XCVI.—*The Diazo-derivatives of the Monoacetylated Aromatic Para-diamines.*

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A STUDY of the diazonium salts derived from camphor- β -sulphonyl-*p*-phenylenediamine and benzenesulphonyl-*p*-phenylenediamine showed that these substances readily gave rise to a new type of diazo-compound, of which benzenesulphonyl-*p*-phenylenediazoimide,

is the simpler example.

The investigation has now been carried a step further with the object of ascertaining whether the condensation occurs with the sulphonyl derivatives of other para-diamines, and also whether any

change of this kind occurs when the sulphonyl complex is replaced by another acyl group.

The results indicated in the experimental part of this communication show that the reaction represented by the following equation :

is fairly general for aromatic para-diamines containing a complex of the type $\text{RSO}_2 \cdot \text{NH}$, and altogether seven examples of this series have now been studied.

On the other hand, no indication could be obtained of the production of similar diazo-anhydrides with acyl-*p*-diamines containing formyl, acetyl, succinyl, and benzoyl groups, so that at present the fundamental reaction represented by the foregoing equation must be regarded as being restricted to the mono-acylated *p*-diamines having one RSO_2 residue.

The changes observed in the case of benzoyl-*p*-phenylenediamine are somewhat singular. The sparingly soluble hydrochloride of this base yields on treatment with nitrous acid a soluble diazonium salt, which does not give rise to an anhydride with concentrated aqueous sodium acetate. When, however, the concentrated diazo-solution is poured into cold aqueous potassium hydrogen carbonate, a very pale yellow, crystalline precipitate is produced, which consists of a sparingly soluble *diazonium carbonate* having the formula

This substance is quite stable in the dry state, and does not explode either on heating or by percussion. It evolves carbon dioxide on treatment with cold hydrochloric acid, and the solution yields the azo-compound, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, when poured into an alkaline solution of β -naphthol. When boiled with water or aqueous solutions of mineral acids, the diazo-complex is destroyed, and benzoyl-*p*-aminophenol, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ (m. p. 205—207°), is obtained.

In a similar manner, when the acetic acid solution of the diazotised benzoyl-*p*-phenylenediamine is poured into cold aqueous sodium nitrite, a sparingly soluble crystalline, yellow *diazonium nitrite*,

is deposited.

This compound resembles the diazonium carbonate in readily yielding azo-derivatives with the phenols and aromatic diamines, the facility with which this condensation occurs indicating that the salt is a true diazonium compound, in spite of its distinctly yellow hue. The

appearance of colour in this case is probably to be attributed to the presence of a nitrite ion rather than to any rearrangement in the configuration of the diazo-complex.

On subjecting the monoformyl and monoacetyl derivatives of *p*-phenylenediamine to a similar series of operations, these substances did not furnish insoluble carbonates, no precipitate being formed on pouring the diazo-solutions into aqueous sodium or potassium hydrogen carbonate. The diazo-solution of the acetyl derivative (*p*-aminoacetanilide), when treated with aqueous ammonia, gave rise to a bulky brown precipitate, which, when washed with water and dried on porous tile, had the properties of, and gave analytical numbers corresponding with, the nitrosoamine, $\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NO}$. When dissolved in aqueous alkali and treated with β -naphthol, no azo-derivative was produced, the formation of the compound,

taking place only when the nitrosoamine is first dissolved in cold concentrated hydrochloric acid, and the diluted solution then added to an alkaline solution of the naphthol.

An attempt made to obtain a diazo-anhydride by treating an aqueous solution of *p*-aminoacetanilide hydrochloride with the calculated quantity of sodium nitrite and then adding aqueous sodium acetate led to the production of the diazoamino-compound,

This substance could be crystallised from alcohol, whereas the foregoing nitrosoamine was decomposed on boiling with this solvent.

The results obtained with formyl-*p*-phenylenediamine were quite similar. Its diazotised solution yielded no insoluble compound either with sodium acetate or potassium hydrogen carbonate, but gave a brown precipitate of the nitrosoamine on treatment with ammonia. The hydrochloride of the formyl base, when diazotised and combined with a molecular proportion of the free base, gave rise to a diazoamine, which, however, was not obtained in a state of purity.

p-Aminosuccinanilic acid, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_2\text{H}_4 \cdot \text{CO}_2\text{H}$, which was obtained by reducing *p*-nitrosuccinanil and partially hydrolysing the resulting *p* aminosuccinanil, when diazotised in hydrochloric acid, yields a *diazonium chloride*, $\text{CO}_2\text{H} \cdot \text{C}_2\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Cl}, \text{H}_2\text{O}$. This salt crystallises from a fairly concentrated solution and is quite stable in the dry state; its aqueous solutions do not yield insoluble diazo-derivatives with aqueous sodium acetate, potassium hydrogen carbonate, and ammonia.

An attempt to prepare the diazoamine of benzenesulphonyl-*p*-phenylenediamine showed that the tendency to form the cyclic diazoimide inhibits the production of this derivative. A glacial acetic acid

solution of the diazonium chloride and the original base, when treated with aqueous sodium acetate, yielded merely a mixture of the diazoimide and uncombined benzenesulphonyl-*p*-phenylenediamine.

EXPERIMENTAL.

I. *Arylsulphonyldiazoimides of the Aromatic p-Diamines.*

(1) *Naphthalene- α -sulphonyl-*p*-phenylenediazoimide,*

*Naphthalene- α -sulphonyl-*p*-nitroanilide*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_{10}\text{H}_7$, was obtained by heating together for 3 hours 20 grams of *p*-nitroaniline, 17 grams of naphthalene- α -sulphonic chloride, and 100 c.c. of dry toluene, the solvent being then evaporated and the residue boiled with excess of sodium carbonate. The filtered solution was cooled, the precipitated nitroaniline removed, and the final filtrate acidified with hydrochloric acid. The precipitate, when thrice crystallised from alcohol, separated in lemon-yellow needles melting at $205\text{--}206^\circ$.

0.4695 gave 36.7 c.c. nitrogen at 19° and 747 mm. $\text{N} = 8.84$.

$\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ requires $\text{N} = 8.56$ per cent.

*Naphthalene- α -sulphonyl-*p*-phenylenediamine,*

was prepared by reducing the preceding compound (12 grams) with 10 grams of iron, 300 c.c. of water, and 4 c.c. of glacial acetic acid, the yield being 10.5 grams; it does not crystallise readily, being somewhat too soluble in the ordinary organic solvents; after two crystallisations from benzene, it separated in clusters of brown needles and melted at 175° .

0.2454 gave 21.1 c.c. nitrogen at 19° and 747 mm. $\text{N} = 9.72$.

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ requires $\text{N} = 9.39$ per cent.

The hydrochloride of the base is only sparingly soluble, but when suspended in water, cooled and treated with the requisite amount of sodium nitrite the salt dissolves and the solution, when filtered into an excess of aqueous sodium acetate, yields an insoluble cyclic diazoimide which, when washed successively with water, alcohol, and light petroleum, decomposes indefinitely* at $164\text{--}167^\circ$, sintering and darkening at about 120° .

* The decomposition points of these diazoimides vary considerably with the rate of heating.

0·1694 gave 20·5 c.c. nitrogen at 19° and 746 mm. N = 13·65.

0·1542 „ 0·1235 BaSO₄. S = 10·99.

C₁₆H₁₁O₂N₃S requires N = 13·59 ; S = 10·35 per cent.

This cyclic compound dissolves in concentrated hydrochloric acid and the solution, when diluted and mixed with alkaline β -naphthol, gives an azo-compound which, as is usual in this series, separates in the form of its sparingly soluble alkali salt.

(2) *Naphthalene- β -sulphonyl-p-phenylenediazoimide.*

Naphthalene- β -sulphonyl-p-nitroanilide, prepared in the same manner as its α -isomeride, crystallises from benzene in yellow needles melting at 168—169°.

0·5706 gave 41·4 c.c. nitrogen at 21° and 761 mm. N = 8·28.

C₁₆H₁₂O₄N₂S requires N = 8·56 per cent.

Naphthalene- β -sulphonyl-p-phenylenediamine, obtained by reducing the preceding nitro-compound in the manner just indicated, crystallises from ethyl acetate or acetone in reddish needles melting at 231—232°. The reduction should be carried out in about 1½ hours, more prolonged heating leading to the formation of tarry products,

0·2430 gave 20·0 c.c. nitrogen at 18·5° and 768 mm. N = 9·55,

C₁₆H₁₄O₂N₂S requires N = 9·39 per cent.

The cyclic diazoimide was obtained by diazotising the preceding base in the usual way and treating the filtered solution with sodium acetate, when the product separated as a yellow, microcrystalline precipitate which, when washed successively with water, alcohol, and light petroleum and dried in the desiccator, decomposed violently at about 130°.

0·1170 gave 14·2 c.c. nitrogen at 18·5° and 745 mm. N = 13·72.

0·2137 „ 0·1618 BaSO₄. S = 10·40.

C₁₆H₁₁O₂N₃S requires N = 13·59 ; S = 10·35 per cent.

The diazoimide dissolves in concentrated mineral acids to form a diazonium salt which combines with alkaline β -naphthol; the azo-derivative, after two crystallisations from glacial acetic acid, melted at 220°.

(3) *Benzenesulphonyl-2:5-tolylenediazoimide,*

Benzenesulphonyl-5-nitro-o-toluidine, NO₂·C₆H₄·(CH₃)·NH·SO₂Ph, was first prepared by condensation in toluene, but the yield was so

poor (2 grams of product from 20 grams of the nitro-base) that this process was abandoned in favour of the following method.

The calculated amount (1 mol.) of benzenesulphonic chloride was added to 10 grams of the nitro-base dissolved in 30 c.c. of warm pyridine, and the mixture gently heated for $1\frac{1}{2}$ hours, and then cooled and extracted with cold hydrochloric acid. The insoluble portion was thoroughly washed with water and dissolved in aqueous caustic soda; the benzenesulphonyl compound was precipitated from the cooled filtered solution with hydrochloric acid, the yield being 17 grams. The reaction in concentrated pyridine solution is at first quite vigorous and is accompanied by a considerable rise of temperature; after two crystallisations of the product from dilute alcohol, amber-yellow, prismatic crystals were obtained melting at $157-159^\circ$.

0.5088 gave 43.0 c.c. nitrogen at 18° and 770 mm. $N = 9.89$.

$C_{13}H_{12}O_4N_2S$ requires $N = 9.59$ per cent.

Benzenesulphonyl-2:5-tolylenediamine, $NH_2 \cdot C_6H_3(CH_3) \cdot NH \cdot SO_2Ph$, obtained by reducing the preceding nitro-base in the usual way, crystallised from hot water in colourless, hair-like needles melting at 147° .

0.2347 gave 22.0 c.c. nitrogen at 20° and 769 mm. $N = 10.85$.

$C_{13}H_{14}O_2N_2S$ requires $N = 10.68$ per cent.

The cyclic diazoimide was prepared by mixing the base with cold concentrated hydrochloric acid, when it yielded at first a plastic mass which rapidly changed to the crystalline hydrochloride. Crushed ice was now added, the mixture diazotised with a slight excess of aqueous sodium nitrite, and the filtered solution treated with sodium acetate, when a precipitate was at once produced consisting of small, light yellow needles which decompose explosively at 163° .

0.1412 gave 18.8 c.c. nitrogen at 17° and 760 mm. $N = 15.22$.

0.2450 „ 0.2186 $BaSO_4$. $S = 12.27$.

$C_{13}H_{11}O_2N_3S$ requires $N = 15.38$; $S = 11.71$.

The *azo-β-naphthol* derivative, when isolated by acid from its sodium salt, produced by dissolving the cyclic diazoimide in cold concentrated hydrochloric acid and adding the diluted solution to alkaline β -naphthol, crystallises in prismatic crystals and melts at $184-185^\circ$.

(4) *Benzenesulphonyl-p-xylylene-2:5-diazoimide*,

Benzenesulphonyl-5-nitro-p-xylylidine, $NO_2 \cdot C_6H_2(CH_3)_2 \cdot NH \cdot SO_2Ph$, was produced by condensing 10 grams of 5-nitro-*p*-xylylidine (m. p.

142°) with benzenesulphonic chloride in about 50 c.c. of pyridine, removing the solvent with hydrochloric acid, extracting the residue with aqueous sodium hydroxide, and precipitating the filtered solution with mineral acid; it was crystallised twice from dilute alcohol, when it separated in yellow, prismatic crystals melting somewhat indefinitely at 160—163°.

0.2151 gave 17.2 c.c. nitrogen at 18° and 760 mm. $N = 9.23$.

$C_{14}H_{14}O_4N_2S$ requires $N = 9.15$ per cent.

The sodium derivative of this compound is sparingly soluble in aqueous sodium hydroxide, and separated in the course of the foregoing preparation in long, yellow needles, which dissolved again on warming the solution.

Benzenesulphonyl-p-xylylene-2:5-diamine,

was prepared by reducing the corresponding nitro-compound by the method already adopted for its lower homologues; it crystallises from water in straw-coloured needles melting at 144—146°.

0.1724 gave 15.3 c.c. nitrogen at 20° and 767 mm. $N = 10.23$.

$C_{14}H_{16}O_2N_2S$ requires $N = 10.14$ per cent.

The diazoimide was produced by diazotising the acylated diamine in a dilute solution containing excess of hydrochloric acid, filtering from a very slight residue, adding aqueous sodium acetate cautiously until a faint yellow precipitate became permanent, filtering again, and finally precipitating with excess of the alkali acetate. The bright yellow diazoimide was somewhat viscous at first, but hardened on triturating with cold water; it decomposed explosively at 125—130°.

0.1876 gave 23.9 c.c. nitrogen at 19.5° and 771 mm. $N = 14.83$.

0.2434 „ 0.1980 $BaSO_4$. $S = 11.17$.

$C_{14}H_{13}O_2N_3S$ requires $N = 14.63$; $S = 11.14$ per cent.

The *azo-β-naphthol* derivative, prepared by dissolving the diazoimide in concentrated hydrochloric acid and filtering into an alkaline solution of β-naphthol, separates in the form of the sparingly soluble alkali salt, which is decomposed by glacial acetic acid, yielding the free azo-compound, which separates in prismatic needles, and after two crystallisations melted at 215°.

(5) *Benzenesulphonyl-1:4-naphthylenediazoimide*,

The 4-nitro- α -naphthylamine required in this preparation was produced by the nitration of aceto- α -naphthalide in glacial acetic acid and the partial hydrolysis of the mixed 4- and 2-nitroaceto- α -naphthalides according to Lellmann and Remy's directions (*Ber.*, 1886, 19, 797). The product of the latter operation, which consists of the required base and the unaltered 2-nitroaceto- α -naphthalide, was, however, resolved into its components simply by dissolving the mixture in just sufficient hot ethyl acetate and cooling the solution rapidly. In these circumstances, practically the whole of the acetyl derivative crystallises out, whereas the 4-nitro- α -naphthylamine remains in solution until the greater portion of the solvent has been distilled off, when it separates from the concentrated solution as an orange, crystalline precipitate melting at 187° . A diazotisation experiment showed that the base was almost entirely free from 2-nitroaceto- α -naphthalide, and after one crystallisation from alcohol it melted at 191 – 192° (Lellmann and Remy give 191°). The 2-nitroaceto- α -naphthalide, which separated from the dilute ethyl acetate solution, was also extremely pure; it melted at 199 – 200° (corr., m. p. 199°) and was shown by successive treatment with nitrous acid and alkaline β -naphthol to be practically free from any 4-nitro- α -naphthylamine. In our hands, this mode of separation gave much more satisfactory results than the process of separation with dilute alcoholic sulphuric acid employed by Lellmann and Remy (*loc. cit.*).

Benzenesulphonyl-4-nitro- α -naphthylamine, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH} \cdot \text{SO}_2\text{Ph}$, could not be prepared by heating its generators in toluene, but it was found that a fairly good yield was obtained by condensation in quinoline or pyridine, the more volatile medium being preferable. Ten grams of benzenesulphonic chloride (1 mol.) were slowly added to a solution of 10 grams of 4-nitro- α -naphthylamine in 40 c.c. of pyridine; a vigorous action ensued which was completed by boiling the mixture for one and a half hours. The product was extracted successively with dilute hydrochloric acid and aqueous sodium hydroxide and the filtered solution from the latter extraction acidified, when 17 grams of the benzenesulphonyl derivative separated; it was crystallised twice from water, when spherular aggregates of bright yellow, fern-like crystals were obtained, melting at 158° .

0.2079 gave 15.3 c.c. nitrogen at 19° and 762 mm. $\text{N} = 8.48$,

$\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ requires $\text{N} = 8.53$ per cent.

Benzenesulphonyl-1:4-naphthylenediamine, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH} \cdot \text{SO}_2\text{Ph}$, was prepared by reducing the foregoing nitro-compound, but the reduction proceeded less smoothly by the iron and acetic acid method than was the case with the corresponding benzene derivatives. In many experiments, indefinite tarry products were the only result, but ultimately the following mode of procedure led to a more satisfactory conclusion.

Four grams of the nitro-compound were dissolved in about 200 c.c. of hot alcohol, 8 grams of tin were introduced, and 25 c.c. of concentrated hydrochloric acid gradually added with shaking, the mixture being boiled until test portions on treatment with water no longer exhibited any yellow coloration. The liquid was then transferred to a basin, the residual alcohol evaporated off, and about 5 c.c. of concentrated hydrochloric acid added. The colourless precipitate thus obtained was collected at the pump, washed free from tin salts with concentrated hydrochloric acid and finally water, dissolved in dilute aqueous caustic soda and the acylated base precipitated from the filtered solution with dilute acetic acid.

0.2237 gave 18.2 c.c. nitrogen at 20° and 767 mm. $\text{N} = 9.40$.

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ requires $\text{N} = 9.39$ per cent.

The base crystallises from benzene in clusters of colourless needles and melts at $186\text{--}187^\circ$.

The cyclic diazoimide was prepared by suspending the diamine in excess (20 mols.) of concentrated hydrochloric acid, adding crushed ice, and diazotising with a slight excess of sodium nitrite. The sparingly soluble diazonium salt was collected, dissolved in a mixture of glacial acetic and concentrated hydrochloric acids and the solution filtered into aqueous potassium acetate. The yellow diazoimide, which separated immediately as an amorphous, yellow powder, was collected and washed successively with water, alcohol, and light petroleum.

0.1849 gave 21.1 c.c. nitrogen at 20° and 769 mm. $\text{N} = 13.22$.

0.2351 „ 0.1705 BaSO_4 . $\text{S} = 9.94$.

$\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3\text{S}$ requires $\text{N} = 13.59$; $\text{S} = 10.35$ per cent.

All the diazoimides hitherto studied are extremely sensitive to light, and the foregoing naphthalene derivative seems in this respect to be even more readily affected than its benzenoid homologues.

It dissolves in a mixture of glacial acetic and concentrated hydrochloric acids, and the diluted solution, when added to alkaline β -naphthol, yields an *azo-derivative* which crystallises from glacial acetic acid and melts at 261° .

II.—*Action of Nitrous Acid on other Monoacylated (Formyl, Acetyl, Succinyl, and Benzoyl) Derivatives of p-Phenylenediamine.*

(1) *Acetyl-p-phenylenediamine.*

The acetyl-*p*-phenylenediamine (*p*-aminoacetanilide) required in the following experiments was prepared from a specimen of *p*-nitroacetanilide kindly supplied by the firm of Messrs. Levinstein. A solution of this acylated diamine in dilute hydrochloric acid (3—5 mols.), when diazotised and added to concentrated aqueous sodium acetate, gave no precipitate corresponding with the diazoimides obtained from the arylsulphonyldiamines, neither was any insoluble product isolated by pouring the solution into concentrated aqueous potassium carbonate (compare the benzoyl derivative, p. 933). The addition of ammonia, however, gives rise to a voluminous brown precipitate which has the properties of a nitrosoamine,

When collected, washed, and dried on porous tile it was found to dissolve in dilute acid or aqueous caustic alkali; the former solution at once gave the azo-condensation with alkaline β -naphthol, the latter only slowly. The compound could not be obtained in a crystalline form from the ordinary organic solvents. An estimation of nitrogen in the dried amorphous preparation agreed more closely with the percentage of a nitrosoamine than with that of a cyclic diazoimide or a diazoamino-compound.

0.1740 gave 35.2 c.c. nitrogen at 17° and 742 mm. $\text{N} = 22.94$.

$\text{C}_8\text{H}_9\text{O}_2\text{N}_3$ requires $\text{N} = 23.47$ per cent.

This substance decomposed somewhat indefinitely at about 85°.

A specimen of acetyl-*p*-phenylenediamine hydrochloride, obtained by passing hydrogen chloride into an acetone solution of the diamine, was dissolved in ice-cold water and treated successively with exactly one molecular proportion of sodium nitrite and excess of sodium acetate; a yellow precipitate was thus obtained, which decomposed suddenly at 195° and could be crystallised from alcohol, when it separated in small, brownish-yellow crystals decomposing somewhat indefinitely through a range of temperature from 190° to 200°. The substance retains water very tenaciously, its weight becoming constant only after prolonged heating in the steam oven.

0.1214 gave 24.3 c.c. nitrogen at 19° and 751 mm. $\text{N} = 22.74$.

$\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}_5$ requires $\text{N} = 22.50$ per cent.

This result agrees with the formula for a diazoamine,

which apparently indicates that only half the nitrite was required in the foregoing preparation. The compound was accordingly prepared by diazotising completely one molecular proportion of the hydrochloride suspended in moderately concentrated hydrochloric acid, and adding to the filtered solution excess of sodium acetate followed by one molecular proportion of the hydrochloride. The diazoamine separated immediately and this preparation decomposed at about 190° and resembled that obtained in the foregoing experiment. The substance is very sensitive to light, darkening rapidly on exposure.

(2) *Formyl-p-phenylenediamine* (*p-Aminoformanilide*).

This base was obtained by reducing with iron and dilute acetic acid formyl-*p*-nitroaniline, a substance formerly prepared by Osborn and Mixer (*Amer. Chem. J.*, 1886, **8**, 346) by nitrating formanilide and described as melting at $187-194^{\circ}$; our specimen melted at $194-195^{\circ}$ and gave the following numbers on analysis:

0.2448 gave 0.4514 CO_2 and 0.0881 H_2O . C = 50.29; H = 3.99.

0.2822 „ 41.8 c.c. nitrogen at 19° and 756 mm. N = 16.94.

$\text{C}_7\text{H}_6\text{O}_3\text{N}_2$ requires C = 50.60; H = 3.61; N = 16.86 per cent.

The acylated diamine crystallises from hot water in pale brown needles and melts at $125-127^{\circ}$. The crystallisation must be carried out rapidly, as the base quickly darkens if left in contact with the solvent. The hydrochloride, which is readily soluble in water, was prepared by saturating an acetone solution of the base with hydrogen chloride.

0.2074 gave 37.5 c.c. nitrogen at 20° and 748 mm. N = 20.36.

$\text{C}_7\text{H}_8\text{ON}_2$ requires N = 20.58 per cent.

When diazotised, it yields a solution from which neither sodium acetate nor alkali carbonates precipitate any insoluble diazo-derivative; ammonia, however, gives rise to a dark brown compound resembling the nitrosoamine obtained from the acetyl derivative (see p. 930). An ill-defined diazoamine, $\text{COH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COH}$, was obtained in the manner indicated for the acetyl diamine on p. 930; it was not, however, obtained crystalline, but when analysed in the crude state gave numbers approximating to the foregoing formula (N = 23.3, the calculated amount being 24.73 per cent.). The compound, when heated with cold mineral acid, undergoes the ordinary diazoamino-fission into its generators.

(3) *p*-Aminosuccinanilic Acid (*Succinyl-p-phenylenediamine*).

Succinanil (Menschutkin, *Annalen*, 1872, 162, 182) was nitrated and the *p*-nitro-derivative (m. p. 205—208°) then separated from the ortho-isomeride, simultaneously produced by extracting out the latter with alcohol.

p-Aminosuccinanilic acid is conveniently obtained by suspending 4.4 grams of *p*-nitrosuccinanil in 100 c.c. of water and adding 1 gram of glacial acetic acid and 4 grams of iron filings, the metal being introduced gradually and the solution then boiled for 15 minutes. The mixture was rendered alkaline with 2 grams of anhydrous sodium carbonate, boiled for 8 minutes, and then filtered at the pump. The filtrate, when rendered neutral by the successive addition of acetic acid and powdered calcite, yielded the *p*-amino-acid, which was thus obtained in colourless needles melting at 183°, this melting point being identical with the temperature recorded by R. Meyer (*Annalen*, 1903, 327, 39), who prepared the compound from *p*-phenylenediamine and succinic anhydride. *p*-Aminosuccinanil (m. p. 236°) is obtained by reducing the nitro-compound in the foregoing manner, excepting that the mixture is filtered immediately after the addition of the sodium carbonate, which in this case is added only in sufficient quantity to neutralise the acetic acid.

Succinyl-p-aminobenzenediazonium chloride,

was obtained on diazotising the amino-acid in a cold fairly concentrated solution in dilute hydrochloric acid; it is a perfectly stable compound which burns quietly and does not explode on percussion.

0.1610 gave 21.0 c.c. nitrogen at 15° and 759 mm. N = 15.27.

0.3120 „ 0.1529 AgCl. Cl = 12.12.

$\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_3\text{Cl}\cdot\text{H}_2\text{O}$ requires N = 15.32; Cl = 12.98 per cent.

The diazonium salt is readily soluble in water and its solution does not yield insoluble products with sodium acetate, alkali carbonates and ammonia; when poured into moderately concentrated alkaline β -naphthol, the alkali salt of the azo- β -naphthol is precipitated. This product, which readily dissolves in water, is decomposed by glacial acetic acid, yielding the free azo- β -naphthol derivative,

a substance which separates from glacial acetic acid as a crystalline powder and melts at 230—231°.

0.2300 gave 22.8 c.c. nitrogen at 18° and 768 mm. N = 11.58.

$\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}_3$ requires N = 11.54 per cent.

(4) *Benzoyl-p-phenylenediamine (p-Aminobenzanilide).*

This compound, formerly obtained by Hübner (*Annalen*, 1881, 208, 295) by reducing *p*-nitrobenzanilide with tin and hydrochloric acid, is readily prepared in quantitative yield from the nitro-compound by the iron and dilute acetic acid method of reduction. When the sparingly soluble hydrochloride is diazotised with sodium nitrite and hydrochloric acid, a soluble diazonium chloride is formed, the solution of which does not yield a precipitate with saturated aqueous sodium acetate. When, however, the solution is poured into cold aqueous sodium or potassium carbonate, a pale yellow, micro-crystalline precipitate is produced, which is only very sparingly soluble in cold water.

Benzoyl-p-aminobenzenediazonium carbonate,

is a remarkably stable example of a diazo-carbonate, and may be dried in the water-oven without undergoing any appreciable change beyond a slight darkening in colour. The substance, although so stable in the dry state, could not be recrystallised, as it is decomposed on boiling with alcohol or water; in the former case, the replacement of the diazonium complex by hydrogen appears to take place, for the odour of acetaldehyde is very marked; with the latter solvent, the diazo-group is replaced by hydroxyl, and this change also occurs when the salt is boiled with aqueous mineral acid; the carbon dioxide evolved was in several instances absorbed in weighed soda-lime tubes, the percentage amount varying from 12.8 to 13.1 per cent., this being about 84 per cent. of the quantity calculated for the pure carbonate.

The *p*-hydroxybenzanilide (*N*-benzoyl-*p*-aminophenol), produced by the decomposition of the diazo-compound by water, crystallises from water in colourless needles melting at 205–207°. This melting point, although differing considerably from the number (227.5°) given by Hübner (*Annalen*, 1881, 210, 378), is identical with the constant recorded for the substance by Hantzsch (*Ber.*, 1891, 24, 4042).

The diazonium carbonate dissolves with effervescence in cold concentrated hydrochloric acid, and the diluted solution, when introduced into alkaline β -naphthol solution, gave a practically quantitative yield of the azo-compound, the amount in two experiments being 124 and 128 per cent., whilst the calculated value is 128.8. A specimen of the carbonate prepared from carefully purified benzoyl-*p*-phenylenediamine furnished the following data on analysis:

0.1952 gave 25.5 c.c. nitrogen at 19.5° and 757 mm. $\text{N} = 14.95$.

$\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}_3$ requires $\text{N} = 14.73$ per cent.

The diazonium carbonate is sensitive to light, but if kept in the

dark may be preserved unchanged for an indefinite time. When shaken up with cold water, the carbonate yields a solution having a very faint alkaline reaction to red litmus. It readily condenses with amines and phenols, the addition of alkali accelerating the change in the case of the latter compounds. The hydrochloride of its azo-derivative with α -naphthylamine dissolves in alcohol to an intense bluish-purple solution.

It was hoped that this product might, on account of its great stability, be employed in the application of azo-compounds to the printing of textile fabrics, but comparative dye tests showed that the colours of its azo-derivatives could not compare in brilliancy with those obtained from diazotised *p*-nitroaniline. In this connexion, the compounds with "R salt" and "chromotrope acid" were examined, and the insoluble azo-compound with β -naphthol was recrystallised and analysed.

Benzoyl-p-aminobenzenazo- β -naphthol,

when crystallised successively from glacial acetic acid and alcohol, separates as a micro-crystalline powder and melts at 211° . With concentrated sulphuric acid, it develops a crimson coloration.

0.2808 gave 27.9 c.c. nitrogen at 20° and 767 mm. $\text{N} = 11.47$.

$\text{C}_{23}\text{H}_{17}\text{O}_2\text{N}_3$ requires $\text{N} = 11.44$ per cent.

Benzoyl-p-aminobenzenediazonium Nitrite,

—The solution obtained by adding excess of sodium acetate to the hydrochloric acid solution of benzoyl-*p*-aminobenzenediazonium chloride, when treated with excess of sodium nitrite, yields a crystalline, yellow precipitate, which dissolves in water to an almost colourless solution.

0.2162 gave 39.0 c.c. nitrogen at 19° and 763 mm. $\text{N} = 20.83$.

$\text{C}_{13}\text{H}_{10}\text{O}_3\text{N}_4$ requires $\text{N} = 20.74$ per cent.

The aqueous solution of the diazonium nitrite, when treated with potassium iodide, does not liberate iodine until dilute acetic acid is introduced, when the liberation of the halogen occurs immediately. The diazonium salt condenses readily with phenols and aromatic amines, yielding azo-derivatives.

A solution of the diazonium nitrite or acetate, when poured into a saturated solution of sodium hydrogen sulphite, yields at first an orange-coloured precipitate, which rapidly changes to a pale yellow substance which is also sparingly soluble in cold water. The orange compound interacts at once with alkaline β -naphthol, whereas the

yellow product does not at first yield any azo-derivative ; when, however, the mixture is kept for some time, a coloration is slowly developed.

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