heated together on the steam-bath for three hours. The product was steam-distilled until the distillate became clear. On acidification of the distillate ω-bromostyrene separated as an oil. It was extracted with ether and distilled; yield 5.4 g. (36.6%), b. p. 219° (19 mm.). The liquid residue from the steam distillation was acidified and the needle-like crystals, 6.8 g., were removed by filtration. All attempts to separate the cinnamic and bromocinnamic acids quantitatively failed; hence the mixture was analyzed for bromine by the method of Carius.

Anal. Calcd. for $C_9H_7O_2Br$: Br, 35.3. Found: Br, 14.2.

Evidently there was sufficient bromine present to account for the bromo acid to the extent of 40.3% of the mixture. Assuming the mixture of acids to contain nothing but cinnamic and bromocinnamic acids, the yields were: cinnamic acid, 4.1 g., 34.1%; bromocinnamic acid, 2.7 g., 14.7%. Pure cinnamic acid and pure α-bromocinnamic acid in small amounts were obtained by fractional crystallization of the analyzed mixture.

Experiments in aqueous solution using pyridine, or sodium carbonate, or mixtures of the two invariably resulted in the formation of ω-bromostyrene in 65–75% yields. The remainder of the product consisted again of a mixture of cinnamic and α-bromocinnamic acids.

Summary

1. Improved methods of preparation of quinaldine and γ-picoline chlorals have been developed.

2. Quinolyl- and pyridylacrylic acid dibromides have been prepared and their dehalogenations studied. Quinolylacrylic acid dibromide was found to have different properties than those previously described for it in the literature.

3. The dehalogenations of the above two dibromo acids with a series of bases led in every case to the formation of the original acrylic acids as the principal products. This constitutes a new type of reaction for the α,β-dibromo acids, differing in degree but not in kind from the dehalogenations of other similar acids.

4. Attention has been called to the similarity between the above-mentioned dehalogenations and the action of anhydrous pyridine upon cinnamic acid dibromide. Apparently the heterocyclic nitrogen atoms in the pyridyl and quinolyl acids influence the course of the dehalogenations even in the presence of other bases.

5. As an example of the heterocyclic acetylenes, β-pyridylacetylene has been prepared and its properties described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Action of Sulfur on Aniline and Similar Amines

BY MAURICE L. MOORE[1] AND TREAT B. JOHNSON

The desire of securing certain new derivatives of 4,4′-dihydroxydiphenyl sulfide led the authors to study the reaction of sulfur with aromatic amines in the presence of lead oxide, and we now offer an explanation of the mechanism of this reaction.

Hodgson and others[2] have isolated and identified the different products of the reaction between aniline and sulfur, 2,2′-diaminodiphenyl sulfide, 2,2′-diaminodiphenyl disulfide, 2,4′-diaminodiphenyl sulfide, 4,4′-diaminodiphenyl disulfide, and 4,4′-diaminodiphenyl sulfide being among the chief products formed. The presence of lead oxide[2c] promotes the formation of *para*-substituted derivatives, thereby increasing the yield of *p*-thioaniline and at the same time lowering the temperature at which the reaction occurs. The conditions under which this reaction proceeds with the optimum results have been established by Hodgson,[2a] although a considerable amount of dark colored tarry material is obtained and the ultimate yield of the thioaniline is very low. Shukla[3] has found that iodine will lower the reaction temperature as indicated by the evolution of hydrogen sulfide even though his final yield was only 1 g. of thioaniline from 50 g. of aniline.

In determining the extent of this reaction it was found that Merz and Weith[2c] have prepared thioacetanilide by the action of sulfur on acetanilide in the presence of lead oxide. Hodgson[4] obtained thio-*o*-toluidine from *o*-toluidine by the same reaction. The results of these workers led us to examine the reaction with other compounds of a similar nature, namely, benzalaniline,

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(1) A. Homer Smith Research Fellow in Organic Chemistry 1934–1935.

(2) (a) Hodgson, *J. Chem. Soc.*, **125**, 1855 (1924); (b) Hofmann, *Ber.*, **27**, 2807 (1894); (c) Merz and Weith, *ibid.*, **4**, 384 (1871).

(3) Shukla, *J. Indian Inst. Science*, **10A**, pt. 3, 33 (1927).

(4) Hodgson and France, *J. Chem. Soc.*, 296 (1933); 1140 (1934).

monomethylaniline and dimethylaniline. The expected sulfides produced from these compounds could be identified by conversion with acid hydrolysis to thioaniline or else compared with compounds of known structure. Of the compounds mentioned, monomethylaniline was the only one to react with sulfur, under the conditions of the experiment, to give thio-monomethylaniline. Benzalaniline and dimethylaniline failed to react and were recovered as such.

These findings with those previously mentioned are of considerable theoretical interest in view of the fact that only those compounds which have at least one labile hydrogen on the nitrogen atom will undergo a reaction with sulfur to give the corresponding sulfide. This leads us to postulate the intermediate formation of a sulfanilide type of compound I in which the sulfur is initially connected to nitrogen with the evolution of hydrogen sulfide. This compound is then immediately rearranged under the conditions of the experiment to the corresponding *para* sulfide II. The formation of this intermediate sulfanilide compound I offers an excellent explanation of the fact that one obtains so many products from the reaction mixture because the rearrangement could occur in successive steps, and also in the *ortho*- or *para*-positions.[5] Benzalaniline, dimethylaniline and those compounds which do not have a labile hydrogen on the nitrogen atom could not form such an intermediate compound, hence would not be expected to react with sulfur to form the final thio derivatives. Aniline, monomethylaniline, *o*-toluidine, acetanilide and those compounds which have a labile hydrogen on the nitrogen atom could form this intermediate and, therefore, would be expected to react with sulfur forming the amino sulfides, as observed from the experimental results. A molecular rearrangement of this type extends to other series of compounds as exemplified by the benzidine, methylene[6] and sulfonyl[7] rearrangements.

$$2C_6H_5NH_2 + S \longrightarrow \underset{\text{I}}{C_6H_5NHSNHC_6H_5} \longrightarrow \underset{\text{II}}{H_2NC_6H_4SC_6H_4NH_2}$$

To establish conclusively this reaction mechanism, one ought to isolate the intermediate compound and subsequently subject it to a high temperature and determine if it undergoes rearrangement. The intermediate products in the case of the benzidine, methylene and sulfonyl compounds have been isolated and their rearrangements,[6,7] observed. Since the temperature of the aniline–sulfur reaction is so high as to destroy completely all of the intermediate compound if it is formed, it was decided to prepare a series of comparable compounds and study their behavior upon heating. In the following paper of this series we shall discuss the preparation and rearrangement of a series of sulfanilide compounds of the type $C_6H_5SNHC_6H_5$ which supports our postulations.

In studying the reaction of the above compounds with sulfur and lead oxide, it was found convenient to modify and combine the methods of preparation as described by Hodgson[4] and Shukla[3] to the extent that the final material was isolated as the sulfate. The yields and purity of the products were considerably increased by doing so. The large amount of colored, tarry material formed, with the tedious steps necessary for purification, leaves much to be desired in using this reaction for laboratory preparations.

Experimental Part

Thioaniline, 4,4′-Diaminodiphenyl Sulfide.—From several experiments, involving variations in the time of heating, the temperature, the amount of lead oxide and different procedures for purification, the following procedure was found to give the maximum yield with a minimum amount of tar. Freshly distilled aniline (93 g.), b. p. 181–182°, and sulfur (32 g.) were placed in a round-bottomed flask, equipped with a mechanical stirrer, on an oil-bath at a temperature of 135–145°. Lead oxide (160 g.) was slowly added over a period of five and one-half hours with vigorous stirring and heating continued for thirty minutes longer at the same temperature. The dark oily mixture was allowed to cool, 30 ml. of 20% sodium hydroxide added, and then extracted three times with boiling alcohol (500 ml.). The alcohol was removed by distillation on an oil-bath and 8 ml. of unaltered aniline was recovered by steam distillation. The oily residue was then removed, treated with dilute hydrochloric acid and the solution evaporated to dryness. The solid was taken up with a large volume of water and boiled vigorously with Norite. The solution was filtered and neutralized with 10% sodium hydroxide solution and the precipitate washed free of alkali. The oily solid was then dissolved in an ether–alcohol mixture, boiled with Norite and the sulfate of thioaniline precipitated with dilute sulfuric acid. Upon drying, a yellowish gray powder was obtained in a yield of 65 g. The sulfate was dissolved in hot water, boiled with Norite and

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(5) This type of change is not suggested in the papers by Hodgson (*loc. cit.*), and neither Edeleano [*Bull. soc. chim.*, [3] **5**, 173 (1891)] nor Schmidt [*Ber.*, **11**, 1168 (1878)] postulate such a mechanism in their respective studies on the action of sulfur chloride on amines and acetanilide.

(6) (a) Von Braun and Kruber, *Ber.*, **45**, 2977 (1912); (b) Cohn and Fischer, *ibid.*, **33**, 2586 (1900); (c) Meyer and Rohmer, *ibid.*, **33**, 250 (1900); (d) Eberhardt and Welter, *ibid.*, **27**, 1804 (1894).

(7) Witt and Truttwin, *ibid.*, **47**, 2786 (1914).

finally precipitated with 5% sodium hydroxide. The free base was crystallized from 35% alcohol and melted at 106–108°. After several recrystallizations it melted at 107–108°.

The Diazotization of Thioaniline by a Modification of the Method of Bass and Johnson.[8]

4,4'-Dihydroxydiphenyl Sulfide.—Thioaniline sulfate (10 g.) was suspended in 75 ml. of glacial acetic acid and 5 ml. of concentrated sulfuric acid in an ice-bath at 0–5°. Isoamyl nitrite (5 g.) was slowly added over a period of thirty minutes with vigorous stirring for thirty minutes longer. A solution of 100 ml. of concentrated sulfuric acid and 80 ml. of water was heated to boiling (160°) and the diazotized solution slowly added, when a dark oil separated. After heating the solution to boiling for about forty-five minutes it was then diluted with water and cooled. The oil was separated and dissolved in 5% sodium hydroxide solution and boiled with Norite. Upon cooling, the solution was neutralized with dilute hydrochloric acid. The straw-colored precipitate was dissolved in 50% alcohol, decolorized with Norite and crystallized; yield, 2.5 g., m. p. 149°.[9]

Action of Sulfur on Benzalaniline.—Benzalaniline (180 g.) and sulfur (32 g.) were heated at 140–150° in the presence of lead oxide (160 g.) for six hours. On working up the reaction mixture after digestion with hydrochloric acid we obtained only benzaldehyde and aniline the hydrolysis products of benzalaniline. No thioaniline was formed.

Action of Sulfur on Dimethylaniline.—Freshly distilled dimethylaniline, b. p. 190–192° (121 g.), was heated with sulfur (32 g.) and lead oxide (160 g.) at 140–150° for six hours. Upon extraction with alcohol and steam distilling, 110 ml. of unused dimethylaniline was recovered. The water solution remaining contained no thiodimethylaniline.

Bis - (4 - monomethylaminophenyl) Sulfide.—Monomethylaniline, b. p. 193–195° (90 g.), sulfur (28 g.) and lead oxide (125 g.) were heated together in the usual manner for six hours at 140–160°. Upon extraction and steam distilling, 25 ml. of unused monomethylaniline was recovered. The remaining material was purified according to the above method. The sulfate did not precipitate completely from the alcohol–ether mixture, so it was evaporated and 25 g. of a gray powder obtained. This was dissolved in hot water, boiled with Norite several times, neutralized with 5% sodium hydroxide, and finally crystallized as a colorless solid from an ether–petroleum ether mixture, m. p. 58–60° (Beilstein, m. p. 60°). The material turned purple upon standing in the air.

Summary

The action of sulfur on certain aromatic amines, namely, aniline, benzalaniline, monomethylaniline and dimethylaniline, has been studied in which it was observed that benzalaniline and dimethylaniline do not react to form the corresponding sulfides. These results together with those for *o*-toluidine and acetanilide, lead the writers to propose a possible mechanism for the explanation of this reaction, involving the intermediate formation of a sulfanilide type of compound through the replacement of a labile hydrogen on the nitrogen atoms with sulfur. This compound under the conditions of the experiment immediately undergoes a rearrangement to the corresponding amino-sulfide. The research will be continued.

An improvement has been noted in the technique for the purification of the products obtained from this reaction.

NEW HAVEN, CONN. RECEIVED APRIL 25, 1935

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(8) Bass and Johnson, THIS JOURNAL, **52**, 1146 (1930).

(9) Tassinari, *Gazz. chim. ital.*, **17**, 83 (1887), (m. p. 150–151°); Krafft, *Ber.*, **7**, 1165 (1874), m. p. 143–144°.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies on the Polymethylbenzenes. XI. The Nitration of Pentamethylbenzene and of Hexamethyl- and Hexaethylbenzene[1,2]

BY LEE IRVIN SMITH AND S. ARTHUR HARRIS

The nitration of pentamethylbenzene was investigated in 1887 by Gottschalk,[3] who by adding the hydrocarbon to fuming nitric acid at 0° obtained a small amount of a dinitrotetramethylbenzene, m. p. 178°, together with much oily material. Willstätter and Kubli[4] obtained the same solid product from the hydrocarbon by nitrating it with a mixture of sulfuric acid and fuming nitric acid in the presence of chloroform. Both investigators assigned to this product the ortho dinitro structure, regarding it as dinitroprehnitene.

The work of Barbier[5] and of Alfthan[6] indicates that in those nitrations of benzene derivatives in which a nitro group displaces an alkyl or acyl group, the group displaced is always meta to the first entering nitro group. On this basis, the

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(1) Paper X, THIS JOURNAL, **56**, 2169 (1934).

(2) Abstracted from a thesis by S. Arthur Harris, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science, July, 1934.

(3) Gottschalk, *Ber.*, **20**, 3287 (1887).

(4) Willstätter and Kubli, *ibid.*, **42**, 4151 (1909).

(5) Barbier, *Helv. Chim. Acta*, **11**, 157 (1928).

(6) Alfthan, *Ber.*, **53**, 78 (1920).