LX.—*Researches on Secondary and Tertiary Azo-Compounds.* No. I.

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Introduction.

THE series of compounds containing the diazo-group —N=N— , first discovered by Griess, have of late years largely occupied the attention of chemists, both on account of their great scientific interest and their technical importance as colouring matters. The bodies of this class have, as is well known, supplied to commerce a splendid series of dye-stuffs, ranging from brilliant yellow and orange, through various shades of scarlet and brown, to bluish-violet. The discovery of these “diazo-colours” has indeed created quite new branches of the tinctorial industry, and the utilisation of those portions of coal-tar which, like the higher homologues of benzene and naphthalene, were at one time waste products, but which are now consumed in enormous quantities, is almost entirely due to their introduction.

Up to the present time attention has chiefly been directed to the investigation of those bodies constructed on the type of azobenzene:—

the phenyl (or naphthyl) residues on one or both sides of the diazo-group containing acid or basic substituents, such as HO , HSO_3 , COOH , NH_2 , $\text{N}(\text{CH}_3)_2$, $\text{C}_6\text{H}_4\text{.NH.C}_6\text{H}_5$, &c. Adopting the nomenclature proposed by Wallach (*Ber.*, 1882, 2812), the compounds of this class may conveniently be termed *primary* azo-compounds.

The *secondary* azo-compounds containing the —N=N— group twice, fall under two distinct types:—

(I.) Those in which the diazo-groups are both in the phenol residue; represented by Griess’s “phenol-bidiazobenzene” (*Ber.*, 1876, 628)—

and by Weselsky and Benedikt’s phloroglucinol-bidiazobenzene (*Ber.*, 1879, 226), which has the formula—

The bodies of this class have recently formed the subject of in-
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teresting papers by Wallach and others (*Ber.*, 1882, 22; 2814, 2825, and 3020).

(II.) The azo-compounds of the second class may be regarded as being constituted on the type of azo-azobenzene—

and are represented by Caro and Schraube's oxyazo-azobenzene (*Ber.*, 1877, 2230)—

or by the corresponding β -naphthol-compound described by Nietzki (*Ber.*, 1880, 1838)—

To this class belong the well-known and important commercial products, the “Biebrich”* and “Croceine”† scarlets, &c.

The compounds of the first class are formed by the successive introduction of two similar or dissimilar diazotised nuclei into a phenol (Wallach's “disazo-compounds”).‡

The bodies of the second type, to which I have confined my investigations, have hitherto been prepared by two methods:—

(1.) By the action of a diazotised amidoazo-compound (or its sulphonic acid) upon a phenol or substituted phenol.

(2.) By the neutralisation of one amido-group in an aromatic diamine by an acid radicle (acetyl), the diazotising of the remaining amido-group, and the copulation of the diazo-compound thus formed with a phenol. The acid radicle is then eliminated, and the restored amido-group diazotised and copulated with a second phenol residue (Wallach, *Ber.*, 1882, 2825).

Having for some years past been interested in the technical pro-

* Nietzki, *Ber.*, 1880, pp. 800 and 1838; W. v. Miller, *ibid.*, pp. 542, 803, and 980; Léo Vignan and J. B. Boasson, *ibid.*, p. 1060; Grässler, *Germ. pat.*, No. 38919, 1880; Krügener, *Germ. pat.*, No. 36792, 1880; also F. Bayer and Co. (Amidonaphthalene-tetrazobenzene-sulphonic acids), *Germ. pat.*, No. 20000, 1882; Farbwerk. Meister, Lucius and Brüning, *Germ. pat.*, No. 22010, 1882.

† F. Bayer and Co., *Germ. pat.*, No. 18027, 1881.

‡ Diamidoazo-compounds of the Chrysoidine class appear also capable of being converted into disazo-compounds by the introduction of a second diazotised radicle. See *Germ. pat.*, No. 22714 of the *Aktiengesellschaft für Anilinfabrikation*, 1883.

[Since writing the above note a paper has just been published by Dr. Griess (*Ber.*, 1883, p. 2028), in which are described several secondary azo-compounds of the class referred to, viz., $\text{R—N=N—R(NH}_2)_2$, as well as tertiary compounds of the mixed

type $\text{R—N=N—R—N=N—R} \begin{matrix} \text{N=N—R} \\ \text{<} \\ \text{(NH}_2)_2 \end{matrix}$].

duction of azo colouring-matters, I commenced last year a series of experiments, having for their object the extension of our knowledge of the secondary azo-compounds and the production of the hitherto imperfectly known tertiary compounds. It occurred to me that the desired results could be most simply arrived at by starting from a nitro-derivative of an amidoazo-compound—

Such a body when diazotised and united with a phenol residue (Ph) would give rise to the formation of a secondary nitroazo-compound of the type—

A body of the above type would, if it were possible to reduce the nitro-group without at the same time splitting up the azo-groups, give by a repetition of the foregoing processes a tertiary compound of the formula—

The same result would also be obtained by first reducing the nitro-amidoazo-body so as to obtain a diamidoazo-compound of the type—

then diazotising the two amido-groups simultaneously, and finally combining the product with 2 mols. of a phenol. As the result of the present investigations, I have thus far found that this last process alone works in a satisfactory manner.

Up to the present time, nitro-derivatives of the amidoazo-compounds have been but little studied, and experiments were therefore in the first place directed to the production of some of these bodies, the most obvious method that suggested itself being the action of diazotised nitroamido-derivatives of aromatic hydrocarbons upon primary monamines. Thus, in the case of the benzene series:—

The experiments herein recorded were all made with paranitraniline.*

* To prepare this compound in large quantities, the following method was adopted:—Equal volumes of nitric acid (sp. gr. 1·420) and strong sulphuric acid are mixed and well cooled. Acetanilide is then gradually introduced and the mixture agitated after each addition so as to dissolve the solid crystals. When no more acetanilide is taken up, the solution is left at rest for about half an hour, and kept thoroughly cooled during this time. The contents of the flask are then

ACTION OF DIAZOTISED PARANITRANILINE UPON PRIMARY MONAMINES.

I. *Action upon Metaxylidine.*

Some preliminary experiments having shown that the most decided results were given by the action of diazoparanitrobenzene salts upon *meta*-monamines, such as metatoluidine or metaxylidine, the last-named substance was employed. Throughout these investigations the following method of diazotising was adopted:—The nitraniline is powdered and mixed with a small quantity of water, and then strong hydrochloric acid is added till the crystals just dissolve. The theoretical quantity of sodium nitrite dissolved in water is then slowly added, and the mixed solutions kept thoroughly cool. The diazo-compound is immediately formed, and by this means practically the whole of the nitraniline is converted, whereas by departing from this method, a considerable quantity of the nitraniline is apt to be converted into an insoluble yellow compound, probably a dinitroamidoazo-benzene.

Paranitrobenzene-azoamidometaxylene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_8\text{H}_8\cdot\text{NH}_2$, is formed by filtering a solution of paranitrodiazobenzene chloride (1 mol.) into an alcoholic solution of metaxylidine hydrochloride (1 mol.). A bulky reddish precipitate soon separates, causing the contents of the beaker to become semi-solid. This precipitate consists of the diazo-compound $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_8\text{H}_8$, which, on standing for a few hours, becomes converted into the isomeric azo-compound, the latter forming a bright scarlet hydrochloride. This salt was collected, washed with alcohol acidulated with hydrochloric acid, and finally with water. Ammonia liberates the base as a brown substance which crystallises from dilute alcohol in brick-red needles, having a melting point of 141°C . The base is readily soluble with an orange colour in alcohol, acetone, benzene, and chloroform. It dissolves also with an orange colour in strong sulphuric acid. A platinum salt was formed by adding PtCl_4 and HCl to a dilute alcoholic solution of the base. The salt separates out in minute scales having a metallic green reflection.

0.2314 gram gave 0.477 gram Pt.

Theory for $2(\text{C}_6\text{H}_4\text{N}_2\text{NH}\cdot\text{C}_8\text{H}_8\cdot\text{NH}_2\cdot\text{HCl})\text{PtCl}_4$.		Found.
Pt	20.72 per cent.	20.61

stirred into a large bulk of cold water, and the nitro-compound is collected, washed, and crystallised from boiling water. On saponification by boiling NaHO solution, paranitraniline separates out on cooling. By following this method but a very small quantity of orthonitraniline appears to be produced, and one or two crystallisations from water furnish the para-compound in a state of perfect purity.

The salts of this base are very insoluble in alcohol, and separate out in beautiful red needles having a violet reflection when HCl, H₂SO₄, or HNO₃, is added to a hot alcoholic solution. With respect to the constitution of this substance, the following observations may be offered:—

The three known metaxylylidines possess the constitutional formulæ:—

When a diazotised radicle combines with an amine, the N₂-group always takes up the para-position with respect to the amido-group. This is shown by the circumstance that diazotised paranitraniline gives no definite compound with paratoluidine, whilst with ortho-toluidine it gives a small yield, and with metatoluidine a rich yield of an azo-compound. All three metaxylylidines occur in the xylidine from coal-tar xylene, but the α -modification can take no part in the present reaction, and the body described is therefore most probably a mixture of the two modifications:—

By complete reduction both these compounds would give rise to paradiamidobenzene and the *same* diamidoxylylene, so that the relative positions of the NH₂ and —N₂.C₆H₄.NO₂-groups with respect to the CH₃-groups, cannot be determined by this method. The formula of the new compound may thus be written:—

II. Action of Diazoparanitrobenzene upon α -Naphthylamine.

Paranitrobenzene-azoamido- α -naphthalene,

was prepared in precisely the same manner as the xylene compound. On mixing the solutions a deep crimson colour is developed, and a bulky brown precipitate forms. The substance was purified by washing with alcohol acidulated with HCl, and finally with hot water. By treatment with ammonia the base was obtained as a brown substance, somewhat difficultly soluble in boiling alcohol. The solution is of a fine crimson colour, and minute needles are deposited on cooling. The base dissolves in benzene and its homologues with an orange colour, and crystallises therefrom in brown glistening needles. A specimen crystallised from toluene had a melting point of 252° . On adding hydrochloric acid to a hot alcoholic solution, the hydrochloride crystallises out in hair-like needles, having a faint violet shimmer. The base dissolves in strong sulphuric acid with a violet colour. The platinum salt was obtained as a violet non-crystalline precipitate on adding HCl and PtCl_4 to hot solution of the base in alcohol.

0.1052 gram gave 0.0205 gram Pt.

Theory for $2(\text{C}_6\text{H}_4 \cdot \overset{\text{NO}_2}{\underset{1}{\text{N}}} \cdot \overset{4}{\text{N}} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2 \cdot \text{HCl}) \text{PtCl}_4$.	Found.
Pt 19.81 per cent.	19.48

By complete reduction this substance is resolved into paraphenylenediamine, and a naphthylene diamine yielding α -naphthoquinone on oxidation. Its constitution is therefore :—

III. Action of Diazoparanitrobenzene upon β -Naphthylamine.

Paranitrobenzene-azoamido- β -naphthalene,

This body was prepared in a similar manner to the α -compound, but it was found more advantageous in this case to work with an aqueous instead of an alcoholic solution of the naphthylamine hydrochloride, as

the salts of the nitroamidoazo- β -compound are readily soluble in alcohol, and do not separate out on dilution in a convenient state for purification. Great care must also be taken to avoid an excess of sodium nitrite in diazotising the paranitraniline; otherwise amido-azo- β -naphthalene is apt to be formed, and is most difficult to separate from the substance required.

On mixing the solutions containing the theoretical quantities of paranitrodiazobenzene and β -naphthylamine hydrochloride, a bronzy-looking precipitate immediately separates. This was collected, washed with water, basified and dried. On dissolving in boiling alcohol a red solution was obtained, which on cooling deposited magnificent needles, having a bright metallic golden lustre and melting at 180°C . The base possesses the following properties:—It dissolves in alcohol, acetone, and chloroform, with a red colour, whilst its solutions in benzene, toluene, &c., are orange-coloured. It dissolves in strong sulphuric acid with a violet colour, becoming red on dilution with water. The salts of the base, unlike those of the corresponding α -compound, are readily soluble in alcohol, so that nothing separates out when hydrochloric acid is added to the alcoholic solution. The platinum salt was obtained as a reddish-brown amorphous powder, by adding PtCl_4 to a strong alcoholic solution of the hydrochloride.

0.1713 gram gave 0.0335 gram Pt.

	Theory.	Found.
Pt	19.81 per cent.	19.55

0.2319 gram burnt with CuO gave 38.4 c.c. N at 18.2° , and 752.3 mm. bar. = 0.0438 gram N.

Theory for $\text{C}_6\text{H}_4\text{N}_2\text{C}_{10}\text{H}_6\text{NH}_2$	Found.
N	18.88

I have not yet succeeded in obtaining from this substance by complete reduction the naphthylenediamine giving β -naphthoquinone on oxidation. Its constitution is, however, most probably*—

* The extreme stability of the substance is opposed to the idea that we may here have the isomeric diazo-compound, $\text{C}_6\text{H}_4\text{N}_2\text{C}_{10}\text{H}_6\text{NH}_2$.

The behaviour of this body both on reduction and when acted upon by HNO_2 , as will be seen hereafter, is in many ways remarkable, and I propose to make its investigation the subject of special study on some future occasion.

REDUCTION OF THE NITROAMIDOAZO-COMPOUNDS.

Paraamidobenzene-azoamidometaxylene, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}\cdot\text{C}_8\text{H}_8\cdot\text{NH}_2$.

—The nitroamidoazo-compound obtained by the action of paranitrodiazobenzene chloride upon metaxylidine was converted into a state most suitable for reduction by dissolving it in alcohol and stirring the solution into cold water. The bulky red semi-gelatinous precipitate was collected, washed with water till free from alcohol, and then warmed for some hours with ammonium sulphide. The colour of the precipitate gradually changes to yellow, and the diamido-base separates in a crystalline form. The latter was purified by crystallisation from boiling water, and was obtained in the form of beautiful golden-yellow scales melting at 163° . This base is extremely soluble in alcohol, benzene, and most solvents. Its solution in strong sulphuric acid is yellow, changing to orange on dilution. The solutions of the hydrochloride, sulphate, and nitrate are orange-coloured, and these salts are extremely soluble in water. By adding excess of acid the biacid salt is precipitated; thus on adding an excess of HCl to a solution of the hydrochloride, the salt, $\text{C}_6\text{H}_4\cdot\text{N}(\text{NH}_2)\cdot\text{N}(\text{NH}_2)\cdot\text{C}_8\text{H}_8\cdot\text{NH}_2\cdot 2\text{HCl}$, separates out as a bulky brown non-crystalline precipitate. A platinum salt was precipitated as a brown amorphous powder by adding PtCl_4 to the aqueous solution of the hydrochloride.

0.0958 gram gave 0.0289 gram Pt.

Theory for $(\text{C}_6\text{H}_4\cdot\text{N}(\text{NH}_2)\cdot\text{N}(\text{NH}_2)\cdot\text{C}_8\text{H}_8\cdot\text{NH}_2)\cdot 2\text{HCl}\cdot\text{PtCl}_4$.	Found.
Pt 30.21 per cent.	30.16

Paraamidobenzene-azoamido- α -naphthalene,

was prepared in the same manner as the last compound. The brown gelatinous nitroamidoazo-body, on digestion with ammonium sulphide, became converted into a mass of ochreous needles, melting when dry at about 159 — 160° . The salts of this diamido-base dissolve readily in water, giving solutions of a magenta-like red; excess of acid precipitates the biacid salts. The base is readily soluble in alcohol, acetone, benzene, and chloroform. Its solution in strong sulphuric acid is of a

fine red colour. The platinum salt is similar in appearance, and was prepared in the same manner as the last.

0.1174 gram gave 0.0342 gram Pt.

Theory for $(C_6H_4<N_2C_{10}H_6.NH_2)2HCl.PtCl_4$.		Found.
Pt	29.27 per cent.	29.13

On acting upon an aqueous solution of the hydrochloride with zinc-dust complete reduction takes place, and the solution becomes colourless. The excess of zinc was filtered off, and ferric chloride added to the filtrate, which, on standing, deposited a brownish crystalline substance. The latter was collected, washed, boiled with water, and filtered. The filtrate on cooling deposited a mixture of small yellow and larger red needles, the two kinds of crystals being easily separable when dry. The melting points proved that the yellow crystals were benzoquinone and the red crystals α -naphthoquinone, thus establishing the constitutional formula previously assigned.

Reduction of Paranitrobenzene-azoamido- β -naphthalene.

It was not found possible to obtain this substance in a convenient form for reduction in an aqueous solution with ammonium sulphide, as the bronzy paste precipitated by water from an alcoholic solution soon becomes crystalline, and is then unacted upon by the reducing agent. Rapid reduction takes place, however, when ammonium sulphide is added to a cold alcoholic solution of the base. The colour of the solution immediately changes from red to yellow, and on pouring into water a bright orange precipitate is thrown out. This substance is not simply the diamidoazo-compound, but it appears to contain sulphur, and is readily fusible in boiling water. I propose to study this reaction in greater detail hereafter.

The diamidoazo-compounds described above are the first known members of a series of bases isomeric with the "chrysoïdine" series discovered by Dr. O. N. Witt. They differ from the latter in having the amido-groups in different aromatic nuclei:—

These new bases are yellow or orange dye-stuffs, and are best applied in a neutral or slightly alkaline bath. By the action of nitrous acid both amido-groups are readily diazotised, thus affording a means, as will be seen subsequently, of preparing a whole series of new tertiary azo-compounds.

SECONDARY NITRAZO-COMPOUNDS.

Nitrous acid acts readily upon paranitrobenzene-azoamidometaxylene, the amido-group becoming diazotised, and thus furnishing a starting point for the production of a series of secondary nitrazo-bodies. After various experiments the following method was adopted:—The theoretical amount of NaNO_2 dissolved in a small quantity of water, was added to the solution of the base in alcohol, and the mixture whilst kept thoroughly cooled acidulated with hydrochloric acid. The hydrochloride of the base is first precipitated, but this soon redissolves, and an orange-coloured solution of the tetrazo-salt is obtained. The latter was then poured with constant stirring into a cold aqueous solution containing the theoretical quantity of the phenol dissolved in an alkali. Of the various compounds thus obtained, the β -naphthol-body was alone studied in detail, as this was the only one that could be obtained easily in a state of purity by crystallisation.

Paranitrobenzene-azometaxylene-azo- β -naphthol,

On mixing the solutions of the tetrazo-chloride and sodium β -naphtholate in the manner above described a brown precipitate separated, which was collected, washed with water till the filtrate was no longer yellow, and dried. A green metallic powder was thus obtained, which was dissolved in boiling aniline, and the crimson solution on cooling deposited small brilliant metallic-green needles, which were collected, washed with alcohol, and dried. The aniline filtrate contained a small quantity of a substance apparently identical in all respects with the green needles, so that no soluble isomeride appears to be produced in this reaction. A specimen was purified for analysis by another crystallisation from toluene, in which solvent the substance dissolves at the boiling point with a crimson colour, and separates on cooling in green glistening scales having a fusing point of 278° .

- I. 0.2745 gram gave 0.6816 gram CO_2 and 0.1202 gram H_2O .
 II. 0.1387 gram gave 20 c.c. N at 19.3° and 755.4 mm. bar. = 0.0228 gram N.

		Found.	
		I.	II.
C	Theory for $\text{C}_{24}\text{H}_{19}\text{N}_5\text{O}_3$. 67.76	67.71	—
H	4.47	4.86	—
N	16.47	—	16.43

The substance is but very slightly soluble in alcohol or glacial acetic acid, even when boiled with these solvents. It dissolves somewhat more freely in boiling alcoholic potash, the solution being violet at first, but becoming red on standing. It is soluble in boiling nitrobenzene with a magenta-like red colour, and it gives a green colour in strong sulphuric acid, changing to violet on dilution. Fuming sulphuric acid (80 per cent. anhydride) converts it into a sulphonic acid having no particular tinctorial properties. Although this compound, like the nitroamidoazo-body from which it is derived, probably contains two isomeric modifications, the two isomerides, if present, differ to so small an extent in their degree of solubility and other properties that no separation could be effected. The constitutional formula may be written:—

The secondary nitroazo-compounds represented by the present substance did not appear to furnish promising starting-points for the preparation of tertiary azo-compounds, since the nitro-group was not readily reducible, and even when reduced the resulting secondary amido-compound could not be diazotised. The following members of the series were not studied in much detail.

Paranitrobenzene-azometaxylene-azo- α -naphthol—

This body resembles the foregoing in its general characters, but is rather more soluble in alcohol, glacial acetic acid, &c. The solutions are redder than those of the β -naphthol-compound, but the substance is not readily crystallisable.

Paranitrobenzene-azo-metaxylene-azo- β -naphtholsulphonic acid—

The ammonium salt of this acid was precipitated as a reddish gelatinous substance on mixing the solution of the tetrazo-salt with a solution of the ammonium salt of Schäffer's β -naphtholsulphonic acid, and adding ammonia. The salts of this acid are all very insoluble, and from an acid bath dye silk and wool of a claret-red.

The corresponding compound from α -naphtholsulphonic acid is similar to the above, but dyes of a reddish-brown shade.

Paranitrobenzene-azometaxylene-azophenol—

This substance was obtained in the form of an orange powder,

slightly soluble in boiling alcohol and toluene, and readily soluble in hot aniline. All its solutions are orange-coloured; the addition of NaHO to the alcoholic solution changes the colour from orange to reddish-violet. The substance dissolves in sulphuric acid with a fine blue colour.

Paranitrobenzene-azometaxylene-azoresorcinol,

was obtained as a dark brown amorphous substance, dissolving with some difficulty in boiling alcohol, toluene, and glacial acetic acid, the solutions being of an orange colour. A specimen purified by deposition from hot toluene had a melting point of 231° . The substance dissolves in alcoholic soda with a fine red colour, which becomes violet on adding excess of alkali. It dissolves also with red colour in alcoholic ammonia and with blue colour in strong sulphuric acid. The alkaline solution poured into an acid-bath enables wool and silk to be dyed of a rich brown very similar to that imparted by triamidoazobenzene.

Secondary nitroazo-compounds analogous to the foregoing could not be obtained from the α -naphthylamine compound

as the amido-group does not appear to be diazotised by the action of nitrous acid. By acting with NaNO_2 and an acid upon the corresponding β -naphthylamine compound a body having all the characters of a nitroso-derivative was obtained. This substance, which crystallises from alcohol in bright orange scales, and dissolves in alcoholic potash with a violet colour, is undergoing further investigation.

TERTIARY AZO-COMPOUNDS.

For reasons already explained, the secondary nitroazo-compounds could not be made available for the preparation of tertiary azo-bodies, but the diamidoazo-compounds previously described lent themselves readily to this reaction.*

* The constitutional formulæ here assigned to the new tertiary azo-compounds may safely be ascribed to the chief products of the action of the diazotised diamido-azo-bases upon alkaline solutions of phenols. The production of isomerides, as observed by Wallach in the preparation of his diazo-compounds, and by myself in the present case, considerably complicates the question of the relative positions of the substituents in these extremely complex bodies. The problem of the constitu-

β-Naphtholparaazobenzene-azo-α-naphthalene-azo-β-naphthol,

The diamidoazo-base, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH}_2 \\ \text{N}=\text{N}-\text{C}_{10}\text{H}_6.\text{NH}_2\alpha \end{array}$, was dissolved in dilute hydrochloric acid, and the theoretical quantity of sodium nitrite (2 mols.) gradually added to the well-cooled solution. The diazotising of the amido-groups is indicated by the change of colour of the solution from red to orange. On mixing this orange solution with an aqueous alkaline solution of *β*-naphthol a dull metallic green powder was precipitated, and this, after being collected and washed, was crystallised from boiling aniline. By this treatment the substance was separated into two distinct bodies, one of which (insoluble modification) crystallised out in small needles with a metallic green reflection, whilst the other remained in the aniline filtrate (soluble modification).

The crystalline portion dissolves in aniline with a violet colour; it is practically insoluble in boiling alcohol, acetone, or glacial acetic acid, and but very slightly soluble in chloroform and the benzene hydrocarbons. Boiling nitrobenzene dissolves the substance, giving a solution which is reddish-violet when hot, and blue-violet when cold. The melting point is above 295°.

The soluble modification was separated by diluting the filtrate with alcohol and neutralising the aniline with hydrochloric acid. A bulky violet precipitate was obtained, which after being collected and washed was purified by dissolving in alcoholic potash and filtering into water acidulated with HCl. This modification is more soluble in all solvents than the crystalline portion. It could not be obtained in a crystalline form.

The following results were obtained on analysis:—

Insoluble Modification.

I. 0.1794 gram gave 0.4950 gram CO₂, and 0.0762 gram H₂O.

II. 0.1666 gram gave 21.3 c.c. N at 18°, and 767 mm. bar. = 0.0248 gram N.

tion of the subsidiary isomeric products can of course be attacked with the greatest hope of success in the case of bodies of simpler constitution than those here dealt with. I may add that I have in the course of my experiments obtained results which seem to indicate that the production of the isomeride is to some extent governed by the conditions of the experiment, *i.e.*, the nature of the alkali and the solvent employed.

Soluble Modification.

- I. 0.2907 gram gave 0.8025 gram CO₂, and 0.1216 gram H₂O.
 II. 0.2902 gram gave 37.3 c.c. N at 19°, and 761.5 mm. bar. = 0.0429 gram N.

Theory for C ₃₆ H ₂₄ N ₆ O ₂ .		Found.			
		Insol. modification.		Sol. modification.	
		I.	II.	I.	II.
C	75.52	75.25	—	75.29	—
H	4.19	4.71	—	4.64	—
N	14.68	—	14.88	—	14.78

These numbers show that the two bodies are isomeric, a result which has already been observed by Wallach in the preparation of disazo-compounds. The more striking characters of the two isomerides with respect to their behaviour towards solvents are set forth in the following table:—

Reagent.	Insoluble modification.	Soluble modification.
Glacial acetic acid..	Insoluble	Soluble at boiling point of acid. Solution violet when hot, blue when cold.
Alcoholic potash ..	Very difficultly soluble. Solution blue.	Readily soluble with a violet colour.
Strong H ₂ SO ₄	A deep inky blue, becoming bluish-green and finally violet on dilution.	A clear indigo-blue, becoming brighter on dilution, and finally changing to violet.

A disulphonic acid corresponding to the foregoing compound, viz.:—

was obtained by mixing a solution of the diazotised diamidoazo-compound with an alkaline solution of β -naphtholsulphonic acid (Schäfer's). The salt (ammonium) of the acid is precipitated as a violet semi-gelatinous substance soluble in boiling water. Mineral acids precipitate the free disulphonic acid which is insoluble in boiling water. The acid possesses no tinctorial power.

The corresponding α -naphthol compound,

is very similar to the β -naphthol body. It forms a bronzy powder dissolving in alcoholic potash with a blue colour. The aniline solution is red, and it dissolves in strong sulphuric acid with an indigo-blue.

The phenol compound, of which the formula is most probably

was obtained as a dull bronzy-green powder dissolving in boiling alcohol and toluene with an orange colour. The solution in alcoholic potash is violet, and the sulphuric acid solution dark indigo-blue.

The resorcinol compound was precipitated as a brown flocculent substance drying to a bronzy powder. The probable formula is

This substance dissolves in alcohol with a dull red colour, and in alcoholic potash with a violet colour. The colour of the strong sulphuric acid solution is bluish-green.

With the exception of the β -naphthol compound none of the foregoing tertiary azo-compounds were readily crystallisable, and were not therefore examined in such detail.

β -Naphtholparaazobenzene-azometaxylene-azo- β -naphthol,

The diamidoazo-base was diazotised as before, and the orange-coloured solution gradually stirred into a solution of β -naphthol (2 mols.) in caustic soda. A deep violet precipitate was thrown down, and this, after being collected and washed, dried to a dull metallic-looking powder. The latter was dissolved in boiling aniline; the solution on cooling deposited small needles of a dull bronzy-green. The aniline filtrate was examined for an isomeride by dilution with alcohol and neutralisation with HCl and water, but only a very small quantity of a brown substance was thus obtained, and it was not possible to decide by analysis whether this was an isomeride or simply a trace of some bye-product.

A specimen of the crystalline substance was purified for analysis by dissolving it in boiling xylene. When cold the small green needles were collected and washed with pure benzene.

- I. 0.1532 gram gave 0.4146 gram CO_2 , and 0.0652 gram H_2O .
 II. 0.1109 gram gave 14.4 c.c. N at 20.6° , and 768 mm. bar. = 0.0166 gram N.

		Found.	
		I.	II.
Theory for $\text{C}_{34}\text{H}_{26}\text{N}_6\text{O}_2$.			
C	74.18	73.81	—
H	4.73	4.73	—
N	15.27	—	14.96

The substance dissolves in aniline with a reddish-violet colour, which becomes bluer on cooling. Its xylene-solution is also violet. It is practically insoluble in alcohol and glacial acetic acid, but dissolves in hot alcoholic potash with a bluish-violet colour. With concentrated sulphuric acid it gives a dull greenish-blue, becoming bright blue on dilution, and finally violet, and precipitating. It is transformed by the action of fuming sulphuric acid into a sulphonic acid which dyes silk and wool of a dull violet colour.

ACTION OF DIAZOTISED PARANITRANILINE UPON SECONDARY MON-AMINES.

Action upon Diphenylamine.

The starting point of this series of compounds was the body already described by Roussin and Poirrier (*Dingl. polyt. J.*, 1879, p. 423; *Chem. Industrie*, 1879, **2**, p. 293), obtained by the action of diazoparanitrobenzene upon diphenylamine.

On mixing an aqueous solution containing one molecule of diazotised paranitraniline with an alcoholic solution of diphenylamine (one molecule), a deep reddish-violet colour is produced, and the mixture soon becomes semi-solid from the separation of a dense brown precipitate. The latter was collected, washed with water, and basified by ammonium carbonate. A dull red substance was obtained which after crystallisation from dilute alcohol, formed brown leaflets having a melting point of 151° .

Paramitrobenzene-azodiphenylamine, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{NO}_2 \\ \text{N}=\text{N} \end{smallmatrix}\text{.C}_6\text{H}_4\text{.NH.C}_6\text{H}_5$, is readily soluble in alcohol with an orange colour, which changes to violet on the addition of hydrochloric acid, and the hydrochloride separates out in clusters of small needles having a beautiful violet reflection. The salt is extremely unstable, being instantly decomposed by water or by exposure to the air. The base dissolves in strong sulphuric acid with a violet colour.

Paramidobenzene-azodiphenylamine, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{NH}_2 \\ \text{N}=\text{N} \end{smallmatrix}\text{.C}_6\text{H}_4\text{.NH.C}_6\text{H}_5$,—

The reduction of the nitro-base was effected by adding ammonium sulphide to the cold alcoholic solution. In the course of a few minutes the colour of the solution changed from orange to yellow, and on diluting with water an orange crystalline substance slowly separated out. The amido-base thus obtained was mixed with a small quantity of some secondary product containing sulphur, from which it could not be entirely freed even by repeated solution in dilute HCl, filtration, and reprecipitation by ammonia. It was found, however, that this impurity was removed by the diazotising process, so that no further attempts at purification were made, and the following remarks apply to the crude substance.

The melting point of the crude base is 90—91° C. Its salts dissolve readily in water with a magenta colour. The base itself is but slightly soluble in boiling water, but dissolves readily in alcohol, acetone, chloroform, and the benzene hydrocarbons with a yellow colour. On adding hydrochloric acid to the alcoholic solution, a green colour is first produced, and this on the further addition of acid passes into red. The solution in concentrated sulphuric acid is violet passing into red on dilution. The salts act as dye-stuffs, imparting a bright yellowish-orange shade to silk and wool.

β-Naphtholparaazobenzene-azodiphenylamine,

In order to diazotise the amido-base, $\text{C}_6\text{H}_4 \cdot \text{N}^{\text{H}_2} \text{C}_6\text{H}_4 \cdot \text{N} < \text{C}_6\text{H}_5$, it was found most advantageous to dissolve it in alcohol with the addition of hydrochloric acid, and then add the theoretical quantity of NaNO_2 dissolved in water little by little to the well cooled solution. The orange-coloured solution was then gradually mixed with an aqueous solution of sodium *β*-naphtholate. A reddish precipitate was obtained which was collected, washed and dried. Purification was effected by dissolving the substance in alcoholic soda, filtering, and precipitating by an acid. This operation was repeated several times, and finally a violet precipitate was obtained which, after being collected and washed with water till free from saline impurity, dried to a dull bronzy powder. After crystallisation from hot glacial acetic acid it was obtained in the form of warty scales having a dull bronzy lustre and melting at 203—204° C.

I. 0.3301 gram gave 0.9128 gram CO_2 , and 0.1471 gram H_2O .

II. 0.1558 gram gave 21.2 c.c. N at 22° and 767.1 mm. bar = 0.0242 gram N.

		Found.	
Theory for $C_{28}H_{21}N_5O$.		I.	II.
C	75·84	75·41	—
H	4·74	4·98	—
N	15·80	—	15·53

This new secondary azo-compound is characterised by the following properties :—It dissolves slightly in boiling alcohol and readily in benzene with a red colour. It is dissolved by glacial acetic acid, the solution being red when hot, and reddish-violet when cold. It dissolves in strong sulphuric acid with a greenish-blue colour, changing to reddish-blue on standing. Alcoholic potash or soda dissolves the substance with great facility, the solution being red. A most characteristic property of this compound is the fine blue coloration produced by adding hydrochloric acid to its dilute solution in alcoholic potash.

These researches have been conducted in the course of technological studies carried on in the laboratory of Messrs. Brooke, Simpson, and Spiller at the Atlas Works, Hackney Wick; and it is with great pleasure that I record my thanks to this firm. The investigations will be extended to the action of diazoparanitrobenzene upon tertiary monamines and phenols, and the corresponding series of reactions with the isomeric nitranilines and their homologues.