[CONTRIBUTION FROM THE LABORATORY FOR ORGANIC CHEMISTRY OF THE TECHNICAL HIGH SCHOOL, DELFT, HOLLAND]

The Character of the Diazonium Group.[1] The Tetrazotization of Para-Phenylenediamines

BY H. A. J. SCHOUTISSEN

The use of a diazo and tetrazo compound derived from *p*-phenylenediamine has become of very great practical importance in the manufacture of azo dyes, but as it is essential that *a single compound and not a mixture of diazo and tetrazo compounds should be prepared and further, that no large excess of nitrous acid should be present these compounds have hitherto been prepared in an indirect way.* For this purpose either *p*-nitraniline or *p*-aminoacetanilide is used as the starting point. Hitherto it has not been possible to tetrazotize *p*-phenylenediamine in a quantitative way. The tetrazotization of negatively substituted *p*-phenylenediamines presents still greater difficulties.

Griess[2] found that it was impossible to convert *p*-diaminobenzoic acid into the tetrazo compound as it became exclusively *p*-aminodiazobenzoic acid. It has also been observed that nitrous acid converts only one of the amino groups of *p*-phenylenediaminosulfonic acid.[3] The same behavior is shown by 1,4-naphthalenediamino-3-sulfonic acid;[4] a similar example is *o*-nitro-*p*-phenylenediamine as appears from the researches of Bülow and Mann.[5] Benda[6] examined the possibility of tetrazotizing *p*-phenylenediaminoarsenic acid; in spite of all the methods which he applied, he only succeeded in diazotizing *one* of the two amino groups.

The question arises why these *p*-phenylenediamines are diazotized partially. Cain and Morgan[7] have tried in vain to give a satisfactory explanation. However, the present author succeeded in giving a logical explanation by observing the following rules. (1) The reaction of diazotization proceeds between the *salt* of the amine and free nitrous acid.[8] (2) The group diazonium is extremely negative, being much stronger than the nitro group.

Observing these results the author has succeeded too in finding a method of tetrazotization which gives good results for these diamines.

It is a well-known fact, that the character of aromatic amino compounds is changed in a high degree by the introduction of substituents in the nucleus. The nitro group, *e. g.*, decreases to a large extent the basicity

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(1) Schoutissen, *Rec. trav. chim.*, **40**, 763 (1921).

(2) Griess, *Ber.*, **17**, 603 (1884).

(3) German Patent 160,170; *Friedländer*, **8**, 133.

(4) German Patent 102,160; *Friedländer*, **5**, 508.

(5) *Ber.*, **30**, 877 (1897).

(6) Benda, *Ber.*, **44**, 3300 (1911).

(7) Cain, *J. Chem. Soc.*, **91**, 1049 (1907); Cain, "The Chemistry and Technology of the Diazo Compounds," London, 1920, p. 188–189; Morgan, *J. Chem. Soc.*, **91**, 1315, 1505 (1907); **95**, 1319 (1909); **93**, 617 (1908); **97**, 2561 (1910).

(8) Schoutissen. These, Delft, 1926.

of the aromatic amines. So, for example, 1,2-diamino-4-nitrobenzene is a monoacidic base,[9] 1,2-diamino-3,5-dinitrobenzene gives salts which are hydrolyzed into acid and free base,[10] while the salt of hydrogen chloride from 1,3-diamino-2,4,6-tribromobenzene yields hydrogen chloride when exposed to the air.[11] *p*-Phenylenediamine gives salts with both amino groups. This is still the case with monochloro-*p*-phenylenediamine[12] as well as probably with the symmetrical dichloro-*p*-phenylenediamine.[13] Bülow,[14] on the contrary, found that the salt of mononitro-*p*-phenylenediamine contains merely *one* mole of hydrogen chloride. It was found by Wolff[15] that 2,6-dichloro-*p*-phenylenediamine combines only with *one* mole of hydrogen chloride, trichloro- and dinitro-*p*-phenylenediamine have a still more reduced basicity. Krause[16] found that tetrachloro-*p*-phenylenediamine showed a basicity reduced to such an extent that he could recrystallize this compound from concentrated hydrochloric acid. In this diamine therefore the basicity of *both* the amino groups is very small. Wolff[17] found that the salts of trichloronitro-*p*-phenylenediamine are only stable in concentrated hydrochloric acid and sulfuric acid; both are hydrolyzed on diluting with water, the free base separating.

It follows from these facts that negative substituents reduce the basicity of the amino groups in a very pronounced way. This influence of negative groups on the basicity will be strong for amino groups, in respect to which they occupy the ortho or para position; it will be less pronounced for the amino group in meta position.

Let us now consider *p*-phenylenediamine; the diazotization of *one* of the ammonium groups will present no difficulties and proceed with small concentrations of mineral acid in consequence of the relatively strong basic properties of *p*-phenylenediamine. However, as soon as the diazonium group has entered into the benzene nucleus this substituent will by its strong negative character (resembling at least 2 nitro groups at the positions ortho and para with respect to the substituent) reduce to a great extent the basicity of the second amino group in para position. Therefore it is to be expected that this amino group can only be converted into the ammonium group *and therefore into the diazonium group* with very high concentrations of mineral acid. No wonder that the tetrazotization of *p*-phenylenediamine presents great difficulties in opposition to *m*-phenylenediamine. It is to be expected that the same phenomena will be still more pronounced for the negatively substituted *p*-phenylenediamines.

(9) Gottlieb, *Ann.*, **85**, 27 (1853).
(10) Norton and Elliott, *Ber.*, **11**, 328 (1878).
(11) THIS JOURNAL, **18**, 470 (1896).
(12) Cohn, *Mitt. Techn. Gew. Mus. Wien*, **11**, 211 (1901).
(13) Möhlau, *Ber.*, **19**, 2010 (1886).
(14) Bülow, *ibid.*, **29**, 2284 (1896).
(15) Wolff, These, Berlin, 1909.
(16) Krause, *Ber.*, **12**, 51 (1879).
(17) Wolff, These, Berlin, p. 9.

Therefore the tetrazotization of *p*-phenylenediamines can be reduced to the diazotization of highly negatively substituted amines. It is to be expected that the tetrazotization of these *p*-phenylenediamines will succeed according to the method which was elaborated for the extremely weak basical amines.[18]

According to the data of literature it has not yet been posssible to tetrazotize *o*-phenylenediamine. It has been shown that by the action of nitrous acid this diamine, by internal condensation, is always converted into the *azimino compound.*[19]

This can be also explained with the same rules 1 and 2 mentioned above. The first action of nitrous acid may be the formation of *one* diazonium group. As we know, however, that the basicity of the amino group in *o*-nitroaniline has nearly disappeared, this will be still more pronounced for the remaining amino group in ortho position in this monodiazotized diamine. Tetrazotization will be possible only in very strong mineral acidic medium, otherwise the amino group is able to couple with the diazo group to an azimino compound.

Experimental

1.—***p*-Phenylenediamine chloride** (3.62 g.) is dissolved in 70 cc. of phosphoric acid (d. 1.7). This solution is then cooled in a beaker with an ice-salt mixture. With vigorous stirring a solution of 3 g. of sodium nitrite in 30 cc. of sulfuric acid (d. 1.84) is dropped into it (temp. −5°). After the addition of the nitrosylsulfuric acid the tetrazotization is still continued for about one-half hour, after which 2 g. of finely powdered urea is added. Also in the following experiments the excess of nitrous acid is removed for the purpose of giving convincing evidence that the tetrazotization proceeds really in the original solution.

The reaction mixture is poured after one-half hour into a concentrated solution of 8 g. of potassium iodide, to which some pieces of ice are added. After being kept overnight the mixture is diluted with water and the precipitate filtered off. The pale yellow precipitate is washed with water, sodium thiosulfate and water again; yield 6.5 g., calcd. 6.6 g. After treatment with norit and recrystallization from dilute ethyl alcohol, 6.1 g. of *p*-diiodobenzene was obtained, m. p. 129°. It appears from the above that in these circumstances *p*-phenylenediamine is tetrazotized quantitatively; the mother liquor after being made alkaline showed no trace of *p*-iodoaniline.

2.—The tetrazonium solution of *p*-phenylenediamine is dropped with vigorous stirring into a solution of cuprous chloride (prepared by refluxing 10.8 g. of $CuSO_4 \cdot 5H_2O$, 5.4 g. of NaCl, 45 cc. of water, 150 cc. of HCl (1.19) and 30 g. of copper) cooled to 0°. *p*-Dichlorobenzene passed over on steam distillation; yield about 70% of colorless *p*-dichlorobenzene, m. p. 53°.

3.—A solution of 15 g. of bromine in 15 g. of potassium bromide and 100 cc. of water is cooled with ice. On dropping the tetrazonium solution with vigorous stirring into the latter a red precipitate of the perbromide separates. After one hour copper powder is added with vigorous stirring. On standing overnight the precipitate is filtered off, extracted twice with small quantities of alcohol and filtered again. On diluting the solution with water a white precipitate separates, which is recrystallized from boiling dilute alcohol as beautiful long colorless needles of *p*-dibromobenzene, m. p. 87.5°.

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(18) Schoutissen, These, Delft, 1926; THIS JOURNAL, **55**, 4531 (1933).

(19) Ladenburg, *Ber.*, **9**, 219 (1876); **17**, 147 (1884).

4.—The perbromide of the tetrazonium compound of *p*-phenylenediamine is suspended in ice water and gradually added with vigorous stirring to 100 cc. of concentrated ammonia, temp. 0°. The crude product is filtered off and purified by steam distillation; yield 2.2 g. On recrystallization from warm alcohol the substance appears in beautiful hexagonal leaflets, m. p. 83°. The properties correspond with those of bistriazobenzene, described by Griess.[20]

***p*-Phenylenediamine sulfonic acid** is tetrazotized in the same way. The tetrazonium solution is dropped into potassium iodide cooled with ice and salt. Instantly a strong evolution of nitrogen begins. After being kept for two and one-half hours at 0° the solution is gradually warmed and free iodine is removed by steam distillation. The diiodide separates on cooling in flat pointed needles. It is easily soluble in water, slightly soluble in strong mineral acids, moderately soluble in ether.[21]

The barium salt was prepared by adding a concentrated solution of barium chloride to the warm solution of the ammonium salt. It was obtained in long, bright leaflets; at 160° these crystals lose their water of crystallization.

The potassium salt was obtained in a similar way; it crystallizes in long, colorless needles with 1 mole of water of crystallization. After removing this water the potassium salt of 1,4-diiodobenzene sulfonic acid was treated with phosphorus pentachloride by heating to 100–140°; m. p. of the crude product after extraction with water 130°. After one crystallization from cold chloroform the sulfochloride is obtained in colorless needles, m. p. 131.[21] The compound dissolves readily in ether and chloroform and is insoluble in water.

If a quick stream of chlorine dried by sulfuric acid is passed through the solution of this compound in chloroform, the 1,4-diiodobenzene sulfochloride-dichloride precipitates. It crystallizes in pale yellow, short, sparkling quadrilateral prisms, m. p. 128°.[21]

Nitro-*p*-phenylenediamine is tetrazotized according to the indications given above. The tetrazonium solution is poured after about one and one-half hours into a concentrated solution of potassium iodide. A dark resin was formed. After the mixture has been kept overnight it is isolated and washed with water. After adding 50 cc. of 2 *N* potassium hydroxide diiodonitrobenzene passed over on steam distillation; yield 1 g. of crude product, m. p. 109°. The compound crystallizes from petroleum ether in weak yellow needles, m, p. 109–110°. It appears from the melting point and the analysis that this product is really 2,5-diiodonitrobenzene.

Anal. Calcd. for $C_6H_3NO_2I_2$: I, 67.72. Found: I, 67.63, 67.59.

The non-volatile mass is acidified with dilute sulfuric acid. On steaming a yellow product (1 g.) passed over. This compound was freed from iodine by a sodium thiosulfate solution and afterward purified from small quantities of mixed diiodonitrobenzene by dissolving it in 2 *N* alkali, m. p. of the crude product 80–81°. The compound crystallized from boiling petroleum ether in big citron yellow, quadrilateral prisms, m. p. 81°. In sodium hydroxide the substance dissolves with an orange-red color; the salt crystallizes in red needles.

Anal. Calcd. for $C_6H_4O_3NI$: I, 47.91. Found: I, 47.9, 48.0.

It appears from analysis and m. p. that the compound is 4-iodo-2-nitrophenol. The origin of this by-product can be explained from the easy decomposition of the tetrazonium compound while it is being poured into the potassium iodide solution. No unaltered amine could be shown in the filtrate.

2,5-Dichloro-*p*-phenylenediamine was dissolved in concentrated sulfuric acid, mixed with the theoretical quantity of nitrosylsulfuric acid and dropped into twice the volume of phosphoric acid (d. 1.7) temp. −10–0°. The tetrazonium solution thus ob-

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(20) Griess, *Ber.*, **21**, 1559 (1888).

(21) Boyle, *J. Chem. Soc.*. 1701 (1909).

tained was dropped into cuprous chloride (obtained by boiling 10.8 g. of $CuSO_4 \cdot 5H_2O$, 5.4 g. of NaCl, 45 g. of water, 90 cc. of HCl (1.19) and 31 g. of copper powder), to which some pieces of ice are added. After some time the reaction mixture is warmed to 60° and afterward diluted with water; the precipitate is filtered off and extracted by hot benzene. Upon evaporating the benzene solution tetrachlorobenzene crystallizes; yield 64%, m. p. 131°. After one recrystallization from alcohol colorless needles were obtained identical with 1,2,4,5-tetrachlorobenzene.[22]

2,6-Dichloro-*p*-phenylenediamine is tetrazotized in the same way as the 2,5 compound. The weak red colored tetrazonium solution is then poured into a solution of 20 g. of cuprous chloride in 100 cc. of hydrochloric acid (1.19) and 150 cc. of water, temp. about 20°. Instantly a strong evolution of nitrogen begins and after the reaction mixture has been warmed for two hours to 80° the precipitate is filtered off. By steaming the alkaline suspension 1,2,4,6-tetrachlorobenzene is obtained; on recrystallization from ethyl alcohol colorless needles, m. p. 50–51°.[23]

Anal. Calcd. for $C_6H_2Cl_4$: C, 33.4; H, 0.9; Cl, 65.7. Found: C, 33.5; H, 0.8; Cl, 65.3.

2,6-Dibromo-*p*-phenylenediamine is tetrazotized in exactly the same way. The reaction mixture is dropped into a concentrated aqueous solution of potassium iodide to which some pieces of ice are added. After the mass has been kept overnight the precipitate is filtered off and washed with sodium thiosulfate and water; yield 95%. The compound was purified by recrystallization from warm alcohol 1:1 after decoloration with norit as colorless needles, m. p. 115°. It is easily soluble in benzene and chloroform. likewise in alcohol, ether and carbon tetrachloride, little however in petroleum ether.

Anal. Calcd. for $C_6H_2Br_2I_2$: Br, 32.78; I, 52.05. Found: Br, 32.4; I, 51.8.

The filtrate, obtained after converting the tetrazonium solution with potassium iodide, was made alkaline; no precipitate of 2,6-dibromo-4-iodoaniline has been observed. The diamine has been tetrazotized quantitatively.

Trichloro-*p*-phenylenediamine.—Twenty grams of 2,6-dichloro-*p*-phenylenediamine is dissolved in 100 cc. of acetic anhydride; in order to catalyze the acetylation a drop of concentrated sulfuric acid is added. The reaction mixture is boiled for some time under a reflux condenser. After the addition of 50 cc. of glacial acetic acid the solution is poured into water; the diacetyl product separates in small colorless needles. It is recrystallized from glacial acetic acid, m. p. 225°. At room temperature the diacetyl compound is little soluble in the usual solvents; on warming it dissolves readily in ethyl alcohol (96%) and glacial acetic acid. The chlorination of this compound cannot be carried out in a direct way with free chlorine; however, the interaction of calcium hypochlorite is successful.[15]

A solution of $^3/_{20}$ mole of $Ca(OCl)_2$ is added in small quantities to a solution of 13 g. ($^1/_{20}$ mole) of diacetyldichloro-*p*-phenylenediamine in 150 cc. of glacial acetic acid. In the beginning a yellow tough mass is obtained which however in a few days turns into the crystalline state. Moreover colorless crystals separate from the mother liquor. The crude product is crystallized from glacial acetic acid and finally from 96% alcohol as small colorless needles, m. p. 289°.

The diacetyltrichloro-*p*-phenylenediamine has been saponified with 70% sulfuric acid. The diamine is precipitated from this solution by adding ammonia. It can be crystallized by the gradual addition of ligroin to the solution in chloroform. In this way the diamine is obtained in colorless needles, m. p. 198°. The compound dissolves readily in the usual solvents, little however in water.

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[22] *Ann.*, **152**, 248 (1869); **192**, 236 (1878); **296**, 67 (1897); *Ber.*, **29**, 875 (1896).

[23] *Ann.*, **141**, 105 (1867); **192**, 237 (1878).

It is tetrazotized in exactly the same way as described for 2,5-dichloro-*p*-phenylenediamine. The tetrazonium solution is dropped with vigorous stirring into a solution of cuprous chloride in hydrochloric acid cooled to 0°. After one hour the solution is warmed to 60° and then the pentachlorobenzene is steamed over. The compound separates in colorless crystals, yield 80%. It is recrystallized with warm alcohol (60%); on cooling it separates in long colorless needles, m. p. 86–87°.[24]

***o*-Phenylenediamine**, 3.24 g., finely powdered, m. p. 102°, is tetrazotized in the same way, the temperature not being allowed to exceed −5°. About one hour after the first addition of phosphoric acid (1.7) the tetrazotization has ceased and the reaction mixture is poured into a solution of 25 g. of potassium iodide in 100 cc. of water to which some pieces of ice are added A brown oil separates with a strong evolution of nitrogen. After the mixture has been kept for twelve hours at room temperature, the reaction is brought to an end by warming. The iodine is removed with sodium bisulfite. The *o*-diiodobenzene has been separated by steam distillation. The formed weak yellow oil has been shaken with dilute potassium hydroxide to remove the eventually formed *o*-iodophenol. The oil is washed with water and finally dried in a desiccator over concentrated sulfuric acid; yield about 1 g. The boiling point,[25] as the average of several determinations, was found to be 287°, 768.5 mm. This agrees with the b. p. of *o*-diiodobenzene.[26] After steaming, 2.5 g. of resinous product remains which solidifies after cooling to a brownish mass. We have not succeeded in separating definite compounds from this product.

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Summary

1. The technical importance of a method of tetrazotizing *p*-phenylenediamine and its substituted derivatives in a quantitative way has been shown.

2. Starting from the very negative character of the diazonium group and taking account of the fact that the reaction of diazotization proceeds between the *salt* of the amine and nitrous acid a logical and simple explanation is given why negatively substituted *p*-phenylenediamines could only be diazotized hitherto at *one* of the amino groups. Therefore the theories of Cain and of Morgan on this subject must be cast aside.

3. The tetrazotization of *p*-phenylenediamines corresponds with the diazotization of very negatively substituted amines. The same procedure which makes possible diazotizing these amines also serves in tetrazotization of *p*-phenylenediamines. *p*-Phenylenediamine and its derivatives, *e. g.*, nitro-*p*-phenylenediamine, *p*-phenylenediamine sulfonic acid, 2,5-dichloro-*p*-phenylenediamine, 2,6-dichloro-*p*-phenylenediamine, 2,6-dibromo-*p*-phenylenediamine, trichloro-*p*-phenylenediamine, can be tetrazotized in a quantitative way. The two diazo groups were eliminated with cuprous chloride or potassium iodide with a good yield.

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(24) *Ann.*, **141**, 96, 152, 247 (1867); **154**, 182 (1870); **172**, 344 (1874).

(25) Determined after the method of Siwoloboff, *Ber.*, **19**, 795 (1886); Tschitschibabin and Jelgasin, *ibid.*, **47**, 1848 (1914).

(26) Körner and Wender found 286.5°, 751 mm., *Gazz. chim. ital.*, **17**, 491 (1887).

4. It appears that *o*-phenylenediamine is tetrazotizable; however, as would be expected, different factors (lesser stability of the tetrazo compound, coupling with products of decomposition and the formation of an azimino compound) have an unfavorable influence on the yield.

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The Character of the Diazonium Group.[1] A New Method of Preparing Mixed Disazo Dyestuffs[2]

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It is a well-known fact that the equilibrium diazonium $\rightleftarrows$ diazo shifts with the alteration of the concentration of mineral acid: acids transpose the diazo into the diazonium compound. Substituents in the nucleus also have a pronounced influence upon the situation of this equilibrium.[3] The equilibrium shifts to diazo compound if the substituents are more negative. As the reaction of coupling takes place between the *diazo* compound and the azo component in connection with the experiments of Hantzsch on the situation of the equilibrium diazonium $\rightleftarrows$ diazo for different diazo compounds, it may be expected that diazo compounds with strong negative substituents in the nucleus will be able to couple in much greater concentrations of mineral acid as compared with the less negatively or positively substituted diazo compounds. For, notwithstanding the great concentration of mineral acid, still a proper amount of diazo compound is present for the former. K. H. Meyer and Lehnard[4] found that not only phenols and naphthols but also their ethers are capable of coupling with some diazo compounds. The reaction of coupling however proceeds much more slowly with the ethers in comparison with the respective phenols and naphthols and proceeds only rapidly in a mineral acid solution if the diazo compound is *very negatively* substituted. Table I shows the comparative behavior of some diazo compounds with regard to β-naphthol and anisole as to the velocity of the reaction of coupling in a medium of 1 volume of sulfuric acid (d. 1.84) and 2 volumes of phosphoric acid (d. 1.7).

It appears that coupling with anisole proceeds only if *two nitro groups* in the positions ortho and para with respect to the diazo group are present. If two nitro groups are in meta position and their negative influence upon the diazo group therefore is smaller, no coupling appears with ethers. A similar behavior follows from the experiments with β-naphthol.

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(1) Schoutissen, *Rec. trav. chim.*, **40**, 763 (1921).

(2) Schoutissen, communicated in the section meeting for applied chemistry of the Dutch Chem. Soc., April 21, 1922, Delft; see also *Chemisch Weekblad*, **19**, 217 (1922).

(3) Hantzsch, *Ber.*, **33**, 2166 (1900).

(4) K. H. Meyer and Lehnard, *Ann.*, **398**, 74 (1913).