Explanation of Table I.—0.02 Mole of the amines mentioned in this table is dissolved in sulfuric acid (15 cc. (d. 1.84)) and after cooling to 0° mixed with a solution of 1.44 g. of sodium nitrite in 15 cc. of sulfuric acid (1.84). Now the mixture is dropped into 60 cc. of phosphoric acid (1.7), cooled with an ice and salt mixture to $-10°$. After the addition of the final quantity of nitrosylsulfuric acid, the diazotization (tetrazotization) is still continued for one-half hour; afterward 2 g. of finely powdered urea is added in order to remove nitrous acid, for this might involve the production of colored matters in consequence of the nitrosation of the azo component. For each case the velocity of the reaction of coupling has been studied during one and one-half hours with the azo components β-naphthol and anisole, by determination of the quantity of dye which is produced in a definite time. *It appears from these observations that the character of the diazonium group is at least as strongly negative as the behavior of two nitro groups in the positions ortho and para with respect to the substituent.*

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Summary

1. The character of the diazonium group agrees with the influence of *two nitro groups* in the positions ortho and para with respect to the substituent.

2. Tetrazotized p-phenylenediamine couples only with *one* mole of the azo component (both *phenols and ethers*) in strongly acidic medium. These diazo-azo compounds can be isolated by pouring onto water and may be afterwards coupled with an azo compound (not with ethers).

ROTTERDAM, HOLLAND

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The Preparation of Para-Phenylene Dihydrazine Hydrochloride

BY H. A. J. SCHOUTISSEN

In previous communications[1] a method was described by which it was possible to tetrazotize p-phenylenediamine in a quantitative way. Now it is of interest to investigate whether this method will enable us to prepare the p-dihydrazinobenzene previously looked for in vain,[2] by reduction of the corresponding tetrazonium compound with stannous chloride, according to the method of V. Meyer and Lecco.[3]

In spite of different attempts to isolate the *free* dihydrazine, I did not succeed, since this compound has a low degree of stability in aqueous

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(1) Schoutissen, These, Delft, 1926, p. 106; THIS JOURNAL, **55**, 4535, 4541 (1933).

(2) Stollé and Leffler, *Ber.*, **57**, 1061 (1924); compare also Wieland, Juchum and Maier, *ibid.*, **64**, 2513 (1931).

(3) V. Meyer and Lecco, *Ber.*, **16**, 2976 (1883).

solutions. However, the hydrochloride was prepared and analyzed. For further evidence *p*-chlorobenzene and *p*-diiodobenzene and also the disemicarbazide were prepared from the dihydrazino salt.

The researches are being continued, especially with regard to the condensation products of *p*-phenylenedihydrazine with aldehydes and ketones.

Experimental

1.—3.24 g. of *p*-phenylenediamine is dissolved with warming in 100 cc. of phosphoric acid (d. 1.7). Nitrosylsulfuric acid (4.32 g. of sodium nitrite and 45 cc. of sulfuric acid (d. 1.84)) is added by drops; time 1 hour, temp. −5°. The solution obtained in this way is poured, with vigorous stirring, into a solution of 35 g. of stannous chloride dissolved in 80 cc. of concentrated hydrochloric acid, cooled at −10°. After one and one-half hours the reduction is stopped, concentrated hydrochloric acid is added and the precipitate deposits in needles. The crude product obtained by filtration is washed with concentrated hydrochloric acid. It is readily soluble in water; this solution becomes quickly colored. On warming it a little a rapid evolution of nitrogen appears. The crude product is dissolved in a small quantity of cold distilled water and filtered. Now the same volume of 2 *N* hydrochloric acid is added, besides some drops of stannous chloride solution. The hydrochloride separates in colorless flat needles. After this crystallization is repeated the precipitate is filtered off and washed successively with 1:1 hydrochloric acid, alcohol and ether. The melting point of the salt could not be determined; on warming a vigorous decomposition has been observed.

Anal. Calcd. for $C_6H_{12}N_4Cl_2$: C, 34.10; N, 26.55. Found: C, 34.09; N, 26.42.

2.—3.24 g. of *p*-phenylenediamine is tetrazotized and reduced in the same way as has been described under 1. The collected precipitate is dissolved in a small quantity of ice-cold water and introduced into a saturated solution of 25 g. of copper sulfate (crystallized). Instantly an evolution of nitrogen begins. The resulting *p*-dichlorobenzene is distilled with steam; yield 2 g., m. p. 53°.

3.—The crude product, according to 1, is dissolved in ice-cold distilled water and a little more than the theoretical quantity of iodine in potassium iodide is added. At once greenish sparkling leaflets or needles separate. If these are warmed in the solution the color turns to brown-red with evolution of gas. After the crystals have been collected and washed with sodium thiosulfate solution, the crude product consists of pale yellow-brown lozenge-shaped crystals, which become colorless on recrystallization from dilute alcohol. The melting point of 128° indicates that the substance is *p*-diiodobenzene.

4.—3 g. of *p*-phenylene dihydrazine hydrochloride, prepared after the method described under 1, is dissolved in 200 cc. of cold distilled water. Now a solution is added of 3 g. of potassium cyanate in 20 cc. of water. A colorless, crystalline precipitate separates. The crude product is recrystallized from distilled water. On cooling slowly pale yellow needles or prisms separate; yield about 2 g. The compound is slightly soluble in the usual organic solvents. No sharp melting point is observed; upon warming the substance colors and carbonizes.

Anal. Calcd. for $C_8H_{12}O_2N_6$: C, 42.85; N, 37.5. Found: C, 42.44; N, 37.72.

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