyl-substituted pyrrolidylalkanols were synthesized by hydrogenation of the corresponding furan amines in acidic aqueous solution in the presence of nickel on diatomaceous earth. Terephthalates, carbamates, and other pyrrolidylalkanol derivatives were obtained. The ability of (2-pyrrolidyl)-3-alkanols to form an intramolecular hydrogen bond was studied by IR spectroscopy.

We have previously reported a new method for the synthesis of (2-pyrrolidyl)-3-alkanols with alkyl substituents in various positions of the pyrrolidine ring by hydrogenation of the corresponding furan amine in acidic aqueous solution in the presence of metal catalysts [1, 2]. The pyrrolidine alcohols are most smoothly obtained in 50-60% yields in the presence of an industrial nickel catalyst on diatomaceous earth. The utilization of this catalyst made it possible to extend the reaction to the synthesis of the previously undescribed phenyl-substituted pyrrolidylalkanols. The latter, in analogy with the structurally similar N-aralkyl-N-alkylaminoalkyl alcohols, may be used for the synthesis of possible neurotropic preparations [3].

We used furan amines (I-III) containing a phenyl ring in the side chain with respect to the furan ring as the starting compounds. The amines were hydrogenated in hydrochloric acid solution (pH 4) at 90°C and an initial hydrogen pressure of 75 atm. The principal reaction

\*See [1] for communication VII.

N. G. Chernyshevskii Saratov State University. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 2, pp. 186-190, February, 1976. Original article submitted July 12, 1974.

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