

RESEARCH ON A NUMBER OF SUBSTITUTED
ARYLAMIDES OF DITHIOCARBOXYLIC ACIDS
XV. OXIDATION OF DITHIOMALONIC ACID ARYLAMIDES
TO SUBSTITUTED 1,2-DITHIOLS

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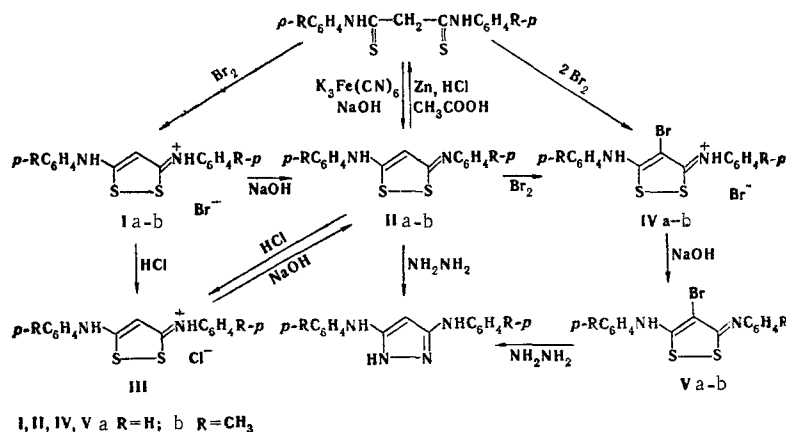
Dithiomalonic acid diarylamides are cyclized to 3,5-diarylamino-1,2-dithiolium halides by oxidation with an equivalent amount of bromine (iodine) in chloroform solution; the same amides are cyclized to 4-bromo-3,5-diarylamino-1,2-dithiolium bromides with excess bromine and to 3-arylamino-5-arylimino-1,2-dithiols in alkaline media with potassium ferricyanide. The behavior of the synthesized substituted 1,2-dithiols with respect to various reagents was studied.

In contrast to derivatives of other dithio acids, dithiomalonic acid amides and N-substituted amides are oxidized to 1,2-dithiol derivatives [1-3] that have found broad practical application [4].

Schmidt [2] and Barnikow [5] obtained 3,5-diarylamino-1,2-dithiolium iodides by oxidation of dithiomalonic acid diarylamides with iodine in alcohol solution. In an attempt to oxidize dithiomalonic acid dianilide with bromine in chloroform solution Barnikow and co-workers were unable to isolate an oxidation product and identified only elementary sulfur [6].

We have obtained 3,5-diarylamino-1,2-dithiolium bromides (Ia, b) by the action of a solution of bromine in chloroform on dithiomalonic acid diarylamides and 3,5-dianilino-1,2-dithiolium iodide, which is identical to the product described in [5], by the action of iodine on dithiomalonic acid dianilide under similar conditions.

In contrast to the data in the literature regarding ring opening and isolation of elementary sulfur [7, 11], ionic halogen is readily split out by the action of basic reagents (NaOH, KSH, $C_6H_5NH_2$, etc.) on bromide I to give 3-arylamino-5-arylimino-1,2-dithiols (IIa, b).



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When Ia is refluxed with concentrated hydrochloric acid, bromine is replaced by chlorine to give the corresponding 1,2-dithiolium chloride (IIIa). Compound IIIa was also obtained by refluxing IIa with hydrochloric acid. A dithiolium salt that is resistant to hydrolytic cleavage at the C=N bond is formed in this reaction.

Like I, on treatment with bases, 1,2-dithiolium chloride IIIa readily splits out ionic halogen and is converted to IIa. The resistance of the 1,2-dithiolium halides that we obtained to basic reagents is apparently explained by the presence of arylamino groups in the 3 and 5 positions, which are responsible for the possibility of the formation of dipolar structures and stabilize the 1,2-dithiolium ring.

The oxidation of dithiomalonic acid diarylamides with 2 or 3 moles of bromine in chloroform solution gives 4-bromo-3,5-diarylamino-1,2-dithiolium bromides (IVa, b). Compound IVa was also obtained by the reaction of IIa with a molar amount of bromine in chloroform.

On treatment with bases, IV readily splits out ionic halogen to give 4-bromo-3-arylamino-5-arylimino-1,2-dithiols (Va, b). The bromine in the 4 position of the 1,2-dithiolium ring is inert with respect to nucleophilic substitution reactions (except for the reaction with hydrazine hydrate). The 1,2-dithiolium salts are decomposed by the action of hydrazine hydrate and arylhydrazines in aqueous solutions, and pyrazole derivatives are formed in anhydrous media [7].

3,5-Dianilinopyrazole, which is identical to the compound we previously obtained in [8], is obtained by heating 3,5-dianilino-1,2-dithiolium bromide in hydrazine hydrate or in an alcohol solution of hydrazine hydrate on a water bath for several hours. The reaction proceeds with hydrogen sulfide evolution. 3,5-Dianilinopyrazole was also obtained by heating Va with an alcohol solution of hydrazine hydrate. Splitting out of halogen apparently occurs during the step involving ring opening after the addition of hydrazine to the 1,2-dithiol [9].

The oxidation of dithiocarboxylic acid diarylamides with potassium ferricyanide has not been described in the literature. It is known only that dithiooxanilide is not oxidized by potassium ferricyanide to the benzothiazol derivative [10]. We carried out the oxidation of dithiomalonic acid dianilide with an equimolar amount of potassium ferricyanide in alkaline media and obtained 3-anilino-5-phenylimino-1,2-dithiol, which was identical to IIa.

On treatment with reducing agents, 1,2-dithiol derivatives are either desulfurized [4] or undergo cleavage of the S-S bond [2]. We obtained dithiomalonic acid dianilide by reduction of 3-anilino-5-phenylimino-1,2-dithiol with zinc in acetic acid.

EXPERIMENTAL

3,5-Dianilino-1,2-dithiolium Bromide (Ia). A solution of 0.6 g (0.003 mole) of bromine in chloroform was added with stirring to a solution of 1 g (0.003 mole) of dithiomalonic acid dianilide in 40 ml of dry chloroform, after which the mixture was allowed to stand at room temperature for 2-3 h. The resulting yellow precipitate was removed by filtration, washed with chloroform, and air dried to give 1.2 g (94%) of a product with mp 177° (from alcohol). Found: Br 22.2%. $C_{15}H_{13}N_2BrS_2$. Calculated: Br 21.9%.

3,5-Di(p-toluidino)-1,2-dithiolium bromide (Ib), with mp 214-216° (from alcohol), was similarly obtained in 89% yield. Found: Br 20.4%. $C_{17}H_{17}N_2BrS_2$. Calculated: Br 20.4%.

3-Anilino-5-phenylimino-1,2-dithiol (IIa). A) A mixture of 1 g (0.003 mole) of 3,5-dianilino-1,2-dithiolium bromide (or chloride) and 20 ml of 5% aqueous sodium hydroxide solution was stirred for 1-2 h. The resulting precipitate was removed by filtration, washed with water, and air dried to give 0.65 g (84%) of a product with mp 161° (from alcohol). Found: S 22.3%. $C_{15}H_{12}N_2S_2$. Calculated: S 22.4%.

B) A solution of 0.2 g of sodium hydroxide in 30 ml of water was added to a solution of 1 g (0.003 mole) of dithiomalonic acid dianilide in 25 ml of alcohol, after which the mixture was cooled to 7-8°, and a solution of 1.2 g of potassium ferricyanide in 10 ml of water was added slowly with stirring. The mixture was then allowed to stand at room temperature for 1-2 h. The resulting yellow precipitate was removed by filtration, washed with water, and air dried to give 0.9 g (90%) of a product with mp 160° (from alcohol). 3-(p-Toluidino)-5-tolylimino-1,2-dithiol (IIb), with mp 160° (from alcohol), was similarly obtained by method A. Found: S 20.0%. $C_{17}H_{18}N_2S_2$. Calculated S 20.4%.

Compounds IIa and IIb were obtained as yellow crystalline substances that were soluble in many organic solvents and stable on heating.

3,5-Dianilino-1,2-dithiolium Chloride (III). A) A mixture of 0.5 g of 3,5-dianilino-1,2-dithiolium bromide and 10 ml of concentrated HCl was heated on a water bath for 10 h, after which it was allowed to stand at room temperature for 48 h. The precipitate that formed on standing was removed by filtration, washed with water, and air dried to give 0.4 g (93%) of a product with mp 193-194° (from alcohol). Found: Cl 10.7%. $C_{15}H_{13}N_2ClS_2$. Calculated: Cl 11.1%.

B) A 0.5-g sample of 3-anilino-5-phenylimino-1,2-dithiol was heated on a water bath with an alcohol solution of hydrochloric acid (1 ml of concentrated HCl in 5 ml of alcohol) for 1-2 h. A portion of the solvent was removed in vacuo, and the resulting light-brown precipitate was removed by filtration, washed with water, and air dried to give a product with mp 194° (from alcohol).

4-Bromo-3,5-dianilino-1,2-dithiolium Bromide (IV). A) A solution of 1.5 g of bromine in chloroform was added slowly with stirring to a solution of 1 g (0.003 mole) of dithiomalonic acid anilide in 10 ml of chloroform. After 1-2 h, the resulting crystalline precipitate was removed by filtration, washed with chloroform, and air dried to give 1.5 g (91%) of a product with mp 142° (from alcohol).

B) A solution of 0.5 g of bromine in 10 ml of chloroform was added with stirring to a solution of 1 g (0.003 mole) of 3-anilino-5-phenylimino-1,2-dithiol in 10 ml of chloroform; the addition of the first portions of the bromine solution was accompanied by the production of a viscous mass that crystallized on further addition of bromine. The yellow precipitate was removed by filtration, washed with chloroform, and air dried to give 1.5 g of a product with mp 141-142° (from alcohol). Found: Br 36.4%. $C_{15}H_{12}N_2S_2Br_2$. Calculated: Br 36.0%.

4-Bromo-3,5-di(p-toluidino)-1,2-dithiolium bromide (IVb), with mp 155-156° (from alcohol), was obtained by method A from dithiomalonic acid di(p-toluidide). Found: Br 34.2%. $C_{17}H_{17}N_2S_2Br_2$. Calculated: Br 33.9%.

4-Bromo-3-anilino-5-phenylimino-1,2-dithiol (Va). A 0.5-g sample of IVa was added to 5 ml of 5% aqueous solution of sodium hydroxide, and the mixture was stirred vigorously at room temperature for 2 h. The precipitate was removed by filtration, washed with water, and air dried to give 0.36 g (90%) of a product with mp 133-134° (from alcohol). Found: Br 20.0%. $C_{17}H_{17}N_2BrS_2$. Calculated: Br 20.4%.

4-Bromo-3-(p-toluidino)-5-(p-tolylimino)-1,2-dithiol (Vb), with mp 160° (from alcohol), was similarly obtained. Found: S 20.3%. $C_{17}H_{20}N_2S_2$. Calculated: S 20.0%.

3,5-Dianilino-1,2-dithiol. A) A 0.4-g (1.4 mmole) sample of 3-anilino-5-phenylimino-1,2-dithiol was dissolved in 10 ml of alcohol, and 2 ml (60 mmole) of 50% hydrazine hydrate was added. The mixture was heated at 60-70° for 6-7 h until hydrogen sulfide evolution ceased completely. A portion of the solvent was removed in vacuo, and the precipitate was removed by filtration, washed slightly with water, and air dried to give a product with mp 199-200° (from alcohol).

B) A 0.5-g (1.3 mmole) sample of 4-bromo-3-anilino-5-phenylimino-1,2-dithiol was heated on a water bath with 4 ml (0.12 mole) of 50% hydrazine hydrate in alcohol solution until hydrogen sulfide evolution ceased. Water (3 ml) was added, the mixture was cooled, and the resulting white crystalline product was removed by filtration, washed with cold water, and air dried to give a product with mp 199° (from alcohol).

Reduction of 3-Anilino-5-phenylimino-1,2-dithiol. A 0.5-g sample of zinc dust was added to a solution of 0.4 g (1.3 mmole) of IIa in 10 ml of acetic acid and 1 ml of hydrochloric acid, and the resulting light-yellow precipitate was removed by filtration and dissolved in methanol. The solvent was removed in vacuo, and the residue was purified by passing a chloroform solution of it through a column filled with Al_2O_3 and subsequently removing the solvent in vacuo to give 0.12 g of a product with mp 147-148°. No melting-point depression was observed for a mixture of this product with dithiomalonic acid dianilide.

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