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]

BY H. A. J. SCHOUTISSEN

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).

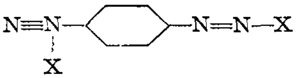
(4) K. H. Meyer and Lehnard, *Ann.*, **398**, 74 (1913).

Table I makes it possible to limit the character of a negative substituent in a relatively simple way. Now in the tetrazotized *p*-phenylenediamine *one* diazonium group behaves according to the nature of the *second.* Therefore, if the diazonium group is an extraordinarily strong negative group, it may be expected that the tetrazotized *p*-phenylenediamine couples as well as diazotized 2,4-dinitroaniline with β-naphthol and anisole in the same conditions; if, however, this group is less negative, at most coupling with β-naphthol appears.

TABLE I

Diazotized	Azo component β-Naphthol	 Anisole
Aniline	No coloration	No coloration
p-Toluidine	No coloration	No coloration
p-Anisidine	No coloration	No coloration
p-Aminophenol	No coloration	No coloration
p-Chloroaniline	No coloration	No coloration
p-Bromoaniline	No coloration	No coloration
p-Iodoaniline	No coloration	No coloration
p-Aminobenzoic acid	No coloration	No coloration
Sulfanilic acid	No coloration	No coloration
2,4-Dichloroaniline	No coloration	No coloration
2,4-Dibromoaniline	No coloration	No coloration
2,4,6-Trichloroaniline	Couples slowly	No coloration
2,4,6-Tribromoaniline	Couples slowly	No coloration
p-Nitraniline	Couples quickly	Couples very slowly
2-Chloro-*p*-nitraniline	Couples quickly	Couples very slowly
2-Bromo-*p*-nitraniline	Couples quickly	Couples very slowly
2,6-Dichloro-*p*-nitraniline	Couples quickly	Couples slowly
2,6-Dibromo-*p*-nitraniline	Couples quickly	Couples slowly
3,5-Dinitroaniline	Couples quickly	No coloration
2,4-Dinitraniline	Couples very quickly	Couples quickly
2,4,6-Trinitroanisidine	Couples very quickly	Couples quickly
2,4,6-Trinitrophenetidine	Couples very quickly	Couples quickly
2,4,6-Trinitroaniline	Couples very quickly	Couples very quickly
p-Phenylenediamine (tet-	Couples very quickly	Couples quickly
Benzidine razotized)	No coloration	No coloration

For, as a strong negative substituent, the one diazonium group effects the transmutation of the other diazonium group to diazo



and gives in this way the possibility of coupling this *diazo* group in the strong acidic medium with β-naphthol; moreover, it may be expected that in consequence of the increased energy of coupling this diazo-diazonium compound couples with ethers such as anisole.

If the speculations mentioned above are exact, it may be predicted also that the coupling *will be restricted to this diazo group,* for as soon as the present diazo group has coupled with a component an *azo* group has been formed, whose nature at most is weakly negative. The remaining diazonium group therefore is not able to change into *diazo* condition in this strongly acidic medium, and it will be possible only to couple this group with an azo component in a weakly basic or weakly acidic solution. The experiments have confirmed our expectations absolutely. The technical importance of this method of procedure, based entirely upon theoretical arguments, appears if one considers the modern preparation of disazo dyes derived from *p*-phenylenediamine.[5]

Operating under the conditions outined below one attains the object more quickly. In the strongly acidic solution a quantitative tetrazotization is accomplished[6] and after that a coupling of one of the diazo groups. Afterward the second desired azo component is introduced under normal circumstances of coupling.

This method enables one at the same time to couple with azo components (e. g., ethers) in the first phase, which is not possible with one of the other methods and which gives an insensibility of the dyes to alkalies. Incidentally it may be observed that the behavior of tetrazotized benzidine in strongly acidic medium in regard to β-naphthol and anisole points to the fact that two substituents in different nuclei influence each other only to a small degree.

Experimental

1.—With warming 2.16 g. of *p*-phenylenediamine is dissolved in 70 cc. of phosphoric acid (1.7). This solution is cooled with stirring with ice and salt. Afterward nitrosylsulfuric acid prepared from 2.88 g. of sodium nitrite and 30 cc. of sulfuric acid (1.84) is added by drops, temp. about −5°. After one-half hour, in order to eliminate the excess of nitrous acid, 2 g. of finely powdered urea is added. After one-half hour a large excess of β-naphthol dissolved in a small quantity of glacial acetic acid is added. After three-fourths hour the mixture is poured into ice water. The *diazonium-diazo compound* separates from this dilute solution (especially after the addition of sodium chloride), in orange-yellow needles, and may be recrystallized from water at 40° without decomposition. As the product obtained dissolves in water it may be concluded that *no disazo compound is formed.* Dilute alkali solution gives a blue coloration (reaction of Nietzki–Meldola for the diazo-azo compounds.

The crude product is now poured into a solution of potassium carbonate cooled at 0° and coupled a second time with β-naphthol. After two hours the disazo compound is filtered off and washed with 2 *N* potassium hydroxide, yield 96%. It is soluble in boiling alcohol and dilute alkalies. The alcoholic suspension gives a violet coloration with a drop of 2 *N* alkali. The compound crystallizes from boiling aniline in small needles with a greenish surface reflex. It dissolves with a beautiful blue color in concentrated sulfuric acid. If this solution is warmed for some time to 100° the compound is sulfonized; on diluting with water no precipitate appears. The product obtained in this way dissolves in dilute alkalies with a beautiful blue color.

Anal. Calcd. for $C_{26}H_{18}N_4O_2$: C, 74.61; H, 5.31. Found: C, 74.48; H, 5.37.

2.—2.16 g. of *p*-phenylenediamine is tetrazotized according to the procedure given under 1. After coupling with 2.88 g. of β-naphthol the diazo-azo compound is combined with phenol; yield 99%. The alcoholic solution becomes blue-violet upon the addition

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(5) Compare Cain, "The Chemistry and Techn. of the Diazo Compounds," p. 25.

(6) Schoutissen, This Journal, **55**, 4535 (1933).

of a little ammonia. The compound crystallizes from methyl alcohol in long filaments or as needles combined to rosets with a greenish surface reflex, m. p. 231–232°. In dilute alkalies the compound dissolves red-violet, in concentrated sulfuric acid greenish-blue.[7]

3.—This time the reaction of coupling is performed with phenol and β-naphthol just as under 2, but in the reversed order of succession; yield 98.5%. The compound appeared to be identical with the disazo compound described under 2, m. p. 231–232°.

4.—2.16 g. of *p*-phenylenediamine is tetrazotized according to the method given under 1. Now the coupling in the strongly acidic medium is performed with 3.5 g. of β-naphthol methyl ether dissolved in 20 cc. of glacial acetic acid, and afterward in potassium solution with 2 g. of phenol; yield nearly the theoretical. The excess of β-naphthol ether is removed by boiling with ether; m. p. of the undissolved portion 229°; after one recrystallization from methyl alcohol m. p. 231°; m. p. of the mixture with β-naphthol-azobenzene-azophenol, 231°. It appears therefore that during the coupling all the naphthol ether is saponified.

5.—Now first of all the tetrazotized *p*-phenylenediamine is coupled with α-naphthol and secondly with phenol. Again the typical coloration to blue has been observed. After two hours the dye is filtered off and washed with dilute alcohol; yield 6.9 g.; theoretical, 7.36 g. In dilute alkalies the compound dissolves red, in concentrated sulfuric acid with an indigo blue color.[7]

6.—The tetrazotized *p*-phenylenediamine is coupled with phenol in two stages. The greenish-yellow precipitate is filtered off and washed with 2 *N* hydrochloric acid and water; yield nearly the theoretical. The compound can be crystallized from hot aniline. On cooling brass-colored leaflets separate which are washed with dilute hydrochloric acid. The substance is recrystallized from boiling benzene: square to lozenge-shaped leaflets, m. p. with decomposition 270°. From 1:1 alcohol it crystallizes in fine, greenish-yellow, silk gleaming crystals. In alkalies the compound dissolves with a red color, in concentrated sulfuric acid with a pure blue color. It is insoluble in petroleum ether and carbon tetrachloride.[7]

7.—The tetrazonium solution is coupled in a first step with 5 g. of anisole and afterward with phenol. During the reaction of coupling in the second stage the color changes from blue to yellow-green. After two hours the disazo compound is filtered off and washed with water; yield nearly the theoretical quantity. It is recrystallized from aniline at 100°; on cooling the disazo compound separates in orange, chaff-shaped leaflets. The crystals are washed with cold aniline, benzene and petroleum ether and finally with dilute hydrochloric acid. After recrystallization from benzene the melting point was found to be 206–207°. The disazo compound dissolves in dilute alkalies with a beautiful red color.

Anal. Calcd. for $C_{19}H_{16}N_4O_2$: N, 16.87. Found: N, 16.72.

8.—2.16 g. of *p*-phenylenediamine is tetrazotized according to the method described under 1. Now 3 g. of phenetole, dissolved in 5 cc. of glacial acetic acid is added to the tetrazonium solution; afterward the diazo-azo compound is coupled with phenol in potassium carbonate solution; yield 6.4 g., calcd. 6.92 g. The crude product is crystallized from aniline at 100° as orange, chaff-shaped leaflets. After washing with dilute hydrochloric acid and recrystallization from boiling benzene the compound is obtained in greenish-yellow leaflets, m. p. 179°.

The compound dissolves readily in warm aniline, less in alcohol, acetone, benzene and toluene and is insoluble in carbon tetrachloride and petroleum ether. With dilute alkalies a beautiful red color appears; in concentrated sulfuric acid the compound dissolves with a blue color, in thick layers the color is red.

Anal. Calcd. for $C_{20}H_{18}N_4O_2$: N, 16.18. Found: N, 15.95, 16.12.

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(7) Meldola, *J. Chem. Soc.*, **47**, 657 (1885).

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).

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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).