IX.—*Studies on the Structure of Azobenzene. The action of Bromine on Azobenzene; production of Tetrabromobenzidine.*

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AMONG coloured substances of simple composition, azobenzene is one of the very few which is represented by a formula of a non-quinonoid type, and moreover by a formula which cannot well be modified so as to bring this compound within the "colour rule" to which Dr. Armstrong has so persistently directed attention in recent years (Proc., March, 1888, 27; 1892, 101, 143, 189; 1893, 52, 206.)

Nietzki, in the introduction to his *Chemie der Organischen Farbstoffe*, calls attention to the peculiarities of azobenzene in the following words:

"Eine Klasse von Farbstoffen, deren Eigenschaften mit Bezug auf ihre Constitution auffallen müssen, sind die Azokörper, speciell aber

ihr einfachster Repräsentant, das Azobenzol. Während wir durch Substitution eines einzelnen Wasserstoffs in einem Benzolring, selbst wenn zwei solche Ringe durch ein zweiwerthiges Radikal verkettet werden, wenig oder gar nicht gefärbte Körper erhalten, ist das Azobenzol eine intensiv gefärbte Verbindung und ein starkes Chromogen. Es liesse dieses an sich fast die Vermuthung aufkommen, dass dem Azobenzol nicht in allen Reaktionen die einfache Constitutionsformel $C_6H_5 \cdot N:N \cdot C_6H_5$ zukommt, und einzelne Thatsachen könnten hier zu weiteren Speculationem verleiten. Die grosse Leichtigkeit mit welcher das Azobenzol, namentlich aber das daraus entstehende Hydrazobenzol, in ein Derivat des Diphenyls, das Benzidin, übergeht, scheint fast darauf hinzudeuten, dass Zwischen den beiden Benzolkernen eine Art von loser Bindung vorliegt. Es liesse sich diese nur mit der Anschauung vereinigen, dass, nach Analogie der Chinone, eine Lösung der doppelten Bindungen im Benzolring stattfindet. Es käme diese Auffassung in

nachstehender Formel zum Ausdruck, . Selbstredend

gehören derartige Formeln in das Gebiet der Hypothese, und können nur als Versuche, die sämmtlichen Farbstoffe unter einen gemeinsamen Gesichtspunkt zubringen, betrachtet werden."

The alternative ortho-formula is not open to

quite the same objection, and is perhaps more in accordance with the marked red colour of azobenzene; but both expressions equally fail to inspire confidence, as the mode of condensation they picture has not hitherto been recognised as occurring between two cycloids, and even the ortho-formula is not a satisfactory expression from Dr. Armstrong's point of view.

Under these circumstances, it appeared desirable to further study azobenzene and its derivatives, and, therefore, at Dr. Armstrong's request, I undertook to examine its behaviour with bromine, as the statements on record are in some respects remarkable; thus Werigo has described a *colourless* tetrabromazobenzene (*Annalen*, 165, 200). The existence of such a compound would undoubtedly, in a measure, serve to confirm the view that azobenzene has not the constitution which is commonly attributed to it. My experiments show, however, that Werigo was in error, and that the compound described by him as tetrabromazobenzene is simply tetrabromobenzidine.

Rodatz has described (*Annalen*, **215**, 217) tetra- and hexa-bromazobenzenesulphonic acids of the formulæ

which are of interest in connection with the question raised in this communication. The salts of the tetrabromo-acid appear to manifest properties such as derivatives of azobenzene might be expected to exhibit; the description given of the derivatives of the hexabromo-acid is somewhat less satisfactory. I have endeavoured to prepare this latter acid, but have not been so successful as Rodatz, and am inclined to think that the action is by no means so simple as is implied in his account. I therefore propose to further study the behaviour of the bromanilinesulphonic acids on oxidation with permanganate.

H. von Reiche has described (*Annalen*, **203**, 64) two azobenzene-tetrasulphonic acids formed by reducing 1:2:4- and 1:3:5-nitrobenzenemetadisulphonic acids. That prepared from the 1:3:5-acid yields colourless salts; when it is mixed with stannous chloride, no action is apparent, and the product resembles the parent substance; but v. Reiche nevertheless regards this "product" as a hydrazo-acid, as it is converted into a benzenemetadisulphonic acid by the action of nitrous acid, &c. There can be no doubt that v. Reiche never had an azobenzene derivative in his hands, and that his product was the amido-acid corresponding with the nitro-acid used. The same is, perhaps, true of the reduction product he prepared from the 1:2:4-nitro-acid, which he describes as β -azobenzenetetrasulphonic acid; some of the salts of this acid are spoken of as coloured, but there is no reference to colour in the case of the sulphonic chloride, and the sulphonamide is described as a *yellowish*, crystalline mass. The corresponding hydrazo-acid is said to yield diazobenzenedisulphonic acid when subjected to the action of nitrous acid. The α -diao-acid, according to v. Reiche, behaves in a peculiar manner with phosphorus pentachloride, but there appears to have been no difficulty in the case of the β -acid in obtaining a sulphonic chloride; as amido-acids do not yield sulphonic chlorides, this latter statement is remarkable, and it will be necessary to revise von Reiche's work.

Action of Bromine on Azobenzene. Azobenzene Perbromide.—Azobenzene, according to Werigo, readily combines with bromine, forming a highly unstable hexabromide; it is easy to prepare this substance by following his directions, but it loses bromine with such readiness

that it must be a matter of great difficulty to satisfactorily determine its composition; on exposure to air, the whole of the bromine is given off, leaving unaltered azobenzene. As it was conceivable that this perbromide might be analogous in composition to a diazoperbromide, it was added to a concentrated solution of ammonia; but no azoimide was formed, the product consisting chiefly of unchanged azobenzene mixed with a small proportion of paradibromazobenzene, m. p. 205°.

With the object of preparing higher derivatives, I have made a number of experiments on the action of bromine on azobenzene in different solvents at temperatures varying from 60° to 90° (compare Janovsky, *Monatsh.*, 1887, 8, 49).

The results show that bromine has very little action on azobenzene dissolved in either acetic acid or chloroform, most of the azobenzene being unattacked. In the case of acetic acid, small amounts of meta-bromazobenzene (m. p. 55—56°) and *o*-dibromazobenzene (m. p. 187°) were obtained, while, on using chloroform as a solvent, *p*-dibromazobenzene (m. p. 205°), *o*-bromazobenzene (m. p. 87°), and *o*-dibromazobenzene (m. p. 187°) were produced, all, however, in very small quantity.

On heating azobenzene with bromine in a sealed tube at 100°, a quantity of symmetrical tribromaniline was formed, the rest of the product being resin.

The resistance which azobenzene opposes to the action of bromine is very striking, and it would seem that the preparation of pure bromo-derivatives by the direct action of bromine is a matter of considerable difficulty.

Conversion of Azobenzene into Tetra-bromobenzidine.—The substance described by Werigo as tetrabromazobenzene was prepared by adding bromine to a hot concentrated alcoholic solution of azobenzene; its preparation in this manner is very easily effected: the azobenzene is dissolved in about twice its weight of hot alcohol, and from three to four times its weight of bromine is poured down the condenser tube when the mixture is nearly boiling; very vigorous action ensues, bromine and hydrogen bromide being given off.

The mixture eventually becomes solid. On filtering off the solid product and well washing it with a little alcohol, a white residue is obtained. On extracting this product with boiling alcohol, a considerable proportion is dissolved; this soluble portion consists of tribromaniline, m. p. 119°. As the substance obtained after extracting the tribromaniline agreed in its properties with the description given by Werigo, in the first instance, I subjected it to the action of stannous chloride: the product was purified without difficulty by recrystallising it from boiling xylene, from which it separated in short, flat needles melting sharply at 284—286° (uncorr.). This sub-

stance was proved by direct comparison to be identical with the tetrabromobenzidine prepared by Claus and Risler from benzidine by direct bromination (*Ber.*, **14**, 86). In the course of the experiments, I was led to notice the very close resemblance of the product described by Werigo as tetrabromazobenzene with this tetrabromobenzidine, and therefore reexamined the crude product; ultimately, by repeatedly recrystallising it from boiling xylene, a product indistinguishable from tetrabromobenzidine was obtained. When impure, the substance chars before it melts, and this, perhaps, accounts for the high melting point observed by Werigo. The difference in composition between tetrabromazobenzene and tetrabromobenzidine is so slight that it is impossible to decide by analysis which compound is dealt with; and the absence of basic properties makes it difficult to differentiate the tetrabromobenzidine.

The following analyses of the product from azobenzene were made.

Subs. 0.1885. AgBr 0.2836 Br 64.02

„ 0.2342. „ 0.3527 „ 64.08

„ 0.1927. „ 0.2892 „ 63.86

Subs. 0.1226. N₂ 6.2 c.c. (moist); *t*. 17°; bar. 758 mm. N 5.96.

Theory for C₁₂H₈Br₄N₂: Br 64.00. N 5.60.

Acetylation of Tetrabromobenzidine and Benzidine.—On merely boiling the tetrabromobenzidine with a large excess (six times its weight) of acetic oxide, a product was obtained which was easily purified by crystallisation from benzene, from which it separated in fine needles melting at about 306° (uncorr.); this substance was also easily soluble in carbon disulphide and chloroform, less easily in alcohol, and insoluble in ether and petroleum spirit.

The results of the analyses made of this substance prove it to be a tetracetate.

Subs. 0.1343. AgBr 0.1512 Br 47.91

„ 0.1434. „ 0.1617 „ 47.97

„ 0.2670. „ 0.3012 „ 48.00

Subs. 0.2073. N₂ 8 c.c. (moist); *t* 22°; bar. 760. N 4.47.

Theory for C₁₂H₄Br₄N₂Ac₄: Br 47.90; N 4.19.

The formation of this *tetracetate* is effected with remarkable readiness; as no corresponding derivative of benzidine has been described, I subjected benzidine to the action of an excess of acetic oxide; the diacetate, m. p. 317°, was almost immediately produced, but prolonged boiling was necessary to effect further acetylation.

Ultimately a product was obtained which still contained diacetate; on boiling this with benzene, a large proportion dissolved, but separated from the liquid on cooling; after recrystallising this product

from a mixture of alcohol and benzene, it was obtained in long, silky needles melting at 214—215°. Analysis shows it to be a tetracetate.

Subs. 0.1307. N_2 9 c.c. (moist); t . 11.5°; bar. 747; N 8.15.

„ 0.2804. „ 18.8 „ t . 11.5°; bar. 747.4; N 7.94.

Theory for $C_{12}H_8N_2Ac_4$: N 7.95.

Benzidine tetracetate is but slightly soluble in benzene and ether, but readily in alcohol and chloroform. It is known that tribrom-aniline is readily converted into a diacetate (Remmers, *Ber.*, **7**, 350), and Claus and Philipson have recently described (*J. pr. Chem.*, [2], **43**, 47—61) diacetates of 1'-bromo- and 1:3'-dibromo-betanaphthylamine; it would seem, therefore, that the two atoms of hydrogen in the NH_2 group of amines are the more readily displaced by acetyl the less basic the amine.

Constitution of Tetrabromobenzidine.—It was to be expected that benzidine would furnish a tetra-ortho-derivative, and this proves to be the case. It is not easy to diazotise tetrabromobenzidine; the method finally adopted was to dissolve it in 15 times its weight of oil of vitriol and to gradually add four-tenths of its weight of finely-powdered sodium nitrite; after several hours, the mixture was poured into 20 times its weight of cooled dehydrated alcohol, and after warming the solution until gas was no longer evolved, it was cooled and the product filtered off. The product could not be obtained in a satisfactory condition by mere recrystallisation, but it was eventually purified by partially oxidising it by boiling with a solution of chromic anhydride in acetic acid; after this treatment it crystallised from benzene, in which it was but moderately soluble, in white, microscopic needles melting at 189°; of this substance, 0.1723 gave 0.2753 AgBr = Br 67.99; the percentage of bromine in tetrabromodiphenyl being 68.08, there was no doubt it was this substance. A satisfactory amount of the diphenyl derivative may be obtained in the manner described if the oxidation be carefully conducted.

Various methods of oxidising the tetrabromodiphenyl were tried, but no satisfactory results were obtained; by boiling it with a solution of chromic anhydride in acetic acid, a relatively small proportion of an acid was obtained which, after recrystallisation from alcohol, melted at 212—213°; as this is the melting point of dimetadibromobenzoic acid, there is little doubt that this acid is formed by oxidising tetrabromodiphenyl from tetrabromobenzidine, and that this latter compound is the tetra-ortho-derivative.

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