

poly(vinyl pyrrolidone) were insoluble in the cold, but dissolved and melted respectively in boiling *N*-methylmorpholine to give reducible mixtures.

In those cases where the reduced polymer, after hydrolysis, was insoluble in *N*-methylmorpholine and precipitated from the solution, it was isolated by extraction of the filtered solids with another organic solvent, usually methanol, followed by precipitation or evaporation (Method B). Those reduced polymers not precipitated because of solubility in the common organic solvents were purified by repeated solution and evaporation of a suitable solvent (Method C). Reduced polymers insoluble in the common organic solvents were dissolved in dilute acetic acid, dialyzed, and isolated by evaporation of the solvent or precipitation with sodium hydroxide solution (Method D).

Analytical values given in the table are the averages of at least two determinations, each of which agreed within 0.4 unit. Since the differences in theoretical hydrogen percentages for the pure, unreduced, and reduced polymers are sometimes quite small and since secondary reactions further complicated the situation, the percentage reduction given in the table is sometimes only a rough estimate.

**Reduction of the Styrene-Methacrylonitrile Copolymer.** A solution of 25 g. (0.145 mole) of this interpolymer in 250 ml. of *N*-methylmorpholine was added, with stirring, over a period of 2 hr. to a suspension of 9.5 g. (0.25 mole) of lithium aluminum hydride in 500 ml. of *N*-methylmorpholine under nitrogen kept at 100–110°. After addition was over, the mixture was stirred for an additional 4 hr. under reflux. After the mixture had cooled, 20 ml. of water, 12 ml. of 25% sodium hydroxide solution, then 20 ml. more water were added dropwise, giving a granular precipitate. After the mixture had been stirred for an additional 3 hr., the precipitate was filtered and discarded. The filtrate was then evaporated down to 100 ml. on a steam-bath under vacuum. On pouring the residual solution into water, the reduced polymer precipitated as a friable powder. It was washed several times with water, filtered, and vacuum-dried. Yield, 19 g. of a white powder, soluble in methanol, dimethylformamide, and dilute acetic acid. It swelled but did not dissolve in acetone.

*Anal.* Calcd. for completely reduced copolymer: C, 82.8; H, 9.7; N, 8.0. Found: C, 84.8, 84.7; H, 9.9, 9.7; N (Dumas), 6.7, 6.7; N (Van Slyke), 4.8, 4.7.

**Acetylation of Styrene-Methallylamine Copolymer.** A solution of 5 g. of the styrene-methallylamine copolymer in 100 ml. of pyridine was treated with 50 ml. of acetic anhydride. The mixture was heated for 1 hr. on a steam-bath, then precipitated in water. It was dissolved in acetone and reprecipitated in water.

*Anal.* Calcd. for complete acetylation of reduced copolymer: acetyl, 16.7. Found: acetyl, 16.4, 16.6.

**Preparation of the  $\gamma$ -Dimethylaminopropylmaleimide-Styrene Copolymer.** Preparation of the Copolymer. A solution of 20.2 g. (0.1 mole) of a styrene-maleic anhydride copolymer (Monsanto Lytron 810) in 200 ml. of dimethylformamide was added dropwise to a stirred, heated (100°) solution of 14 g. (0.14 mole) of  $\gamma$ -dimethylaminopropylamine in 200 ml. of dimethylformamide over a period of 1.5 hr. The temperature was then raised gradually until 100 ml. of solvent had distilled off. During this time, the distillate temperature rose to 152°. The solution was then cooled and poured into water, giving a friable precipitate. This was washed with water, then vacuum-dried, giving 23 g. of a white, voluminous powder which was soluble in acetone and dilute acetic acid.

**Preparation of the *N,N*-Dimethylhydrazone of Poly(methyl Vinyl Ketone).** A mixture of 10 g. of poly(methyl vinyl ketone), 100 ml. of *N,N*-dimethylhydrazine, and 2 drops of glacial acetic acid was tumbled at room temperature overnight. Complete solution resulted. The polymer was precipitated in petroleum ether, redissolved in acetone, and reprecipitated in petroleum ether, giving a soft, water-soluble solid which hardened somewhat on drying. Yield, 7 g.

**Reduction of Poly(methyl Vinyl Ketone) with Sodium Borohydride.** A solution of 7 g. (0.1 mole) of poly(methyl vinyl ketone) in 100 ml. of anhydrous diglyme was added dropwise to a stirred solution of 3.8 g. (0.1 mole) of sodium borohydride in 150 ml. of diglyme, kept at 55° over a period of 0.5 hr. Following addition, the mixture was kept at 65° for 3 hr., then poured into one l. of water. The product was filtered and vacuum-dried. It was dissolved in tetrahydrofuran and precipitated in ether, giving 4.5 g. of a white powder.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

## A Novel Displacement Reaction of the *N*-Nitroso Derivative of *N*-Acetyl-*o*-aminophenyl Benzenethiolsulfonate<sup>1</sup>

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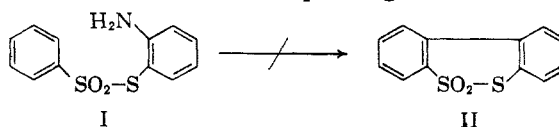
The preparation of *N*-acetyl-*o*-aminophenyl benzenethiolsulfonate is described. Decomposition of its *N*-nitroso derivative gave unexpectedly 1,2,3-benzothiadiazole and benzenesulfonic acid.<sup>3</sup> A mechanism<sup>4</sup> to account for this transformation is proposed.

The initial purpose of this work was to prepare unsymmetrically substituted biphenyl disulfenic

(1) This is the 31st in a series of papers concerned with azo compounds; for the previous paper in this series see C. G. Overberger, George Kesslin and Pao-tung Huang, *J. Am. Chem. Soc.*, **81**, 3779 (1959).

(2) This paper comprises portions of dissertations submitted by Michael P. Mazzeo in partial fulfillment of the requirements for the degree of Master of Science and John J. Godfrey in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

acids in order to study the intramolecular reaction of the sulfinic acid groups with each other. One scheme proposed for this disulfenic acid synthesis involved preparation of unsymmetrically substituted biphenyl thiolsulfonates which could then be converted to the corresponding disulfenic acids.



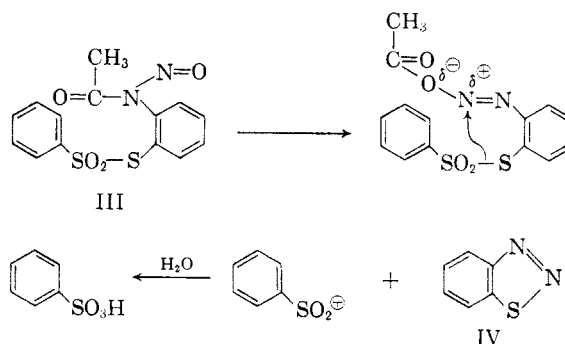
*o*-Aminophenyl benzenethiolsulfonate was prepared as a model intermediate for the study of the ring closure to give the known thiolsulfonate (II) of 2,2'-biphenyldisulfonic acid.<sup>3</sup> This paper describes the attempts to effect the conversion of I to II and the actual product isolated.

*o*-Aminophenyl benzenethiolsulfonate was prepared by the action of silver-*o*-aminothiophenolate on benzenesulfonyl iodide. The aminothiolsulfonate was then diazotized and decomposed by the method of Shetty<sup>4</sup> in the presence of powdered copper in an acidic medium. No biphenyl thiolsulfonate was isolated but only small traces of a white solid, identified as 1,2,3-benzothiadiazole. Strongly acidic conditions similar to the method of DeTar and Sagmanli<sup>5</sup> gave similar results. Cyclization was then attempted by means of the Gomberg-Bachman reaction.<sup>6</sup> Because thiolsulfonates are hydrolyzed with aqueous alkali, only enough aqueous sodium hydroxide was added to neutralize the acid present and form the diazohydroxide from the diazonium chloride. However, no biphenyl thiolsulfonate could be isolated from this reaction, but traces of impure 1,2,3-benzothiadiazole was detected.

Accordingly, the method using nitrosoacetyl-amines for the preparation of biaryl compounds was attempted. *o*-Aminophenyl benzenethiolsulfonate was first acetylated and then nitrosated by means of nitrosyl chloride according to the method of Heilbron<sup>7</sup> to give III. Decomposition of III in an aqueous sodium bicarbonate solution did not yield the expected biphenyl thiolsulfonate, but instead 1,2,3-benzothiadiazole (IV) and benzenesulfonic acid. In addition to these products, a small amount of *N*-acetyl-*o*-aminophenyl benzenethiolsulfonate, the denitrosated product, was isolated.

The formation of IV probably proceeds by way of an intramolecular displacement; a reaction which often occurs with an aromatic diazo compound having an appropriate ortho substituent. Some examples of this are the formation of benzotriazole,<sup>8</sup> 1,2,3-benzothiadiazole<sup>9</sup> and indazole<sup>10</sup> from the corresponding *o*-aminothiol and methyl substituted compounds. The synthesis of hydroxy substituted benzo [c]pyridazines by the diazotization of an enolizable ortho amino ketone<sup>11</sup> is also analogous.

Whereas for the cases just cited the displaced group was a proton, the reaction reported here involves the elimination of a benzenesulfonium ion. The suggested path for this reaction, given below, is analogous to that described for the formation of indazole from *N*-nitroso-*N*-acetyl-*o*-toluidine<sup>12</sup> and for the previously mentioned hydroxy substituted benzo [c]pyridazines.<sup>11</sup>



The benzothiadiazole was identified by comparison of its infrared spectrum with a known sample of 1,2,3-benzothiadiazole prepared by the diazotization of *o*-aminobenzenethiol,<sup>9</sup> and further identified by a mixed melting point and the formation of the 4-nitro derivative.

#### EXPERIMENTAL<sup>13</sup>

*o*-Aminophenyl benzenethiolsulfonate. Benzenesulfonyl iodide was prepared by the method of Otto and Troeger<sup>14</sup> from the sodium salt of benzenesulfonic acid and iodine. Silver *o*-aminothiophenolate was prepared by a procedure similar to that described by Bulmer and Mann,<sup>15</sup> from the reaction of freshly distilled *o*-aminobenzenethiol with silver nitrate.

The procedure was related to that described by Gibson, Miller, and Smiles<sup>16</sup> for the preparation of thiolsulfonates,<sup>5</sup> although no detailed procedures were reported. To 200 ml. of anhydrous benzene cooled in an ice bath was added 13.4 g. (0.05 mole) of benzene sulfonyl iodide with stirring. To this, 12 g. (0.052 mole) of silver-*o*-aminothiophenolate was then added in small portions over a period of 20 min. and after the addition was complete the mixture was stirred an additional 20 min. The pale yellow thiolsulfonate solution was filtered free of silver iodide, the filtrate being collected in an ice cooled receiver. The benzene was then removed under vacuum without the use of heat—towards the end of the evaporation free iodine appeared in the vacuum traps due to the decomposition of unreacted benzenesulfonyl iodide. The yellow solid in the distilling flask was kept at 0.5 mm. pressure for an additional hour in order to ensure removal of all the benzene. The flask was then removed from the vacuum apparatus, 30 ml. of absolute ethanol was added, the contents were mixed thoroughly and placed in a refrigerator. This operation was performed in order to dissolve unreacted sulfonyl iodide and its decomposition products at the expense of some thiolsulfonate, since these contaminants render isolation of the thiolsulfonate diffi-

(3) H. J. Barber and S. Smiles, *J. Chem. Soc.*, 1141 (1928).

(4) G. Shetty, *Helv. Chim. Acta.*, **32**, 24 (1949).

(5) D. DeTar and S. Sagmanli, *J. Am. Chem. Soc.*, **72**, 965 (1950).

(6) W. E. Bachman and R. A. Hoffman, *Org. Reactions*, Vol. II, John Wiley and Sons, Inc., p. 225.

(7) H. France, M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 369 (1940).

(8) A. Ladenberg, *Ber.*, **9**, 219 (1876).

(9) P. Jacobson, *Ber.*, **21**, 3104 (1888).

(10) P. Jacobson and L. Huber, *Ber.*, **41**, 669 (1908).

(11) K. Shofield and J. C. Simpson, *J. Chem. Soc.*, 1170 (1948).

(12) R. Husigen and H. Nakaten, *Ann.*, **586**, 84 (1954).

(13) All melting points are corrected.

(14) R. Otto and J. Troeger, *Ber.*, **24**, 485 (1891).

(15) G. Bulmer and F. G. Mann, *J. Chem. Soc.*, 680 (1945).

(16) D. T. Gibson, S. Smiles, and C. J. Miller, *J. Chem. Soc.*, 1827 (1925).

cult. The thiolsulfonate was then removed by filtration, washed with a minimum amount of cold ethanol and dried in a vacuum desiccator, to give 8.18 g. (61.7%) of *o*-aminophenyl benzenethiolsulfonate, m.p. 83°–83.5°.

*Anal.* Calcd. for  $C_{13}H_{11}NO_2S_2$ : C, 54.32; H, 4.18; N, 5.28; S, 24.16. Found: C, 54.68; H, 4.37; N, 5.58; S, 24.14.

*N*-Acetyl-*o*-aminophenyl benzenethiolsulfonate. In 95 ml. of acetic anhydride was dissolved 24.6 g. (0.093 mole) of *o*-aminophenyl benzenethiolsulfonate. The solution was kept at 50° for 30 min., cooled, and then poured into 200 ml. of ice water. An oil formed which soon solidified. The white solid was removed by filtration, washed with water, and recrystallized from an ethanol-water solution, white needles (94%), m.p. 114.6°–115.4°.

*Anal.* Calcd. for  $C_{14}H_{13}NO_3S_2$ : C, 54.88; H, 4.26; N, 4.56. Found: C, 54.93; H, 4.33; N, 4.49.

*Preparation and decomposition of N-nitroso-N-acetyl-o-aminophenyl benzenethiolsulfonate.* The procedure for the preparation of *N*-nitroso-*N*-acetyl-*o*-aminophenyl benzenethiolsulfonate was a general procedure described by France, Heilbron, and Hey<sup>7</sup> for *N*-acetyl derivatives, by the reaction of nitrosyl chloride with *N*-acetyl amines. This method led to the isolation of the crude *N*-nitroso compound in 85.3% yield; m.p. 77°–79° dec. Attempts to purify the compound by recrystallization from ethanol-water resulted in excessive loss due to ease of decomposition.

To 300 ml. of water in a 1-liter flask equipped with a magnetic stirrer and maintained at 50°–55° was added 24.45 g. (0.072 mole) of *N*-nitroso-*N*-acetyl-*o*-aminophenyl benzenethiolsulfonate and 6.04 g. (0.072 mole) of sodium bicarbonate. The mixture was heated at 50° and continually stirred for a period of 12 hr. to ensure complete decomposition. At the end of this period the yellow nitroso compound had decomposed to give a brown oil which was suspended in the water. The aqueous mixture was then extracted with 250 ml. of ether and the ethereal solution was concentrated to 25 ml., at which time a precipitate formed. The white precipitate was removed by filtration and was observed to be 3.33 g. of *N*-acetyl-*o*-aminophenyl benzenethiolsulfonate, m.p. 114°–115°; a mixed melting point with material melting at 114.6°–115.4° melted at 114°–115°. The remaining ether solution was concentrated and distilled under vacuum to give 4.14 g. (42.3%) of 1,2,3-benzothiadiazole, m.p. 36°–37°; 2.62 g. of charred resinous material remained in the distilling flask. A mixed melting point with an authentic sample of 1,2,3-benzothiadiazole, m.p. 36°–37°, melted at 36°–37°. The infrared spectrum was identical with a known sample.

The benzothiadiazole was characterized further by means of the 4-nitro derivative which was prepared by adding 1 g. of the benzothiadiazole to a mixture of 5 ml. of concentrated sulfuric acid and 5 ml. of fuming nitric acid, heating the solution over a steam bath for 10 min., and then adding it to 50 ml. of ice water. The white solid was recrystallized from an ethanol-water solution, m.p. 93.8°–94.6° (m.p. 95° prepared with potassium nitrate and sulfuric acid).<sup>17</sup>

(17) A. Bernthsen, *Ann.*, **1**, 251 (1888).

A mixed melting point with an authentic sample, m.p. 94°–95° was not depressed, m.p. 94°–95°.

The aqueous phase of the reaction mixture was then evaporated on a rotary evaporator. After the water was completely removed, there remained a brown solid contaminated with a brown oil. The solid was washed with a limited amount of absolute ethanol which dissolved the oil. A total of 5.4 g. (41.5%) of solid crude benzene sulfonate was isolated in this way.

The sodium benzenesulfonate was characterized by means of the aniline salt which was prepared by adding 1 g. of freshly distilled aniline to a saturated 1*N* hydrochloric acid solution of 1 g. of the sodium salt. The white aniline salt which precipitated was recrystallized from water and dried in an oven at 100°, m.p. 237°–239°. A mixed melting point with an authentic sample, m.p. 237°–239° (m.p. 240°),<sup>18</sup> melted at 237°–239°.

*1,2,3-Benzothiadiazole.* The procedure was that described by Jacobson<sup>9</sup> from the diazotization of *o*-aminobenzenethiol. The crude benzothiadiazole was distilled, b.p. 63°/0.5 mm. (57.7%), m.p. 35.4°–36.5° (m.p. 36°–37°).<sup>9</sup>

*Attempted Pschorr reactions and formation of small quantities of 1,2,3-benzothiadiazole.* (A) To 45 ml. of 6*N* sulfuric acid cooled to –5° was added 1 g. of *o*-aminophenyl benzenethiolsulfonate. The amine sulfate formed was insoluble in the medium. A solution of 0.5 g. of sodium nitrite in 5 ml. of water was then added dropwise to the yellow suspension. After the addition, the yellow diazonium salt solution was added in 5-ml. portions to a vigorously stirred suspension of 2 g. of copper powder in 45 ml. of 6*N* sulfuric acid which was kept at 45°–50°. Care was taken to keep the diazonium salt solution cold prior to its addition to the copper suspension in order to minimize decomposition. When all the diazonium solution was added the reaction mixture was brought to 70° and maintained at that temperature for 1 hr. There was no noticeable evolution of nitrogen during the course of the reaction. The mixture was then cooled and the brown oil which had formed was extracted with ether and washed with 1% sodium bicarbonate solution. Upon evaporation of the ether, 0.32 g. of a yellow oil which had a characteristic nitrobenzene odor was isolated. After several attempted recrystallizations some light yellow solid was obtained, m.p. 31°–34°. The infrared spectrum of this compound was identical with the spectrum of authentic 1,2,3-benzothiadiazole. The procedure of ref. (4) was followed and similar results were obtained, namely a small amount of impure 1,2,3-benzothiadiazole was isolated.

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(18) C. M. Keyworth, *J. Soc. Chem. Ind.*, **43**, 341T (1924).