

LXXI.—*The Constitution of Diazobenzeneanilide and its Relation to Amidoazobenzene. II.*

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IN a previous paper (Trans., 1885, 917) we have attempted to show that the isomeric change of diazobenzeneanilide (diazoamidobenzene) into amidoazobenzene, supposed to be brought about through the intervention of aniline hydrochloride, really consists in a splitting up of the molecule by the acid present into diazobenzene and aniline, and that these bodies again combine under the altered conditions with formation of amidoazobenzene. It appeared, however, necessary that the anilide should always be first formed, for under no conditions were we able to obtain a direct combination of diazobenzene and aniline to amidoazobenzene. This is most strikingly shown by the fact that the anilide can be produced at a temperature above 30° C. in the presence of a large excess of aniline hydrochloride or of aniline hydrochloride and aniline, although after standing for a short time it begins to change into the isomeride. Whilst on the other hand, pure diazobenzeneanilide free from aniline, if suspended in dilute hydrochloric acid (1 molecular proportion) is converted in the course of 24 hours at the ordinary temperature into amidoazobenzene hydrochloride, the liquor containing during the whole time some uncombined diazobenzenechloride.

The results obtained on continuing our experiments quite bear out our former conclusions, and we are now extending our investigation to

other diazoamides. The present paper chiefly deals with the constitution of diazobenzeneanilide, concerning which we believe we are able to advance some important evidence.

At the end of our former communication we suggested incidentally that the apparent analogy of diazobenzeneanilide to azoxybenzene was in favour of the symmetrical formula $C_6H_5 \cdot N - N \cdot C_6H_5$. In doing so



we unintentionally somewhat misstated the views of Professor V. Meyer on this point, and now take the opportunity of correcting the error.

V. Meyer (*Ber.*, **14**, 2447, note to a paper by A. Sarauw), whilst admitting the symmetrical formula to be consistent with all the facts then known, yet does not regard it as altogether probable, and considers that the unsymmetrical formula $C_6H_5 \cdot N_2 \cdot NH \cdot C_6H_5$ will explain the facts equally well if a migratory power of the H-atom be assumed (brought about as he considers by addition and subtraction of HCl).

Contrary to our preconceived idea, our experiments have shown that the symmetrical formula is untenable, and that the analogy with azoxybenzene is only superficial. Although azobenzene is converted by sulphuric acid into oxyazobenzene, this isomeric change appears to be quite unlike the change of diazobenzeneanilide, for under no conditions of temperature or dilution could a trace of diazobenzeneanilide had the symmetrical structure it might be produced from azobenzenedibromide, $C_6H_5 \cdot N \cdot N \cdot C_6H_5$, by the action of ammonia: the



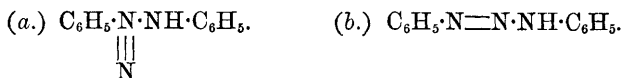
dibromide seems to exist, although it is very unstable, but on passing dry ammonia into its solution in chloroform, azobenzene was regenerated.

A positive proof in favour of an unsymmetrical structure, $C_6H_5 \cdot N_2 \cdot NH \cdot C_6H_5$, was obtained by displacing the hydrogen of the imidogen-group by alcoholic radicles (the reaction taking place with extreme ease), and subsequently splitting up the product $C_6H_5 \cdot N_2 \cdot NRC_6H_5$ by an excess of acid.

A monoalkylated aniline was formed together with diazobenzene, the former of which could not have been obtained from a body of symmetrical structure. A similar proof was attempted some time ago by A. Sarauw (*Ber.*, **14**, 2443) by displacing the H-atom by CO by means of carbonyl chloride, but although his conclusions quite agree with ours, the results he obtained were very unsatisfactory and inconclusive, as from want of knowledge of the properties of diazobenzeneanilide, no precaution was taken to remove the hydrogen chloride

formed during the reaction; this must have acted on the anilide to produce diazobenzene, aniline, amidoazobenzene, tarry products, &c.

The symmetrical formula having been excluded, the only two remaining formulæ are:—



It might fairly be expected that a substance of the constitution (a) would when reduced allow the N-atom outside the chain to be removed in the form of ammonia, and that hydrazobenzene would be produced. Only alkaline reducing agents can be used, since acid reducing agents cause a preliminary decomposition into aniline and diazobenzene, the latter being then reduced to phenylhydrazine. We have tried the effect of various alkaline reducing agents, but the anilide is scarcely attacked by any. In one experiment we dissolved it in absolute alcohol and added a large excess of metallic sodium, a trace of ammonia was evolved, but the greater part of the anilide apparently remained unaltered, and hydrazobenzene was not formed.

Hence there seems little doubt that diazobenzeneanilide has the constitution $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ usually attributed to it.

Diazobenzene-methylanilide (Methyldiazoamidobenzene),
 $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{N}(\text{CH}_3)\cdot\text{C}_6\text{H}_5.$

A solution of sodium ethoxide was prepared by dissolving 30 grams of clean sodium in 300 c.c. of absolute alcohol, and to this a hot solution of 200 grams of diazobenzeneanilide in 500 c.c. of absolute alcohol was added. The mixture was of a deep orange-brown colour; nothing separated from it when it was allowed to cool over lime in an exsiccator, but on exposure to the air it slowly absorbed water and diazobenzeneanilide separated in beautiful crystals.

When the solution was nearly cold, 170 grams of methyl iodide was added and the flask connected with an inverted condenser. A vigorous reaction quickly set in and the mixture boiled violently without the application of any external heat. After an hour's cohobation, half the alcohol was distilled off, and water was added to the residue; the heavy oily layer was separated, washed, and dried over calcium chloride. The product thus obtained was a dark-yellow, heavy oil which only became viscid in a freezing mixture and could not be caused to solidify by any treatment. It decomposed explosively when heated, and did not volatilise with steam, so that it could not be further purified. The yield of crude diazobenzene-methylanilide obtained was 200 grams.

Decomposition by Acid.—If the methylanilide is gently warmed with an excess of hydrochloric acid, diazobenzene can readily be detected in the solution, but is converted into phenol if the mixture is heated. 100 grams of the methylanilide was gradually added to 200 c.c. of hot strong hydrochloric acid: when the violent reaction was over, the solution was diluted with water, made strongly alkaline with caustic soda, and distilled. The crude methylaniline (yield 40 grams) was separated from the distillate, cohobated for some time with an alcoholic solution of carbon bisulphide and a little potash to remove a trace of aniline, separated and rectified. It boiled at 192—193° (uncorr.). Its platinochloride gave on analysis—

Pt.	Calculated for (C ₆ H ₅ ·NHMe, HCl) ₂ PtCl ₄ .	Found.		
		I.	II.	III.
.....	31·52	31·11	31·19	31·32

The acetyl-derivative, obtained by heating the base with an equal weight of acetic anhydride, crystallised from water in beautiful, long, white needles having the constant melting point 101° (uncorr.). The melting point of methylacetanilide is given as 102°. The alkaline residue left after removing the methylaniline by distillation, contains phenol, which after acidifying was distilled off and isolated by adding salt to the distillate. It was identified by conversion into tribromophenol, C₆H₂Br₃OH, which crystallised from dilute alcohol in very fine, white needles, which had the correct melting point 96° (uncorr.).

Hence diazobenzenemethylanilide is decomposed by acids according to the equation—



Diazobenzenemethylanilide (1 mol.) when left in contact with cold dilute hydrochloric acid (1 mol.), is slowly converted in the course of 24 hours into a magma of small, dark crystals. This must consist for the most part of the hydrochloride of methylamidoazobenzene, but we have not yet succeeded in isolating this substance in a pure state, as it is very difficult to separate from a small quantity of amidoazobenzene which it appears to contain.

Diazobenzenebenzylanilide (Benzyl diazoamidobenzene),
C₆H₅·N:N·N(C₇H₇)C₆H₅.

30 grams of sodium were dissolved in 300 c.c. of absolute alcohol, and a hot solution of 200 grams of diazobenzeneanilide in 500 c.c. of absolute alcohol was added. The mixture was cohobated for an hour or two with 140 grams of benzylchloride.

On adding water to the alcoholic solution the product was precipitated as an oil which was washed with hot water; on cooling it solidified.

After one crystallisation from alcohol it weighed 200 grams, which was diminished to 170 grams by a second crystallisation; it then melted at 80° (uncorr.). By further recrystallisation from a mixture of acetone and alcohol the melting point was raised to 81° , at which it remained constant. The pure benzyanilide forms beautiful yellow needles, very soluble in acetone, moderately soluble in alcohol, insoluble in water. A determination of the nitrogen by Dumas' method gave—

	Calculated for $C_{10}H_{14}N_3$.	Found.
N	14.63	14.87

The substance decomposes explosively on heating. When left in contact with 1 molecular proportion of dilute hydrochloric acid, slightly warm, it evidently undergoes change into the isomeric amidoazo-compound, but the benzylamidoazobenzene could not be isolated, as the product always separated as a tar.

Decomposition by Acids.—The diazobenzenebenzyanilide is resolved by an excess of acid into diazobenzene and benzyaniline. If the substance is gently warmed with strong hydrochloric acid diazobenzene can be readily detected in the solution, and phenol is obtained if the mixture is boiled.

50 grams of the benzyanilide was added by degrees to 200 c.c. of nearly boiling strong hydrochloric acid. Part of the benzyaniline hydrochloride separated at once and the rest crystallised out on cooling. The acid mother-liquor which contained the phenol was diluted with water and distilled, and the phenol was separated from the distillate by the addition of salt. It was identified as before by conversion into tribromophenol which melted correctly at 96° (uncorr.). The crude benzyaniline hydrochloride was treated with alkali and the product distilled. The base formed a pale yellowish, crystalline solid, which melted at 33° and boiled above 360° under ordinary pressure. The yield was about 20 grams.

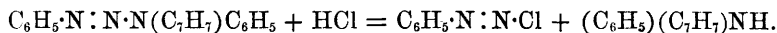
The hydrochloride forms white plates melting at 203° (uncorr.); it is decomposed by water. On combustion with soda-lime it gave—

	Calculated for $(C_6H_5)(C_7H_7)NH, HCl$.	Found.
N	6.38	6.0

The platinochloride formed fine yellow needles melting at 168° (uncorr.), tolerably soluble in water. On analysis it gave—

Calculated for		Found.
{ (C ₆ H ₅)(C ₇ H ₇)NH ₂ ·HCl } ₂ PtCl ₄ .		
Pt.....	25·23	25·14

Hence diazobenzenebenzylanilide is decomposed by acids according to the equation—



We propose to prepare various other substituted derivatives of diazobenzeneanilide and of other diazoamides, and hope by applying this reaction to diazobenzeneparatoluide and paradiazotolueneanilide, C₆H₅·N₃H·C₇H₇, to prove whether these bodies are identical as at present assumed, and to determine their constitution. We hope also to investigate in the same manner the two compounds $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{N}_3\text{H}\cdot\text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_4\cdot\text{N}_3\text{H}\cdot\text{C}_6\text{H}_5 \end{array}$, tetrazodiphenyldianilide and bidiazobenzenebenzidide, which according to our preliminary experiment do not appear to be identical.

In conclusion, we must express our thanks to the firm of Brooke, Simpson, and Spiller, Limited, in whose laboratories at the Atlas Works the above investigation was carried out.
