XVI.—*Researches on the Constitution of Azo- and Diazo-derivatives.*I. *Diazoamido-compounds.*

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IN a paper recently communicated to the Chemical Society (Trans., 1886, 624),* we showed that the hydrogen-atom in the $-\text{N}_2\cdot\text{NH}-$ group of diazoamido-compounds could be readily displaced by alkyl radicles, and we described the ethyl-derivative, paradinitrodiazoamidobenzene, as a type of the class of derivatives thus formed. In the present communication, we give the results of the extension of our experiments to other diazoamido-compounds, these experiments having been undertaken with the hope of being able to throw some light upon the mechanism of the reaction which takes place when these substances are decomposed by acids. Among the points raised in connection with this decomposition was that of a possible intramolecular rearrangement in the $-\text{N}_2\cdot\text{NH}-$ group on treating the compounds with hydrochloric acid (*loc. cit.*, p. 630). A glance at the formula of the dipara-derivative described in the last paper, viz.,

will suffice to show that this question could not be decided by the decomposition of such a substance, since, the two sides of the molecule being symmetrical, we have no means of identifying among the products of decomposition the particular benzene rings attached respectively to the $-\text{N}_2-$ and the $-\text{NH}-$ groups. Our first experiments have therefore been directed to the preparation of mixed unsymmetrical diazoamido-compounds in which the two halves of the molecule could be identified after decomposition.

I. *Action of Diazotised Metanitriline upon Paranitriline.*

Metanitriline (1 mol.) was dissolved in the necessary quantity of dilute hydrochloric acid and diazotised by adding a solution of sodium nitrite (1 mol.) to the cold solution. The solution of the diazo-chloride was then added to a cold dilute solution of paranitriline

* Since the publication of this paper, Dr. Griess has been good enough to point out that one of the compounds described by us, viz., paradinitrodiazoamidobenzene, was obtained by him 24 years ago (*Annalen*, **121**, 271).

hydrochloride (1 mol.). A bright yellow precipitate at once commenced to separate; after being allowed to stand for 12 hours, this was collected, washed with cold water till free from acid, and purified by crystallisation from alcohol, in which it is somewhat more soluble than the isomeric paradinitro-compound. By slow crystallisation from an alcoholic solution, the pure substance was obtained in the form of yellow needles melting at 211° with slight decomposition. The following results were obtained on combustion:—

- I. 0.1568 gram dried at 100° gave 0.2892 gram CO_2 and 0.0460 gram OH_2 .
- II. 0.1048 gram dried at 100° gave 0.1916 gram CO_2 and 0.0301 gram OH_2 .
- III. 0.0786 gram burnt in a vacuum with CuO gave 16.9 c.c. N at 16.5° and 738.4 mm. bar.
- IV. 0.1120 gram burnt in a vacuum with CuO gave 24.2 c.c. N at 17.5° and 736.4 mm. bar.

	Calculated for $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$.	Found.			
		I.	II.	III.	IV.
C.	50.17	50.30	49.86	—	—
H.	3.13	3.25	3.19	—	—
N.	24.39	—	—	24.28	24.22

In its general properties, the substance resembles the isomeric paradinitro-compound, but it is not quite so acid in character, being less soluble in hot aqueous alkaline solution. The solution in caustic potash or soda is not of such a pure magenta-red, but is somewhat more orange in shade than is the case with the isomeride. According to its mode of formation, its formula might be written—

On this point we shall, however, have more to say in a subsequent part of the paper. We have not thought it necessary to study the products of complete reduction, as these would be in all probability a mixture of meta- and para-phenylenediamines,* and would not be of much importance in the present inquiry.

Decomposition by Hydrochloric Acid.

Some of the substance was sealed up in a glass tube with excess of

* Since writing the above, we have satisfied ourselves that this is really the case, by complete reduction and subsequent oxidation, according to the method described further on in this paper. The colour reactions characteristic of a mixture of meta- and para-diamines are immediately shown.

strong hydrochloric acid, and heated in a water-bath for two hours. On opening the tube, nitrogen was given off and the hydrochloric acid solution was filtered in order to separate a dark tarry residue. The latter, on steam distillation, gave an oily distillate which on standing slowly solidified to a crystalline mass intermixed with oil. The crystals, after purification by pressure between filter-paper and crystallisation from alcohol, were identified as paranitrochlorobenzene (m. p. 83°), and the oil on further examination proved to be a mixture of meta- and para-nitrochlorobenzenes.* The pitchy residue left after steam distillation was uncrystallisable and contained no phenolic substance. The hydrochloric acid solution separated from the tarry residue was found to contain a mixture of para- and meta-nitranilines which were separated by fractional crystallisation from water, the paranitraniline being identified by its melting point, while the metanitraniline, which was left in the solution after the removal of the other modification, was identified by reduction to meta-phenylenediamine and then applying the nitrous acid test ("Bismarck Brown") and diazobenzene chloride (chrysoidine).

Identification of a Mixture of Meta- and Para-diamines.—We may here mention that in subsequent experiments where a mixture of meta- and para-nitranilines or alkyl-nitranilines was obtained by the decomposition of the compounds under investigation, the most certain and rapid means of identification was found to be that of reduction to the corresponding diamines and the subsequent oxidation of the mixture. A mere trace of one of the diamines in admixture with the other modification reveals itself by the formation of a deep blue or violet colour ("indamine" series) (O. N. Witt, this Journal, Trans.,

* It was found by experiment that when a mixture of para- and meta-nitrochlorobenzenes containing an excess of the latter is fused under water, it forms an oil which remains fluid for days. The persistent presence of an oil in the above-mentioned steam distillate, led us at first to suspect the presence of nitrobenzene amongst the products of decomposition, and a method of separating this substance from the nitrochlorobenzenes was therefore devised, which may be worth mentioning here, although it led to the conclusion that no nitrobenzene was present among the products examined. The method in question consists in reducing the mixture of nitrobenzene and nitrochlorobenzenes dissolved in alcohol with tin and hydrochloric acid, evaporating off the alcohol and precipitating the tin by sulphuretted hydrogen. The solution of the hydrochlorides of the bases is then evaporated to dryness and acetylated by means of acetic anhydride and sodium acetate. The acetyl-derivatives, after being washed and dried, are nitrated by being dissolved in strong sulphuric acid in the cold, and the sulphuric acid solution gradually dropped into a well-cooled mixture of nitric and sulphuric acids. The nitro-compounds are thrown out by dilution with water, washed, and hydrolysed by boiling with caustic soda solution. Nitraniline (para) can then be separated from the nitrochloranilines, which are not basic, by means of warm dilute hydrochloric acid, and after precipitation is identified by its melting point and other properties.

1879, 356; *Jour. Chem. Soc. Ind.*, 1882, 255; Bindschedler, *Ber.*, 1880, 207; Nietzki, *Ber.*, 1883, 464; Nölting and Collin, *Ber.*, 1884, 267; Schweitzer, *Ber.*, 1886, 150), passing into red on boiling. In order to apply this test, the hydrochloric or acetic acid solution of the nitro-amines is treated with zinc-dust till complete reduction has taken place; ammonium carbonate is then added and the solution boiled and filtered. The filtrate is slightly acidified with acetic acid, and potassium chromate solution added, when the blue colour is immediately developed if both modifications are present, and on boiling the colour changes to red. This method is far more rapid and satisfactory than that of fractional crystallisation of the mixed nitro-amines. In the case of meta- and para-nitranilines, for example, it was found by experiments on mixtures of these two isomerides, that with certain proportions an easily fusible compound is formed which is oily under boiling water, and which caused some trouble during our first examination of the basic products of decomposition of the present dinitrodiazoamido-compound. Owing to this tendency to form a compound, it is most difficult to separate pure paranitraniline from the mixture by fractional crystallisation from water, and this difficulty is greatly increased when, as in the present case, only a small quantity of the mixed nitro-amines is available for examination.

Ethyl-derivative.

This compound was prepared by digesting the potassium salt of the dinitrodiazoamido-compound dissolved in alcohol with the theoretical quantity of ethyl iodide, according to the method described in our previous paper (*Trans.*, 1886, 630). Ethylation takes place very readily, and the ethyl-derivative, after crystallisation from alcohol, was obtained in the form of small yellow needles melting at 148° and at the same time frothing up and decomposing. The following are the results of analysis:—

I. 0.1453 gram gave 0.2836 gram CO_2 and 0.0564 gram OH_2 .

II. 0.0940 gram burnt in a vacuum with CuO gave 18.9 c.c. N at 18.5° and 735.2 mm. bar.

	Calculated for $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{N}(\text{C}_2\text{H}_5) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$.	Found.	
		I.	II.
C	53.33	53.22	—
H	4.12	4.31	—
N	22.22	—	22.39

The substance resembles its isomeride (*Trans.*, 1886, 630) in appearance and general properties. When heated in a sealed tube in a water-bath for three to four hours with excess of strong hydrochloric

acid, it decomposes into nitrogen and a tarry substance, whilst basic compounds remain in the acid solution. The tarry matter, like that obtained by the decomposition of the original substance, furnished an oily mixture of meta- and para-nitrochlorobenzenes on steam distillation. The acid solution contained a mixture of ethylmeta- and ethylparanitraniline. The presence of these two modifications was shown by reduction to the corresponding ethyldiamines; the solution on mere exposure to the air becoming rapidly blue, and giving a deep-blue precipitate immediately on the addition of potassium chromate, this colour changing into red on boiling. A solution of the mixed ethyldiamines prepared for comparison possessed all the foregoing properties. With respect to the constitution of the ethyl-derivative, we shall have some remarks to make further on in this paper.

II. *Experiments on the Decomposition of the Diazobenzene Chlorides by Hydrochloric Acid.*

The results obtained on the decomposition of the compound which, from its mode of formation, might be supposed to have the formula—

although in perfect accordance with the results obtained in similar reactions by other investigators (Griess, *Ber.*, 1874, 1619; Nölting and Binder, *Bull. Soc. Chim.*, **42**, 336), are opposed to the idea that the action of hydrochloric acid is of such a simple character as might appear at first sight. The fact that mixtures of para- and meta-nitrochlorobenzene and of meta- and para-nitranilines are obtained certainly points to the conclusion that intramolecular change occurs in the $\text{---N}_2\text{NH---}$ group, since the simplest mode of decomposition imaginable leads to the supposition that the chief products of decomposition would be metanitrochlorobenzene and paranitraniline, or, if isomeric transformation is supposed to take place, metanitraniline and paranitrochlorobenzene. It appeared of interest therefore at this stage of the work to study the action of hydrochloric acid on the diazotised nitranilines, *per se*, and in presence of similar and dissimilar nitranilines.

1. Paranitraniline was diazotised in the usual way and heated in a sealed tube in a water-bath with excess of strong hydrochloric acid in the presence of an equal weight of paranitraniline. The products of decomposition were nitrogen and paranitrochlorobenzene.

2. Metanitraniline similarly diazotised and heated in the presence of metanitraniline gave metanitrochlorobenzene.

3. Metanitriline diazotised and heated with hydrochloric acid in the presence of an equal weight of paranitriline, gave a mixture of meta- and paranitrochlorobenzenes and of meta- and para-nitrilines.

4. Paranitriline diazotised and decomposed in the presence of metanitriline gave the same products as in the last experiment.

It must be observed that in these experiments the heating of the tubes was commenced as soon as possible after the nitrilines had been diazotised and their solutions mixed, an excess of strong hydrochloric acid being always present, so that the diazoamido-compounds did not in any case separate out. The products of decomposition were, however, precisely the same as those obtained from the corresponding diazoamido-compounds, so that these compounds are actually formed as the first stage in the series of reactions which take place in the sealed tubes, or conversely, the diazoamido-compounds are first resolved into their constituents by the acid, and these products of decomposition then react in some manner, at present inexplicable.

III. *Metadinitrodiazoamidobenzene.*

This compound, first obtained by Griess (*Annalen*, **121**, 272), was prepared by acting with 1 mol. of NaNO_2 upon 2 mols. of metanitriline in dilute hydrochloric acid solution. The substance separates out as a yellowish-white flocculent precipitate which, after being collected, washed, and crystallised from alcohol, was obtained in the form of straw-coloured needles melting at 194° (195.5° Griess) without decomposition.

I. 0.1066 gram burnt in a vacuum with CuO gave 22.9 c.c. N at 17.5° and 746.7 mm. bar.

II. 0.0889 gram burnt in a vacuum with CuO gave 19 c.c. N at 16.5° and 747.4 mm. bar.

Calculated for		Found.	
$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$.		I.	II.
N	24.39	24.42	24.43

This compound differs from the dipara- and unsymmetrical isomerides in being far less acid in character. It is quite insoluble in hot aqueous alkalis, but dissolves in alcoholic potash and soda with an orange-brown colour; the potassium salt separates out from the solution in alcoholic potash, on cooling, in the form of brown glistening crystals. The constitutional formula of the compound is most probably

According to its mode of preparation, this compound might have been expected to be identical with that described by Hallmann (*Ber.*, 1876, 320), but this is certainly not the case. This author states that his substance melts at 175—176° with decomposition, that it dissolves but sparingly in alcohol, and that it is insoluble in acetic acid, &c. He further states that the substance is not decomposed by heating with hydrochloric acid, even at 130°, in a sealed tube, and that it possesses none of the characters of a diazo-compound. Our substance, besides differing in its melting point, is fairly soluble in alcohol, and readily soluble in acetic acid; it is, moreover, easily decomposable by hydrochloric acid, even at ordinary atmospheric pressure, on heating with strong acid, and more completely at 100° in a sealed tube. The products of decomposition are metanitrochlorobenzene and metanitriline; no phenolic substance appears to be formed. Hallmann obtained his compound as a residue formed during the diazotising of metanitriline in a dilute nitric acid solution, and in order to see whether the use of nitric instead of hydrochloric acid would influence the nature of the product we repeated the experiment with this variation, but the only result was a smaller yield of the same product as that obtained in our first experiment. By working in an alcoholic solution as recommended by Hallmann, we have obtained a small quantity of a reddish-brown substance, melting at 175—176°, and agreeing in its properties with the compound described by that author. This, as he suggests, is most probably an amidoazo-compound, and we hope to be able to resume its examination on a future occasion.

This compound was prepared from the foregoing by the action of ethyl iodide on the potassium salt, according to the method already described. After crystallisation from alcohol, it forms small opaque whitish-yellow needles, melting at 119°.

0.1435 gram gave 0.2809 gram CO₂ and 0.0508 gram OH₂.

	Calculated.	Found.
C	53.33	53.38
H	4.12	3.93

This ethyl-derivative on decomposition by hydrochloric acid, gives ethylmetanitriline and metanitrochlorobenzene.* The former com-

* This decomposition can be effected at ordinary pressure by simply boiling with strong hydrochloric acid in a flask, and furnishes a ready method of preparing pure ethylmetanitriline.

pound was identified by its melting point ($59-60^{\circ}$), and by conversion into its nitrosamine (m. p. 47°). Both these compounds have been recently prepared by Nölting and Stricker (*Ber.*, 1886, 546).

IV. *The Identity of Mixed Diazoamido-compounds.*

Since the original discovery by Griess of the interesting fact that the compound formed by combining diazotised bromaniline with aniline is identical with that obtained by combining diazotised aniline with bromaniline (*Ber.*, 1874, 1619), it has been generally admitted that mixed diazoamido-compounds of the type $X \cdot N_2 \cdot NH \cdot Y$ are identical, whether X or Y be diazotised first. In addition to the instance quoted, Griess also gives the following:—The diazoamido-compound formed by the action of diazobenzene on toluidine is identical with that formed by the action of diazotoluene on aniline; the compound formed by the action of diazobenzene on amidobenzoic acid is identical with that formed by the action of diazobenzoic acid on aniline. The identity of these compounds is shown not only by their similarity in physical properties, but also by their giving the same products on decomposition, and Sarauw has shown that they give similar products on treatment with phosgene (*Ber.*, 1881, 2442). Additional confirmation of these results is given by Nölting and Binder (*Bull. Soc. Chim.*, 1884, **42**, 336). Whether a similar identity exists among the secondary diazoamido-compounds obtained by combining tetrazo-salts with amines, and the converse, has not yet been established.

In accordance with the foregoing statements, it might have been anticipated that the compound obtained by acting on metanitriline with paranitrodiazobenzene chloride would be identical with that obtained by combining metanitrodiazobenzene chloride with paranitriline, *i.e.*, with the compound described in the previous portion of this paper. This anticipation has been confirmed by experiment. On mixing a solution of diazotised paranitriline with a dilute solution of metanitriline hydrochloride, a copious yellow precipitate slowly separates, and this, after purification, forms yellow needles melting at 211° , and giving on decomposition with hydrochloric acid a mixture of meta- and para-nitrochlorbenzenes, and of meta- and para-nitrilines. Its ethyl-derivative melts at 148° , and gives, on decomposition with hydrochloric acid, a mixture of the two nitrochlorbenzenes and the two ethylnitrilines, thus fully establishing the identity of this compound with that previously described.

According to the mode of formation of these compounds, two formulæ are possible, *viz.*:—

Isomeric transformation must thus occur in one or the other method of preparation, and the decision between the two formulæ would therefore lead to the important conclusion as to which nucleus the N_2 -group became finally attached. To throw further light on this point we have studied the action of the diazotised nitranilines on the ethylnitranilines.

(1.) *Action of Diazotised Metanitraniline on Ethylparanitraniline.*—Metanitraniline (1 mol.) was diazotised in the usual way, and the solution mixed with the necessary quantity of ethylparanitraniline* dissolved in dilute hydrochloric acid. After standing for about 14 hours, a copious yellow precipitate had formed; this was collected, washed with water till free from acid, and then the water displaced by alcohol. After crystallisation from boiling alcohol, in which the substance is very sparingly soluble, it was obtained in the form of yellow needles, melting at $174\text{--}175^\circ$.

0.1954 gram gave 0.3824 gram CO_2 and 1.0770 gram OH_2 .

	Calculated for	Found.
	$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{N}(\text{C}_2\text{H}_5) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$	
C	53.33	53.37
H	4.12	4.37

This compound is accordingly isomeric with that of melting point 148° described in the previous part of this paper. Its constitutional formula is in all probability

this formula corresponding with that of the ethyl-derivative of No. I. When heated in a sealed tube in a water-bath with strong hydrochloric acid, this substance decomposes, with the formation of ethyl-

* The ethylparanitraniline employed in these experiments was obtained by the decomposition of the ethyl derivative of paradinitrodiazoamidobenzene by hydrochloric acid. It was purified by conversion into its nitrosamine, and the latter, after crystallisation from alcohol, was decomposed by cobotation with hydrochloric acid and alcohol. Ethylmetanitraniline was prepared in a similar way from meta-dinitro-diazoethylamidobenzene.

paranitraniline and metanitrochlorobenzene, thus differing from its isomeride of melting point 148° , which under these circumstances gives a mixture of the two nitrochlorobenzenes and the two ethylnitranilines. On complete reduction and oxidation, it gives the intense blue colour characteristic of the "indamines."

(2.) *Action of Diazotised Paranitraniline on Ethylparanitraniline.*—On mixing the solutions in the usual way, a bulky yellow precipitate separated, which, after crystallisation from alcohol, was obtained in the form of small yellow needles melting at 192° , and identical with the paranitrodiazoethylamidobenzene described in our previous paper (Trans., 1886, 630).

(3.) *Action of Diazotised Paranitraniline on Ethylmetanitraniline.*—The yellow precipitate formed on allowing the mixed solutions to stand was purified by crystallisation from alcohol, in which it dissolves but sparingly, and then formed orange-yellow needles, melting at 187° . The appearance and properties of this substance show that it is probably an amidoazo-compound, possibly having the formula

Under no conditions have we been as yet able to obtain a diazoethyl-amido-compound by the action of diazotised paranitraniline upon ethylmetanitraniline. The crude precipitate is always contaminated with a certain quantity of paradinitrodiazoamidobenzene, which can be dissolved out by treatment with alcoholic potash, and the compound thus left, after being crystallised from alcohol, is quite different in appearance from any of the diazoethylamido-derivatives which we have prepared. The distinct tinctorial properties of this substance, taken in conjunction with the fact that its melting point is considerably higher than that of the unsymmetrical compound

obtained in the foregoing experiment (1), make it extremely probable that we have here a true amidoazo-compound, and we propose to submit this substance to further investigation.

(4.) *Action of Diazotised Metanitraniline upon Ethylmetanitraniline.*—The solutions were mixed as before, and gave on standing an ochreous resinous-looking deposit, which, after washing with water and crystallisation from alcohol, presented the appearance of small opaque whitish-yellow needles melting at 119° , and thus identical with the compound already described as being obtained by the direct ethylation of metadinitrodiazoamidobenzene.

The precise significance of these experiments will be considered subsequently. It may be here remarked, with reference to the product obtained in Experiment 3, that the ethylnitraniline (meta) having the para-position with respect to the $\text{NH}\cdot\text{C}_2\text{H}_5$ -group open, offers every facility for the formation of an amidoazo-compound. We have made some preliminary experiments with this substance in order to see in what respects it differs from its isomeride of m. p. $174-175^\circ$, obtained by the action of diazotised metanitraniline on ethylparanitraniline, and we find that on complete reduction and oxidation, it gives a violet colour very distinct from the pure blue of the "indamine" reaction, as given by the reduction and oxidation of the other ethyl-derivatives. This colour may arise from the oxidation of a mixture of paradiamidobenzene and ethyltriamidobenzene, but this point will require further investigation. The substance is readily decomposed by acids, but we have not as yet examined the products. If further examination should confirm the view that the substance is an amidoazo-compound, it will have to be classed with the β -naphthylamine azo-derivatives described by one of us (Trans., 1883, 430, and Trans., 1884, 116), which, according to Lawson (*Ber.*, 1885, 796), behave like diazo-compounds when decomposed by acids.

V. Benzyl-derivatives.

In order to test the wider applicability of the method described in our previous paper, we have extended our experiments by preparing the benzyl-derivatives of the foregoing diazoamido-compounds. These derivatives are readily formed by boiling the alcoholic solution of the potassium salts with the necessary quantity of benzyl chloride, the only precaution necessary being that the alcoholic solution should not be too dilute, otherwise some of the benzyl chloride is directly decomposed by the alkali, and the yield of benzyl-derivative is correspondingly diminished. The benzylation is generally complete in from two to three hours.

(1.) *Paradinitrodiazobenzylamidobenzene*, formed by the benzylation of the paradinitrodiazoamido-compound, crystallises from alcohol, in which it is but sparingly soluble, in minute yellow needles melting at 187° . The substance dissolves very readily in benzene, and a specimen crystallised from this solvent had a melting point of 190° .

0.0675 gram burnt in a vacuum with CuO gave 10.8 c.c. N at 14.7° and 764.3 mm. bar.

Calculated for		Found.
$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$.		
N	 18.57	18.87

On heating with strong hydrochloric acid in a sealed tube in a

water-bath for 3—4 hours, decomposition takes place in the same manner as with the ethyl-derivative. The contents of the tube consisted of a clear solution containing silvery laminated crystals and a reddish resinous mass. The crystals consisted of the hydrochloride of benzylparanitraniline, but the greater portion of this substance remained in the insoluble resin, owing to its feebly basic properties. On submitting this resin to steam distillation, paranitrochlorobenzene passed over and the benzylnitraniline was extracted from the residue by warm acetic acid (equal parts glacial acid and water), and crystallised out as the solution cooled.

Benzylparanitraniline, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_7\text{H}_7 = 1:4$, after purification by crystallisation from dilute alcohol, forms golden-yellow scales, readily soluble in alcohol and benzene, and melting at $142\text{--}143^\circ$. It is but very feebly basic, and does not form a platinochloride. The *nitrosamine* was obtained by adding the necessary quantity of sodium nitrite to the solution of the substance in alcohol and dilute hydrochloric acid. On dilution with water, a whitish flocculent precipitate is thrown out, which, after being collected and washed with water, was crystallised from dilute alcohol and then from dilute acetic acid. It forms flat, straw-coloured needles, with a silvery lustre readily soluble in cold alcohol and benzene, and melting at $107\cdot5^\circ$.

0·0994 gram burnt in a vacuum with CuO gave 14·1 c.c. N at $16\cdot5^\circ$ and 752·2 mm. bar.

	Calculated for $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{NO})\text{C}_7\text{H}_7$.	Found.
N	16·34	16·32

(2.) *Metadinitrodiazobenzylamidobenzene*.—This substance, obtained from the corresponding diazoamido-compound, crystallises from its alcoholic solution in pale-yellow needles, which glisten in the mother-liquor with brilliant prismatic colours. It is more soluble in alcohol than the preceding isomeride, and, like the latter, dissolves readily in benzene; its melting point is 142° .

0·1659 gram gave 0·3680 gram CO_2 and 0·0620 gram OH_2 .

	Calculated for $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$.	Found.
C.....	60·48	60·49
H	3·97	4·15

On decomposition with hydrochloric acid, it gives metanitrochlorobenzene and *benzylmetanitraniline*. The latter is more basic than the corresponding para-compound, and can be dissolved out from the contents of the tube by warm hydrochloric acid, the hydrochloride separating on cooling in the form of large silvery scales.

The free base, when allowed to crystallise slowly from dilute alcohol, forms magnificent golden-yellow laminae melting at 107° .

0.1280 gram gave 0.3182 gram CO_2 and 0.0610 gram OH_2 .

	Calculated for $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_7\text{H}_7$.	Found.
C.....	68.42	67.79*
H.....	5.26	5.29

The *nitrosamine*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{NO})\text{C}_7\text{H}_7 = 1 : 3$, is readily formed on adding sodium nitrite to the solution of the substance in acetic acid, and separates out on dilution with water as a viscid oil, which does not solidify on long standing.

(3.) *Benzyl-derivative of the Unsymmetrical Dinitrodiazamido-compound*.—In confirmation of the results obtained by the action of ethyl iodide, we have found on careful comparison that the benzyl-derivative of the compound resulting from the action of diazotised metanitriline on paranitriline is identical with the benzyl-derivative of the compound obtained by acting on metanitriline with diazotised paranitriline. The substance is almost insoluble in alcohol, but dissolves readily in benzene. After several crystallisations from this last solvent, it forms microscopic yellow needles melting at 180° .

0.2067 gram burnt in a vacuum with CuO gave 32.8 c.c. N at 14° and 748.5 mm. bar.

	Calculated for $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{N}(\text{C}_7\text{H}_7) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$.	Found.
N.....	18.57	18.38

On decomposition by heating with hydrochloric acid, it gives a mixture of benzylpara- and benzylmetanitriline and the two corresponding nitrochlorobenzenes. The mixed benzylitrilines readily give the "indamine" reaction on reduction and oxidation.

(4.) *Action of Diazotised Metanitriline on Benzylparanitriline*.—In order to see whether this compound would be isomeric with the benzyl-derivative referred to in the last experiment, as might have been expected from the previous results with the ethyl-derivatives, diazotised metanitriline was mixed with an alcoholic solution of benzylparanitriline containing hydrochloric acid. The results were, however, somewhat unsatisfactory, doubtless owing to the circumstance that the feebly basic properties of the benzylparanitriline make it necessary to use alcohol as a solvent. The product of the reaction is extremely small and very impure, smelling strongly of nitrochlorobenzene, and probably containing some of Hallman's com-

* The low carbon is probably due to the highly electrical properties of the substance, which render it extremely difficult to weigh out without loss.

pound. After being collected and washed with water, it was extracted several times with hot alcohol, and the residue repeatedly crystallised from benzene. The final product consisted of a very small quantity of a substance crystallising in minute yellowish-white opaque needles, mixed with larger ochreous crystals. The melting point was 185° , further purification being prevented by the small quantity of material at our disposal.

VI. Summary of Results and Theoretical Considerations.

Although at this stage of the investigations it would be premature to attempt to generalise too widely, it nevertheless seems desirable to consider the theoretical bearings of the present experiments, if only for the purpose of putting the facts in a distinct light, so as to clear the ground for the future extension of our researches. The identity of the unsymmetrical compound obtained by the action of diazotised metanitriline on paranitriline with that resulting from the action of diazotised paranitriline on metanitriline can only be brought about by the transference of the N_2 -group to the position occupied by the NH -group in one or the other method of formation. The ethyl-derivatives obtained in the course of the present investigation enable us to conclude with some degree of probability that the transference of the N_2 -group is to the *para*-position. This follows from the fact that the ethyl-derivative of m. p. $174-175^{\circ}$, obtained by the action of diazotised metanitriline on ethylparanitriline, is isomeric, and not identical with the ethyl-derivative (m. p. 148°) of the unsymmetrical compound prepared by direct ethylation. If, as the appearance and properties of the substance indicate, this $174-175^{\circ}$ m. p. ethyl-derivative is a true diazoamido-compound, its formula must be—

that is to say, it must be an ethyl-derivative of the unknown compound—

and the unsymmetrical compound of m. p. 211° (ethyl-derivative 148°) must therefore have the constitution expressed by the formula—

From this it follows that when metanitraniline is diazotised and combined with paranitraniline, the N_2 -group becomes transferred to the paranitraniline half of the molecule.* The one piece of evidence necessary for the direct confirmation of the foregoing conclusion would be the formation of the unsymmetrical ethyl-derivative (m. p. 148°) of which the formula is most probably—

from diazotised paranitraniline and ethylmetanitraniline, but, as already explained, the reaction apparently takes another course in this case, and leads to the production of what seems to be an amidoazo-compound.

With respect to the transference of the N_2 -group to the para-position, we may here point out that evidence of a similar nature is to be found in a paper by Nörling and Binder (*Bull. Soc. Chim.*, **42**, 336), although these authors do not state explicitly the inference which may be legitimately drawn from their experiments. Thus, the diazoamido-compound obtained by the action of diazotised aniline on paratoluidine is identical with that resulting from the action of diazotised paratoluidine on aniline, as already pointed out by Griess. When decomposed by bromine, this compound splits up into paradiazotoluene bromide and tribromaniline, from which the authors conclude that it has the constitution—

When aniline is diazotised and combined with paratoluidine, it appears, therefore, that a similar transference of the N_2 -group takes place.

The migration of the N_2 -group can perhaps be best explained by adopting the suggestion of Victor Meyer (*Ber.*, 1881, 2447) that an intermediate compound is first formed.† According to this view, the changes which occur when a solution of metanitrodiazobenzene chloride is added to a solution of paranitraniline would be thus represented—

* This conclusion is opposed to that arrived at by Sarauw (*Ber.*, 1882, 46), who states that the NH -group becomes attached to the *more negative* radicle. If this statement held good generally, it might have been expected that the NH -group in the present compound would have been attached to the paranitraniline half of the molecule.

† The formation of unstable additive compounds of the benzene-azonaphthols with hydrogen chloride and hydrogen bromide has been observed by Liebermann, *Ber.*, 1883, 2891.

The latter compound, when heated with strong hydrochloric acid, gives a mixture of the two nitranilines and the two nitrochlorobenzenes, so that at a high temperature it must be supposed that the intermediate compound is again formed, and that this splits up in two ways—

The first mode of decomposition would give a diazoamido-compound, which on decomposition by hydrogen chloride would give paranitrochlorobenzene and metanitriline, and the second mode of decomposition would similarly lead to the production of metanitrochlorobenzene and paranitriline. It is not at all improbable that both these reactions go on simultaneously in a sealed tube at 100°. The mixed products obtained by the decomposition of the ethyl- and benzyl-derivatives of the above compound can be accounted for in a similar manner--

In the second mode of decomposition, however, the ethyl chloride is not actually set free, but at the moment of decomposition exchanges C_2H_5 for the hydrogen of the NH -group. On the other hand, when the ethyl-group is already in the more stable para-position, as is the case with the compound of m. p. 174—175°—

the decomposition must be considered to take place in the above more simple manner, the products being, as we have shown, simply ethyl-paranitraniline and metanitrochlorbenzene.

We propose to test these views by further experimental investigation, and hope soon to be able to resume the study of the supposed amidoazo-compound obtained by the action of paranitrodiazobenzene chloride on ethylmetanitriline, this compound offering many points of special interest in connection with the present researches.

In concluding, we have to express our thanks to our students Messrs. H. T. Pentermann and W. P. Dreaper, who have materially assisted us by making many of the foregoing analyses.