

XXXIX.—*Influence of Substitution on the Formation of
Diazamines and Aminoazo-compounds. Part VI.
The Partially Methylated 4 : 6-Diamino-m-xylenes.*

By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

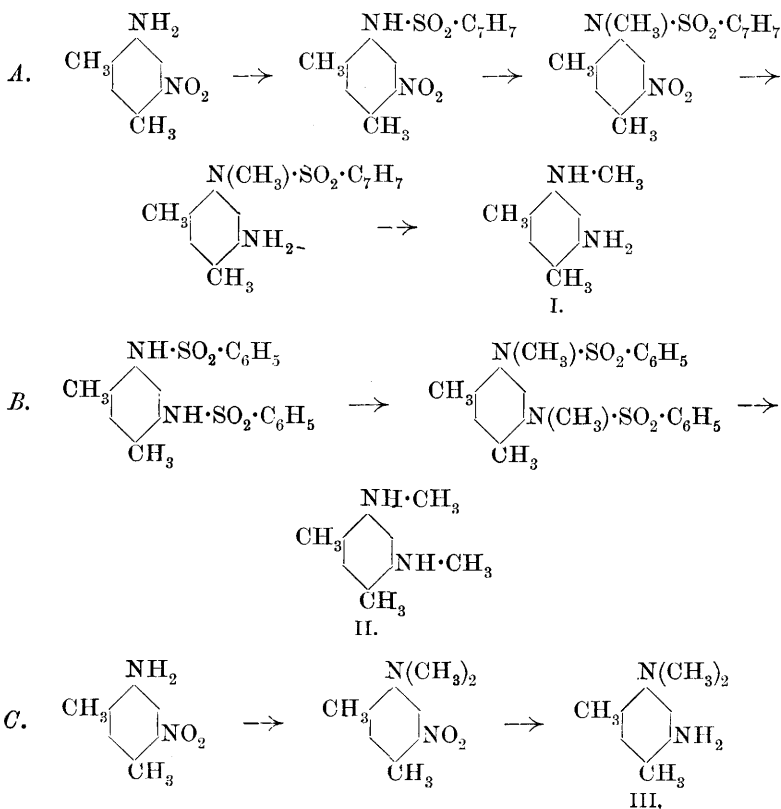
It was previously shown by one of the authors that aminoazo-compounds can be obtained from diazonium salts and 4 : 6-diamino-*m*-xylene, whereas this condensation is entirely inhibited when the aminic hydrogen atoms are completely replaced by alkyl groups as in tetramethyl-4 : 6-diamino-*m*-xylene (Trans., 1902, 81, 89, 656).

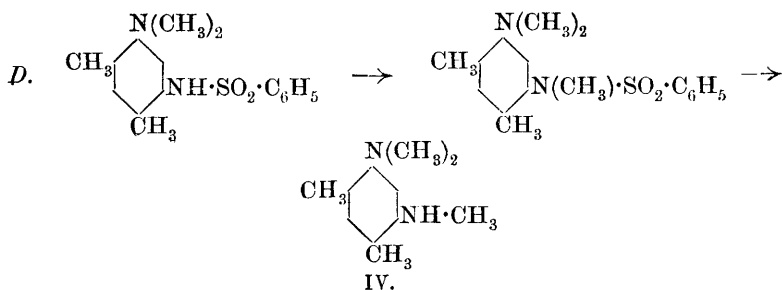
As the partially methylated bases of this series had not been pre-

pared, it seemed of interest to obtain these substances in order to ascertain how the progressive methylation of the primary diamine would affect the formation of azo-derivatives.

One of these partially methylated bases, namely, *s*-dimethyl-4:6-diamino-*m*-xylene, was recently prepared and studied by one of the authors and Mr. A. Clayton (Trans., 1906, 89, 1054), when it was found that the combination with diazo-compounds proceeded with great difficulty, and the product appeared to contain both a diazoamine and an aminoazo-compound.

All the other partially methylated derivatives of 4:6-diamino-*m*-xylene, namely, *methyl*-4:6-diamino-*m*-xylene, *as-dimethyl*-4:6-diamino-*m*-xylene and *trimethyl*-4:6-diamino-*m*-xylene, have now been obtained by methods described in the experimental part of this communication, and, as will be seen from the following diagram, the processes employed were devised to yield as far as possible the required base uncontaminated by other members of the series :





These diamines were readily characterised by their behaviour towards nitrous acid, each furnishing a product of a different type. Methyl-4:6-diamino-*m*-xylene (I) gave a nitroso-diazonium salt, *as*-dimethyl-4:6-diamino-*m*-xylene (III) formed a normal diazonium salt, whilst trimethyl-4:6-diamino-*m*-xylene (IV) gave rise to a mononitrosoamine. *s*-Dimethyl-4:6-diamino-*m*-xylene (II), previously examined, yielded a dinitrosoamine (Morgan and Clayton, *loc. cit.*).

These partially methylated diamines were now submitted in turn to the action of various diazonium salts.

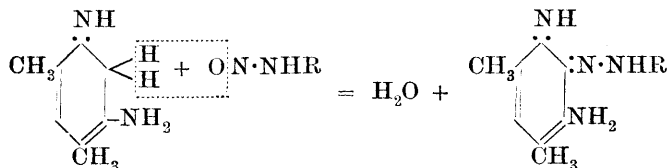
Methyl-4:6-diamino-*m*-xylene, like 4:6-diamino-*m*-xylene itself, furnished only azo-derivatives, but the yields in this case were even smaller than with the unmethylated base, and diazoamines were not isolated.

as-Dimethyl-4:6-diamino-*m*-xylene, on treatment with *p*-nitrobenzenediazonium chloride, furnished a well-defined diazoamine, accompanied only by traces of an azo-derivative. This *as*-dimethyl base may be compared with *s*-dimethyl-4:6-diamino-*m*-xylene which, with the same diazonium salt, gave rise to a mixture of azo-derivative and diazoamine (Morgan and Clayton, *loc. cit.*).

Trimethyl-4:6-diamino-*m*-xylene combined readily with diazotised amines to form well-defined diazoamines accompanied only by traces of azo-derivatives. The diazoamines produced with *p*-nitrobenzenediazonium and toluene-*p*-diazonium chlorides respectively were crystallisable compounds easily isolated in a state of purity and constituting the main product of the condensation.

The experiments on the dipara-substituted *m*-diamines have thus shown that progressive methylation of these bases renders increasingly difficult the formation of *o*-aminoazo-compounds, and that complete methylation altogether prevents this condensation. Now this tendency is entirely absent in the *p*-aminoazo-series where the completely methylated bases form azo-derivatives just as readily as the primary diamines. This striking contrast points to some difference in the mode of formation of the two series of azo-compounds. The presence

of a labile aminic hydrogen atom seems to be essential for the production of an ortho-aminoazo-compound, and this circumstance suggests the view that the condensation actually occurs with a dynamic form of the diamine in which an ortho-quinonoid configuration has been acquired.



The system may then revert more or less completely to the benzenoid form after condensation has been effected.

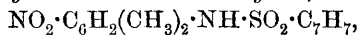
EXPERIMENTAL.

Methyl-4:6-diamino-m-xylene.

m-Xylene was nitrated by adding to 250 grams of the hydrocarbon cooled by salt and ice, a mixture of 500 grams of concentrated sulphuric acid and 575 grams of nitric acid (sp. gr. 1.52). The mixture was subsequently heated for one hour on the water-bath, and then cooled and poured on to ice. The 4:6-dinitro-*m*-xylene was isolated by repeatedly crystallising the product from alcohol, taking at each stage the less soluble crop of crystals.

6-Nitro-4-amino-*m*-xylene was prepared by dissolving the dinitro-compound (20 grams) in 120 c.c. of warm alcohol, adding 10 c.c. of strong ammonia, and saturating the solution with hydrogen sulphide; the addition of ammonia and hydrogen sulphide was repeated after half an hour's heating, and finally, when a considerable amount of a crystalline yellow solid had separated, a small quantity of water was added, and the alcohol was evaporated. The nitro-base was extracted with hydrochloric acid from the washed residue and reprecipitated from the filtered solution by ammonia; the crude product melted at 120°, and was recrystallised until the correct melting point (123°) was obtained.

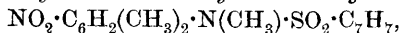
Toluene-p-sulphonyl-6-nitro-4-amino-m-xylene,



was obtained by heating for twenty hours in dry pyridine 20 grams of the nitroxylidine and an excess of toluene-*p*-sulphonic chloride (43 grams); the yield amounted to 33 grams, and the product after crystallisation from alcohol separated in transparent, pale yellow crystals melting at 192°:

0.3716 gave 28.4 c.c. nitrogen at 18° and 756 mm. N = 8.78.

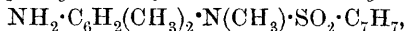
$\text{C}_{15}\text{H}_{16}\text{O}_4\text{N}_2\text{S}$ requires N = 8.70 per cent.

Toluene-p-sulphonyl-6-nitro-4-methylamino-m-xylene,

obtained by methylating the preceding compound in a reflux apparatus with methyl iodide and alcoholic soda, separated from alcohol in colourless, prismatic crystals (m. p. 135—136°) which are insoluble in aqueous alkalis :

0.1996 gave 14.6 c.c. nitrogen at 20° and 778 mm. $\text{N} = 8.57$.

$\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_2\text{S}$ requires $\text{N} = 8.38$ per cent.

4-Toluene-p-sulphonyl-4-methyl-4 : 6-diamino-m-xylene,

was produced by reducing the preceding nitro-compound with iron and dilute acetic acid, but as it did not crystallise satisfactorily from the ordinary organic media it was converted into its *hydrochloride*, which separates from an acid solution in almost colourless prisms melting at 225° :

0.4426 gave 0.1752 AgCl. $\text{Cl} = 9.96$.

$\text{C}_{16}\text{H}_{20}\text{O}_2\text{N}_2\text{S} \cdot \text{HCl}$ requires $\text{Cl} = 10.42$ per cent.

The base yields a very insoluble platinichloride and an *acetyl* derivative, crystallising from benzene in colourless, felted needles, and melting at 176°.

The *azo-β-naphthol* derivative,



crystallises from alcohol or acetic acid in bright red, felted needles, and melts at 177—178°.

Hydrolysis of the Sulphonamide.—This operation was successfully effected by heating for three hours at 120—130° a large number of sealed tubes, each containing 3.5 grams of the crystalline hydrochloride of the sulphonamide and 12 c.c. of concentrated hydrochloric acid. The product was rendered alkaline with ammonia and extracted with chloroform, the extract being then dried with anhydrous sodium sulphate and evaporated on the water-bath. The dark, oily residue thus obtained was distilled under diminished pressure in a current of carbon dioxide, when a colourless oil passed over at 180°/25—30 mm. This fraction when redistilled boiled constantly at 166—167°/10 mm., and solidified in the receiver in stellate clusters of colourless hastate crystals melting at 57° :

0.1739 gave 0.4550 CO_2 and 0.1503 H_2O . $\text{C} = 71.35$; $\text{H} = 9.60$.

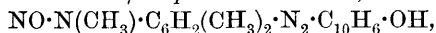
0.1892 „ 0.4978 CO_2 „ 0.1619 H_2O . $\text{C} = 71.75$; $\text{H} = 9.50$.

0.1521 „ 24.6 c.c. nitrogen at 19° and 763 mm. $\text{N} = 18.68$.

$\text{C}_9\text{H}_{14}\text{N}_2$ requires $\text{C} = 72.00$; $\text{H} = 9.33$; $\text{N} = 18.66$ per cent.

This diamine, which is extremely oxidisable, does not crystallise readily from the ordinary organic solvents, but its benzene solution on evaporation deposits transparent, colourless plates. When the hydro-

chloride of this base is treated with excess of sodium nitrite it reacts with two molecular proportions of nitrous acid, forming a soluble nitrosodiazonium chloride; this substance condenses with alkaline β -naphthol to yield an *azo- β -naphthol* derivative,



which separates from benzene in lustrous, red prisms or lath-like crystals, melting at 195—196°:

0.1720 gave 0.4337 CO_2 and 0.0937 H_2O . C = 68.76; H = 6.05.

0.1332 „ 20.2 c.c. nitrogen at 20° and 773 mm. N = 17.66.

$\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_4$ requires C = 68.26; H = 5.38; N = 16.76 per cent.

This substance was analysed only with difficulty owing to the readiness with which it evolves nitrous fumes on heating.

as-Dimethyl-4:6-diamino-m-xylene.

Methylation of 6-Nitro-4-amino-m-xylene.—The recrystallised nitroxylidine (m. p. 123°) was converted into its hydrobromide, and 3 grams of this salt were heated with 12 c.c. of methyl alcohol for five hours at 150—180°, the most suitable temperature being 160°. The sealed tubes then contained a clear red solution quite free from tar. The contents of sixty tubes were diluted with water, boiled with animal charcoal, and then rendered ammoniacal. The methylated nitroxylidine, which was extracted with chloroform, refused to solidify on evaporating off the solvent and cooling the residue. A small portion was converted into its crystalline *picrate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{CH}_3)_2 \cdot \text{N}(\text{CH}_3)_2 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$, which melts with violent decomposition at 170—173°:

0.1174 gave 16.4 c.c. nitrogen at 20° and 777 mm. N = 16.39.

$\text{C}_{16}\text{H}_{17}\text{O}_9\text{N}_5$ requires N = 16.54 per cent.

The main bulk of the oily nitro-base was reduced with a moderate excess of tin and hydrochloric acid; the metal was subsequently removed with hydrogen sulphide and the solution of the hydrochloride of the methylated diamine evaporated to a syrupy consistence. The base set free with ammonia was extracted with chloroform containing a small quantity of ether; the extract after drying with anhydrous sodium sulphate was evaporated at 100°, and the oily residue distilled under diminished pressure, when a viscid, yellow oil passed over at 174°/45 mm. When redistilled in a current of carbon dioxide the oil boiled constantly at 149—150°/21 mm. and was obtained quite colourless:

0.2328 gave 0.6242 CO_2 and 0.2108 H_2O . C = 73.13; H = 10.06.

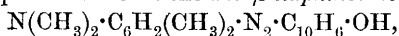
0.1470 „ 21.6 c.c. nitrogen at 18° and 769 mm. N = 17.19.

$\text{C}_{10}\text{H}_{16}\text{N}_2$ requires C = 73.17; H = 9.75; N = 17.07 per cent.

as-Dimethyl-4:6-diamino-m-xylene rapidly assumes a yellow colour

on exposure to the atmosphere and ultimately becomes red; it has a faint but characteristic odour and does not solidify at -10° . Its salts with the mineral acids are fairly soluble in water; its *benzoyl* derivative, $N(CH_3)_2 \cdot C_6H_2(CH_3)_2 \cdot NH \cdot CO \cdot C_6H_5$, crystallises from a mixture of absolute alcohol and light petroleum (b. p. $60-80^{\circ}$) in colourless, glistening plates and melts at 123° .

When treated with excess of sodium nitrite in acid solution the hydrochloride of this diamine reacts with only one molecular proportion of nitrous acid, yielding a soluble diazonium salt which condenses with β -naphthol to form the *azo- β -naphthol* derivative,



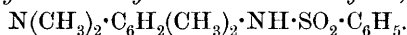
which separates from benzene in stellate clusters of prismatic crystals melting at $140-142^{\circ}$.

0.1883 gave 21.5 c.c. nitrogen at 19° and 763 mm. $N = 13.19$.

$C_{20}H_{21}ON_3$ requires $N = 13.16$ per cent.

Trimethyl-4 : 6-diamino-m-xylene.

Benzenesulphonyl-as-dimethyl-4 : 6-diamino-m-xylene,

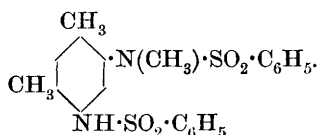


—This sulphonamide was obtained from *as*-dimethyl-4 : 6-diamino-*m*-xylene and benzenesulphonic chloride by the Schotten-Baumann reaction. The main bulk of the product dissolved in the aqueous caustic soda, although a small amount of a substance insoluble in the alkali was isolated. This compound, which crystallised from alcohol or benzene in colourless, transparent plates, melted at $113-115^{\circ}$ and contained 9.38 per cent. of nitrogen; it was not, however, further examined. The alkaline solution, when acidified with excess of hydrochloric acid, yielded (a) a small quantity of insoluble matter; this product when crystallised from alcohol separated in hard, colourless prisms and melted at $136-138^{\circ}$:

0.2690 gave 15 c.c. nitrogen at 19° and 780 mm. $N = 6.56$.

$C_{21}H_{22}O_4N_2S_2$ requires $N = 6.51$ per cent.

This compound appeared to be derived from a small quantity of methyl-4 : 6-diamino-*m*-xylene present in the dimethyl base and its properties (solubility in alkali hydroxides and insolubility in acids) pointed to the formula



This supposition was confirmed by applying the Schotten-Baumann

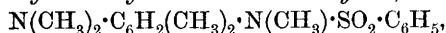
reaction to methyl-4:6-diamino-*m*-xylene when the same compound was produced.

The main hydrochloric acid solution (*a*), after filtration from the preceding compound, was treated with excess of sodium acetate, when the required benzenesulphonyl-*as*-dimethyl-4:6-diamino-*m*-xylene was obtained as a snow-white precipitate; this crystallised from alcohol and was obtained in colourless needles melting at 112—113°:

0.3170 gave 25.2 c.c. nitrogen at 17.5° and 771 mm. $N = 9.33$.

$C_{16}H_{20}O_2N_2S$ requires $N = 9.21$ per cent.

Benzenesulphonyltrimethyl-4:6-diamino-m-xylene,



was prepared from the preceding compound by heating it with methyl iodide and alcoholic potash in a reflux apparatus for nine hours. The product, which was quite insoluble in aqueous caustic soda, was dissolved in warm dilute hydrochloric acid, reprecipitated from the filtered solution by either sodium acetate or ammonia, and crystallised from alcohol, when it separated in transparent, lustrous, colourless needles melting at 122—123°:

0.2216 gave 17.5 c.c. nitrogen at 20° and 779 mm. $N = 9.26$.

$C_{17}H_{22}O_2N_2S$ requires $N = 8.80$ per cent.

Hydrolysis of the Trimethylated Sulphonamide.—Several tubes were each charged with 3 grams of the sulphonamide and 12 c.c. of concentrated hydrochloric acid and heated at 130—150° for four hours. A clear red solution was generally obtained, although in a few instances a small amount of tar was present. The filtered liquid was rendered ammoniacal and extracted with chloroform; the oily residue left after evaporating the dehydrated extract at 100° was distilled under diminished pressure in a current of carbon dioxide. The main portion boiled at 151°/20 mm. and when rectified at 145°/15 mm. was obtained as a colourless oil which slowly solidified to a mass of colourless crystals melting at 40—42°:

0.1432 gave 0.3864 CO_2 and 0.1321 H_2O ; $C = 73.60$; $H = 10.25$.

0.1414 „ 18.8 c.c. nitrogen at 16° and 775 mm. $N = 15.81$.

$C_{11}H_{18}N_2$ requires $C = 74.15$; $H = 10.11$; $N = 15.73$ per cent.

Trimethyl-4:6-diamino-m-xylene, when treated in cold dilute hydrochloric acid with excess of sodium nitrite, yielded only a mononitrosoamine which separated on the addition of excess of sodium acetate as an oil which slowly solidified to a mass of almost colourless crystals melting at 45°; 1 gram of the diamine furnished one gram of its *nitrosoamine*:

0.1428 gave 25.0 c.c. nitrogen at 16° and 775 mm. $N = 20.82$.

$C_{11}H_{17}ON_3$ requires $N = 20.28$ per cent.

This nitrosoamine gave intense colorations in all the phases of the Liebermann reaction.

*Action of Diazonium Salts on the Partially
Methylated 4:6-Diamino-m-xylenes.*

(1) *Methyl-4:6-diamino-m-xylene*.—A comparative dye-test made with diazotised primuline on the cotton fibre showed that this base behaved like 4:6-diamino-*m*-xylene itself towards this diazo-compound, the shades of red produced being very similar in hue and intensity. On treating the new diamine with the simpler diazonium salts it was found extremely difficult to isolate any well-defined condensation products. The substances obtained by means of toluene-*p*-diazonium chloride were tarry, whilst with *p*-nitrobenzenediazonium chloride only a very small yield of any solid azo-derivative was isolated; in neither case was any diazoamine obtained. On adding a solution of the latter diazonium salt to one of the diamine and then treating the mixture with aqueous sodium acetate, a deep brown precipitate appeared, which was accompanied by frothing. This product was collected after twelve hours, and, when dry, extracted with alcohol. A small quantity of a brownish-purple, crystalline substance separated from the alcoholic solution. This product, which contained chlorine, gave an intense reddish-brown coloration with concentrated sulphuric acid, and behaved as the hydrochloride of the azo-compound, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}(\text{CH}_3)_2(\text{NH}_2) \cdot \text{NH} \cdot \text{CH}_3$.

0.1432 gave 24.6 c.c. nitrogen at 20° and 778 mm. $\text{N} = 20.14$.

$\text{C}_{15}\text{H}_{17}\text{O}_2\text{N}_5 \cdot \text{HCl}$ requires $\text{N} = 20.86$ per cent.

This hydrochloride melted at 199—202°.

(2) as-*Dimethyl-4:6-diamino-m-xylene*.—The primuline dye-test indicated a marked diminution in the intensity of the ingrain azo-colouring matter obtained by using this diamine as developer. A comparative experiment made with *s*-dimethyl-4:6-diamino-*m*-xylene showed that the two isomerides give colours of similar hue and intensity.

A condensation of the diamine and *p*-nitrobenzenediazonium chloride effected in the presence of excess of aqueous sodium acetate led to the production of a diazoamine. This compound, which separated as a brownish-yellow precipitate, was obtained in almost quantitative yield, 3.3 grams of the diamine, and 2.76 grams of *p*-nitroaniline, furnishing 5.5 grams of this product. This diazoamine was either decomposed or not dissolved by the available solvents, and was therefore prepared from carefully purified materials and analysed after drying for some days over concentrated sulphuric acid:

0.1784 gave 35.0 c.c. nitrogen at 19° and 751 mm. $N = 22.34$.

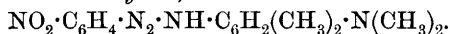
$C_{16}H_{19}O_2N_5$ requires $N = 22.36$ per cent.

A weighed portion, when heated with concentrated hydrochloric acid in the gas-volumeter, evolved the whole of its diazo-nitrogen :

0.4138 gave 29.0 c.c. nitrogen at 17° and 751 mm. $N = 8.03$.

$C_{16}H_{19}O_2N_5$ requires diazo- $N = 8.91$ per cent.

These results show that this substance is *p*-nitrobenzenediazo-*as*-dimethyl-4 : 6-diamino-*m*-xylene,



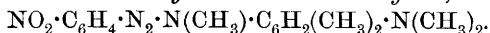
With alcoholic potash it developed the intense purple coloration characteristic of a diazoamine obtained from *p*-nitroaniline and a primary base ; it melted with violent decomposition at 135—140°.

Several attempts were made to transform the diazoamine into the isomeric azo-derivative by warming with the hydrochloride of the diamine in alcoholic solutions and also in solutions of the diamine itself, but in neither case was this change effected. When *as*-dimethyl-4 : 6-diamino-*m*-xylene was treated with toluene-*p*-diazonium chloride in the presence of aqueous sodium acetate, a migration of the diazo-group occurred, with the result that a portion of the diamine became diazotised and then gave rise to tarry phenolic products soluble in caustic soda whilst diazoamino-*p*-toluene (m. p. 116—118°) was produced. The identity of this diazoamine was confirmed by analysis ($N = 18.47$, theory requires $N = 18.60$) and by decomposing it with cold concentrated hydrochloric acid and then condensing the resulting diazonium salt with β -naphthol : the latter compound melted at 132°, the correct value being 134—135°.

This symmetrical diazoamine was not, however, the only product ; a certain amount of viscid material was obtained which was insoluble in aqueous alkalis but gave intense red colorations with concentrated hydrochloric and sulphuric acids. These reactions pointed to the presence of an azo-derivative but the substance could not be isolated in a definite form.

(3) *Trimethyl-4 : 6-diamino-m-xylene*.—The primuline experiment showed that this diamine had only a very slight tendency to form an ingrain azo-colouring matter. This indication was confirmed by the results obtained with simpler diazonium salts, when diazoamines were obtained almost exclusively.

p-Nitrobenzenediazotrimethyl-4 : 6-diamino-*m*-xylene,



This diazoamine separates as a viscid, brownish red precipitate on condensing the diamine and *p*-nitrobenzenediazonium chloride in aqueous sodium acetate. When dried and freed from by-products by washing

with cold alcohol, it was crystallised from this medium and separated in reddish-yellow crystals having a violet reflex:

0.1976 gave 36.2 c.c. nitrogen at 20° and 778 mm. $N = 21.46$.

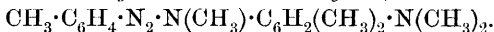
0.1326 „ 0.3028 CO_2 and 0.0742 H_2O ; $C = 62.27$; $H = 6.22$.

$C_{17}H_{21}O_2N_5$ requires $N = 21.40$; $C = 62.38$; $H = 6.45$ per cent.

This diazoamine melted with violent decomposition at 108—115°; it gave no coloration either with cold concentrated sulphuric acid or with alcoholic potash. These negative results indicate respectively an absence of azo-compound or of nitro-diazoamine derived from a primary base. When decomposed with concentrated hydrochloric acid in the gas-volumeter the new diazoamine evolved two-fifths of its nitrogen, a result which corroborates the above view of its constitution.

The alcoholic washings from the crude diazoamine on partial evaporation yielded a dark red, semi-crystalline residue which developed an intense brownish-red coloration with cold concentrated sulphuric acid. This product probably contained an azo-compound but the amount present was too small for more detailed examination:

Toluene-p-diazotrimethyl-4 : 6-diamino-m-xylene,



—Trimethyl-4 : 6-diamino-*m*-xylene, when condensed in the usual manner with toluene-*p*-diazonium chloride, slowly furnished a yellowish-red, viscid precipitate which, when collected and washed with a little cold alcohol, yielded the crude diazoamine. This substance was purified for analysis by dissolving in light petroleum (b. p. 60—80°) and adding to the solution a small quantity of alcohol, when a precipitate of yellowish-white plates was obtained which melted at 70—71°:

0.1034 gave 0.2782 CO_2 and 0.0719 H_2O ; $C = 73.36$; $H = 7.73$.

0.1230 „ 19.6 c.c. nitrogen at 20° and 777 mm. $N = 18.71$.

$C_{18}H_{24}N_4$ requires $C = 72.97$; $H = 8.10$; $N = 18.91$ per cent.

The diazoamine readily underwent fission with cold hydrochloric acid, regenerating the diamine and the toluene-*p*-diazonium chloride; the latter was identified by means of its azo- β -naphthol derivative (m. p. 134—135°). All attempts to transform the two foregoing diazoamines into the isomeric azo-derivatives proved unavailing.

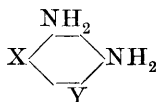
Summary of the Interactions of Aromatic Meta-diamines and Diazo-compounds.

As the investigation described in this paper completes the survey of the interactions of meta-diamines and diazonium salts in a large number of representative cases, it becomes possible to summarise the conclusions which may be drawn from these researches.

1. The mono-substituted meta-diamines and the di-substituted meta-diamines containing one free para-position with respect to an amino-

group interact readily with diazonium salts to furnish para-aminoazocolouring matters* (Trans., 1900, 77, 1205; 1902, 81, 89) and this reaction takes place with equal readiness both with the primary metadiamines of this type and with their completely alkylated derivatives (Trans., 1902, 81, 656).

2. The di-para-substituted primary meta-diamines



interact with diazonium salts to form ortho-aminoazo-derivatives, but the reaction takes place much less readily than with those diamines having one free para-position and the yield of azo-product is frequently very small (Trans., 1902, **81**, 88, 1379 ; 1905, **87**, 935).

3. The nature of the substituents X and Y exerts some influence on the course of the azo-condensation, for when they are methyl groups the base (4:6-diamino-*m*-xylene) reacts with diazotised aniline and its homologues, but when both substituents are halogen atoms (chlorine, bromine, or iodine) the condensation does not occur with these simple diazonium salts, but only with those derived from the nitroanilines. When only one methyl group is replaced by chlorine or bromine, reaction with diazotised aniline and *p*-toluidine still occurs, but the yield of *o*-aminoazo-derivative is extremely small (Trans., 1902, 81, 1379; 1905, 87, 937).

4. The presence of a nitro-group in one of the two substituted para-positions facilitates the azo-condensation, particularly when the diazonium salt also contains a substituent nitro-group (Trans., 1905, 87, 940).

5. The progressive alkylation of the di-para-substituted meta-diamines rapidly reduces their capacity for forming azo-derivatives. The symmetrically and unsymmetrically dimethylated diamines give mixtures of diazoamines and aminoazo-compounds (Trans., 1905, 87, 946; 1906, 89, 1057, and this paper, p. 368), whilst the trimethylated diamines readily furnish diazo-amines and show scarcely any tendency to form azo-derivatives (p. 369). Finally, the interaction of the di-para-substituted *m*-diamines and diazonium salts is entirely prevented by the complete alkylation of these bases (Trans., 1902, 81, 656).

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* Occasionally a small proportion of an ortho-aminoazo-derivative may appear as a by-product (Noelting and Thesmar, *Ber.*, 1902, **35**, 646).