

LVIII.—*A Method of Investigating the Constitution of Azo- and Diazo-derivatives and Analogous Compounds.*

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IN former papers by one of the authors (Meldola, *Trans.*, 1883, 436, and 1884, 117), it was pointed out that the compounds resulting from the action of diazo-salts of para- and meta-nitraniline on β -naphthylamine possessed neither the characters of true azo- nor diazo-compounds, and it was suggested that these substances might be related to the class of azimido-compounds of which the simplest representative is Griess's azimidobenzene:—



According to this view, the general formula of these compounds may be written—



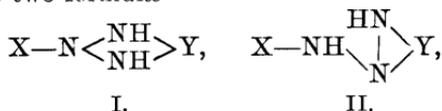
where X and Y may be similar or dissimilar, and the compounds may be regarded as derivatives of the typical hydrazimido-compounds:—



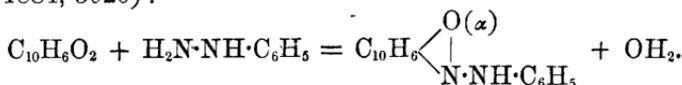
In the paper referred to, it was further suggested that the difference in the constitution of these β -naphthylamine compounds resulted from the interaction of the azo- and amido-groups, which in all probability occupy an ortho-position with respect to one another, so that the investigation of the supposed azo-compounds derived from ortho-amido-compounds becomes a matter of considerable importance. The necessity of continuing the investigation in this direction has always been kept in view, although, since the publication of the paper in question, much additional evidence has been gained by the researches of Zincke and his pupils (*Ber.*, 1885, 3132 and 3142; Lawson, *ibid.*, 796 and 2422, and *Inaug. Diss.*, Marburg, 1885; Sachs, *Ber.*, 1885, 3125).

Among the recent results, the most important in relation to the constitution of the compounds under consideration is undoubtedly the discovery that they can be oxidised to substances of the azimido type (Zincke, *Ber.*, 1885, 3134). Upon this evidence Zincke accepts the

conclusion which had been arrived at on other grounds in the paper published in the Transactions of this Society in 1884, viz., that the compounds in question no longer contain an amido-group, but two NH-groups. With respect to the constitution of these compounds Zincke gives the two formulæ—



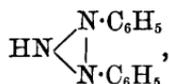
the first of these corresponding with that proposed by one of the authors of the present paper in 1884, and the second corresponding with the formation of β -naphthaquinone-hydrazone from β -naphthaquinone and phenylhydrazine as observed by Zincke and Bindewald (*Ber.*, 1884, 3026):—



The evidence at present available does not render it possible to decide between these formulæ, and further investigation therefore appears necessary.

In a note published by one of the authors (Meldola, *Chem. News*, Dec. 5, 1884), it was suggested among other methods of investigating the constitution of these and analogous compounds, that the behaviour of the alkyl-derivatives, on reduction, might throw light on the question. Thus, with respect to the two formulæ given, a monalkyl-derivative of I would give, on complete reduction, $\text{X}\cdot\text{NH}_2$ and $\text{NH}\cdot\text{Y}\cdot\text{NR}$; and a monalkyl-derivative of II would give either $\text{X}\cdot\text{NHR}$ and $\text{NH}_2\cdot\text{Y}\cdot\text{NH}_2$ or $\text{X}\cdot\text{NH}_2$ and $\text{NH}_2\cdot\text{Y}\cdot\text{NR}$, according to the position of the radicle. A dialkyl-derivative of I would give on reduction $\text{X}\cdot\text{NH}_2$ and $\text{NR}\cdot\text{Y}\cdot\text{NR}$, and of II, $\text{X}\cdot\text{NHR}_2$ and $\text{NH}_2\cdot\text{Y}\cdot\text{NHR}$. The same considerations evidently apply to diazoamido- and amidoazo-compounds, and, as far as we are aware, the decomposition products of the alkyl-derivatives of these compounds have not hitherto been investigated. Thus mono- and di-alkyl-derivatives of true amido-azo-compounds of the type $\text{X}\cdot\text{N}_2\cdot\text{Y}\cdot\text{NH}_2$ would give on reduction $\text{X}\cdot\text{NH}_2$ and $\text{NH}_2\cdot\text{Y}\cdot\text{NHR}$, or $\text{NH}_2\cdot\text{Y}\cdot\text{NR}_2$, whilst diazoamido-compounds of the type $\text{X}\cdot\text{N}_2\cdot\text{NH}\cdot\text{Y}$ could only give monalkyl-derivatives, $\text{X}\cdot\text{N}_2\cdot\text{NR}\cdot\text{Y}$, which, on reduction, would yield $\text{X}\cdot\text{NH}_2$ and $\text{Y}\cdot\text{NHR}$.

It appeared also that the present method would be capable of determining finally the question of the symmetrical or asymmetrical formula of the diazoamido-compounds. The symmetrical formula for diazobenzeneanilide—



is given by Victor Meyer (*Ber.*, 1881, 2447), but is rejected by him as having little probability. The same formula has recently been brought forward by Friswell and Green (*Trans.*, 1885, 924), who state that it appears to them to be more probable than the asymmetrical formula. Supposing the diazo-amido-compounds to have the symmetrical formula above given, it is evident that their monalkyl-derivatives on reduction would give $X \cdot NH_2$, $Y \cdot NH_2$ and NRH_2 .

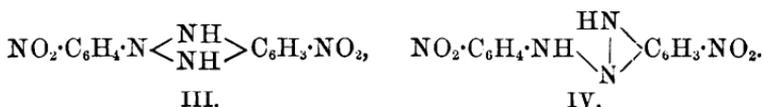
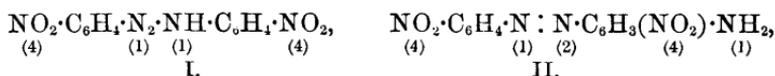
In order to apply the present method, ethyl iodide was used as the exploring agent, and, although we have as yet only studied one compound, the results are sufficiently interesting to warrant their being communicated to the Society.

We propose to extend the investigation to other diazo-, azo-, azimido-, and oxyazo-compounds.

Paradinitrodiazoamidobenzene.

In the present communication, we give the results of the application of the method indicated to the above-named substance, which has not hitherto been prepared, the only analogous compound at present known being the supposed dinitrodiazoamidobenzene obtained by Hallman by the action of nitrous acid on metanitriline (*Ber.*, 1876, 390). We propose to apply our method to Hallman's compound at an early opportunity. In starting from paranitriline for our first experiments, we had two objects in view.

In the first place it appeared probable that the compounds resulting from the action of nitrous acid on the nitrilines would be of a distinctly acid character owing to the presence of the nitro-groups, thus offering the possibility of easy displacement of H by alkyl radicles in NH-groups which might be present, since the acidity of the molecule rendered it probable that the H in the NH-group would be displaceable by metals, and the salts thus formed would be decomposable by alkyl iodides, &c. In the next place, in the case of paranitriline, where the para-position with respect to the NH_2 -group is occupied, it appeared probable that a true diazo-compound would in the first place be formed, and that if this could be transformed into its isomeric amido-azo-compound the N_2 -group would occupy the ortho-position with respect to the amido-group. Thus there might be formed one of the compounds represented by the following formulæ:—



As the result of our experiments, we find that with paranitraniline a true diazo-amido-compound (formula I) is alone produced.

In order to prepare this substance, paranitraniline was dissolved in the minimum quantity of strong hydrochloric acid, and the cold solution diluted with water, but not so much as to throw out the nitraniline. The solution of sodium nitrite (1 mol. to 2 mols. nitraniline) was then gradually added, and the mixed solutions allowed to remain in a cool place for 12—14 hours. The separation of the diazo-compound commenced when the whole of the nitrite had been added, and at the expiration of the time mentioned the contents of the flask had become semi-solid. The pulpy yellow precipitate was collected, washed thoroughly with cold water, and a specimen purified for analysis by crystallisation from alcohol. It forms small yellow needles soluble in boiling alcohol and acetone, but not very readily, and only sparingly soluble in chloroform and the benzene hydrocarbons. It melts at 223°, at the same time frothing up and decomposing. The following results were obtained on analysis:—

- I. 0·1346 gram gave 0·2489 gram CO₂ and 0·0372 gram water.
 II. 0·0843 gram burnt in a vacuum with CuO gave 17·8 c.c. N at 15·5°, and 760·1 mm. bar.

| | Theory for NO ₂ ·C ₆ H ₄ ·N ₂ ·NH·C ₆ H ₄ ·NO ₂ . | Found. |
|--------|---|--------|
| C..... | 50·17 | 50·43 |
| H..... | 3·13 | 3·07 |
| N..... | 24·39 | 24·66 |

The substance, as anticipated, possesses distinctly acid properties, dissolving in cold alcoholic potash or soda with a splendid magenta-red colour, and in boiling aqueous alkalis with a similar colour. The alkaline solutions show a remarkable stability, the substance forming well characterised crystalline salts which separate out from the solutions on cooling. The sodium salt, which probably has the formula NO₂·C₆H₄·N₂·NNa·C₆H₄·NO₂, forms beautiful steel-blue needles, but these are stable only in the presence of excess of alkali; when collected and washed, they gradually decompose on exposure to the air with the liberation of the original yellow substance. The acidity of the substance is sufficiently great to decompose alkaline carbonates, the characteristic red colour being developed on boiling the diazo-compound with a solution of potassium or sodium carbonate. The stability of the substance in the presence of alkalis was shown by boiling some of it for two days with an excess of strong caustic potash solution; the crystalline potassium salt, on being decomposed by dilute sulphuric acid, gave the original substance unaltered. The cold alkaline solution of the compound, when acidified, gives the

original substance in the form of a greenish gelatinous precipitate which gradually becomes yellow on standing; on acidifying the hot alkaline solution, the substance immediately separates in a yellow flocculent state. It is very unstable in the presence of acids, being decomposed by boiling with glacial acetic acid with evolution of nitrogen and the formation of resinous uncrystallisable products. Heated with dilute sulphuric (1 part strong acid to 4 of water) in a sealed tube for 2—3 hours at 100°, the substance is decomposed with the liberation of nitrogen and the formation of paranitraniline and resinous products. No nitrophenol appears to be formed in this reaction. A similar decomposition was effected by heating the substance with water in a sealed tube at 230° for three hours, the product being, as before, paranitraniline and resin.

Products of Reduction.

Supposing the substance to have been an amidoazo-compound, it seemed advisable to study in the first place the action of mild reducing agents in order to see whether a hydrazo-compound could be obtained. By the action of ammonium sulphide on a warm alcoholic solution of the sodium salt, reduction was effected and the magenta-red colour of the solution gradually changed to orange. On dilution with water, a reddish flocculent substance separated out, but this did not appear to be a very definite compound, as it could not be crystallised, and had no definite melting point. It decomposes when heated, and a specimen that had been placed to dry in the water-oven suddenly frothed up and decomposed with carbonisation. The dry substance forms a reddish powder which deflagrates vigorously on ignition. We have since found that more satisfactory results are obtained by reducing the hot aqueous solution of the sodium salt with ammonium sulphide. When the red colour of the solution has disappeared, reddish-brown needle-shaped crystals are deposited on cooling. We propose to make a further study of this reduction product, but the main question of the constitution of the original substance is for the present settled by the fact that on complete reduction it gives only paraphenylenediamine. This was proved by a careful examination of the reduction products obtained by the action of zinc-dust and acetic acid and of tin and hydrochloric acid on the compound dissolved in alcohol. In both cases, paraphenylenediamine was the sole product, and was identified by its characteristic colour reactions with ferric chloride, potassium dichomate, ferric chloride in the presence of hydrogen sulphide, and by the analysis of the diacetyl-derivative. The formulæ II, III, and IV are thus excluded, as these substances on reduction would give a mixture of di- and tri-amidobenzenes, and the substance is therefore a true diazoamido-compound.

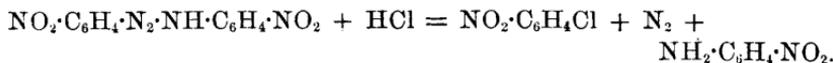
Decomposition by Hydrochloric Acid.

When decomposed by heating with acids in the presence of water, diazoamido-compounds usually break up into amido-derivatives, phenols, and nitrogen. It appears, however, from Lawson's experiments (*Ber.*, 1885, 797) that this mode of decomposition is not confined to diazoamido-compounds, since the compounds obtained by the action of diazotised amines on β -naphthylamine also yield the amine (β -C₁₀H₇·NH₂) and the corresponding phenol (C₆H₅·OH, NO₂·C₆H₄·OH, &c.). That these β -naphthylamine compounds are not true diazoamido-compounds is shown by the fact that they give naphthylendiamine on reduction.* The failure to obtain nitrophenol from the present dinitrodiazoamidobenzene by decomposing it with dilute sulphuric acid is thus a feature in the character of the diazoamido-compounds to which it seems desirable to call special attention. Much more definite results were obtained by decomposing the substance with strong hydrochloric acid, three hours' heating in a sealed tube in a water-bath being sufficient for complete decomposition. Nitrogen is given off on opening the tube, the contents consisting of a mixture of large needle-shaped crystals and a dark tarry substance, together with the excess of acid liquid. The crystals were identified as the hydrochloride of paranitraniline, and the tarry substance, after being repeatedly washed with warm dilute hydrochloric acid to completely remove the paranitraniline, was found to be separable by steam distillation into a white crystalline substance having an odour of bitter almond oil, and a small quantity of a dark oil which remained behind in the flask and solidified on cooling to a brittle resin. The crystalline distillate was purified by redistillation in a current of steam, and proved to be paranitrochlorobenzene: m. p. 83°:—

0·1737 gram burnt with lime gave 0·1590 gram AgCl.

| | Theory for C ₆ H ₄ ·Cl·NO ₂ . | Found. |
|-------------|---|--------|
| Cl. | 22·54 | 22·63 |

The decomposition of the diazoamido-compound by hydrochloric acid may thus be simply represented by the equation—



It seems most probable that the nitraniline residue to the left of the N₂-group in the above formula, that is the nucleus directly

* According to a recent paper by Nietzki and Goll (*Ber.*, 1886, 1281), amido-azo- β -naphthalene can be diazotised under suitable conditions, and thus appears to contain an NH₂-group.

attached to the azo-group, is the one into which the chlorine of the acid enters to displace the N_2 .

This point is, however, sufficiently interesting to examine into further, as it is by no means certain that intramolecular rearrangement may not occur during the decomposition of diazo-compounds, owing to the formation of intermediate additive products. We propose to extend our investigations in this direction by examining the decomposition products of mixed diazoamido-compounds containing dissimilar radicles.

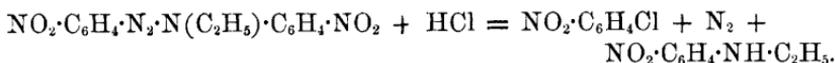
Paradinitrodiazoethylamidobenzene.

In order to prepare this compound, the dinitrodiazoamidobenzene was dissolved in alcohol with the addition of the theoretical quantity of caustic potash to form the potassium salt. The necessary quantity of ethyl iodide was then added and the liquid kept boiling in a flask with an upright condenser for about 10 hours, when the red colour of the solution had disappeared and a heavy yellowish crystalline deposit had separated: 20 grams of the dinitrodiazo-compound gave about 18 grams of the ethyl-derivative, or about 81 per cent. of the theoretical quantity. The ethyl-derivative was collected, washed with water to remove potassium iodide, and crystallised twice from alcohol in which it is but very sparingly soluble. The substance forms small yellow needles, melting without decomposition at $191-192^\circ$.

- I. 0.2825 gram gave 0.5501 gram CO_2 and 0.1072 gram OH_2 .
 II. 0.1456 gram gave 0.2845 gram CO_2 and 0.0550 gram OH_2 .
 III. 0.0958 gram burnt into vacuum with CuO gave 17.9 c.c. N at 13.7° and 757 mm. bar.

| | Theory for $NO_2 \cdot C_6H_4 \cdot N_2 \cdot N(C_2H_5) \cdot C_6H_4 \cdot NO_2$. | Found. | | |
|---------|---|--------|-------|------|
| | | I. | II. | III. |
| C | 53.33 | 53.11 | 53.28 | — |
| H | 4.12 | 4.21 | 4.19 | — |
| N | 22.22 | — | — | 21.9 |

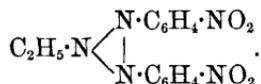
The ethyl-derivative is no longer soluble in alkalis, thus confirming the view that the salt-forming power of the original substance is due to the hydrogen of the $-N_2 \cdot NH-$ group. The compound is quite as unstable towards acids as the original substance, being decomposed by glacial acetic acid, dilute sulphuric acid, &c., but, as before, no nitrophenol is formed. The decomposition with hydrochloric acid was effected by heating in a sealed tube in a water-bath for 2 to 3 hours. The products of this reaction proved to be paranitrochlorobenzene and ethylparanitraniline:—



The last-named compound, which was first described by Weller (*Ber.*, 1883, 31), was identified by its melting point (95—96°) and crystalline form, as well as by the analysis of its nitroso-derivative which has not been hitherto described.

Ethylparanitrophenylnitrosamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{NO}) \cdot \text{C}_2\text{H}_5$.—On adding the necessary quantity of sodium nitrite dissolved in water to the hydrochloric acid solution of ethylparanitraniline, a white flocculent precipitate of the nitrosamine at once separates. This was collected, washed with water, and crystallised from alcohol. It forms large straw-coloured needles melting at 119·5°. The corresponding ethylmetanitrophenylnitrosamine melts at 47° (Nölting and Stricker, *Ber.*, 1886, 546).

The decomposition of the ethyl-derivative by hydrochloric acid into ethylnitraniline and nitrochlorobenzene is conclusive evidence against the symmetrical formula—



We have not yet applied the present method of investigation to the simpler unsubstituted diazoamido-compounds, but we have no doubt that it will be found generally applicable. Alkyl-derivatives of such diazoamido-compounds have however been prepared by Gastiger (*Bull. Soc. Chim.*, **42**, 338) and by Nölting and Binder (*ibid.*, **42**, 336 and 341), by acting with diazobenzene and paradiazotoluene chloride on ethylaniline. The resulting compounds have the formulæ $\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{N}(\text{C}_2\text{H}_5) \cdot \text{C}_6\text{H}_5$, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{N}(\text{C}_2\text{H}_5) \cdot \text{C}_6\text{H}_5$, &c., and behave as true diazoamido-compounds when decomposed by acids, the products being phenol and ethylaniline, and paracresol and ethylaniline respectively.

As the results of this investigation showed that the substance obtained by the action of nitrous acid on paranitraniline is a true diazoamido-compound, an attempt was made to convert it into its isomeric amidoazo-compound by dissolving it in fused paranitraniline containing paranitraniline hydrochloride. Under these circumstances, however, complete decomposition takes place with the evolution of nitrogen and the formation of an uncrystallisable resinous substance.