18. *The Decomposition of Diazo-compounds in Neutral Solution. Part II.* p-*Nitrobenzenediazonium Sulphate.*

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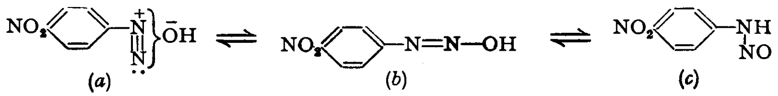
Reaction products identified are *pp'*-dinitrodiazoaminobenzene (*ca.* 40%) by hydrolysis of *p*-nitrobenzenenitrosoamine, 4-nitro-2-*p*-nitrobenzeneazophenol (*ca.* 10%) by solvolytic action of water on *p*-nitrobenzenediazonium hydroxide or salt and subsequent coupling of the *p*-nitrophenol formed with *p*-nitrobenzenediazohydroxide, and a small amount of *pp'*-dinitrodiphenylamine by interaction of the nitrosoamine with the diazonium hydroxide above; the remaining 50% was an inseparable tar.

During work on the decomposition of diazotised amines in solutions neutralised by calcium carbonate, Hodgson and Marsden (*J.*, 1943, 379) found that the neutralised diazonium salt from *p*-nitroaniline, whether prepared in hydrochloric or sulphuric acid solution, afforded a certain amount of 4-nitro-2-*p*-nitrobenzeneazophenol, but the other products were not investigated further at the time. The above azo-compound has now been synthesised by coupling one equivalent of neutralised *p*-nitrobenzenediazonium chloride with *p*-nitrophenol in the presence of sodium hydrogen carbonate, sodium acetate, or calcium carbonate. The product melted appreciably higher (*ca.* 200°) than that formerly isolated from the decomposition mixture (*ca.* 169°); it appeared also to exhibit chromoisomerism. This discrepancy of m. p. has now been traced to the presence of *pp'*-dinitrodiazoaminobenzene as impurity. When two equivalents of the *p*-nitrobenzenediazonium chloride were used, no bisazo-compound was formed, but the excess of the diazonium salt decomposed when the mixture was stirred for some hours in the way about to be described.

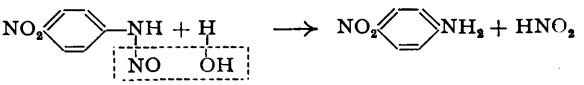
For simplicity, and to avoid the presence of calcium salts in solution, *p*-nitroaniline has been diazotised in aqueous sulphuric acid, and, after neutralisation with calcium carbonate, the solution was neutral to Congo-red and unreactive towards starch–potassium iodide; it was allowed to decompose at room temperature (*a*) without further addition, and (*b*) in the presence of calcium carbonate. In both cases the mixture remained inactive towards Congo-red (even after being kept for a fortnight), but (*a*) developed nitrous acid whereas (*b*) had an enhanced rate of decomposition due to the presence of calcium carbonate which neutralised any acid developed. In contrast, diazotised aniline under conditions (*a*) developed mineral acid rapidly a gave a blue colour with Congo-red paper. It would appear, therefore, that in the neutralisation process the anion of the *p*-nitrobenzenediazonium salt was removed, whereas it would seem to have been retained in the case of benzenediazonium sulphate. In the course of other work with Dr. E. R. Ward, the chemical behaviour of certain aryldiazonium sulphates, when prepared by the method of Hodgson and Mahadevan (*J.*, 1947, 325), and of solutions of the same arylamines, after diazotisation in sulphuric acid solution and neutralisation with calcium carbonate, was markedly different; Dr. Ward suggested that in the latter case the solution might contain the unstable diazohydroxide and not the diazonium sulphate, a viewpoint now supported by the apparent absence of mineral acid development on keeping.

After decomposition and removal of the solid product (D), the residual liquor contained a small amount of *p*-nitrophenol, while from (D), *pp'*-dinitrodiazoaminobenzene (*ca.* 40%) and 4-nitro-2-*p*-nitrobenzeneazophenol (*ca.* 10%) were isolated, together with a small amount of *pp'*-dinitrodiphenylamine; the rest of the reaction product (*ca.* 50%) was an inseparable tar. (D) dissolved completely in acetone, but all separations therefrom contained admixed tar. (D) did not couple with alkaline β-naphthol or with a saturated aqueous solution of β-naphthol, indicating absence of nitrosoamine.

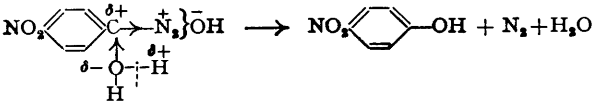
Excluding tar formation, the main reactions would appear to be explained by the varying behaviour of the members of the tautomeric system :



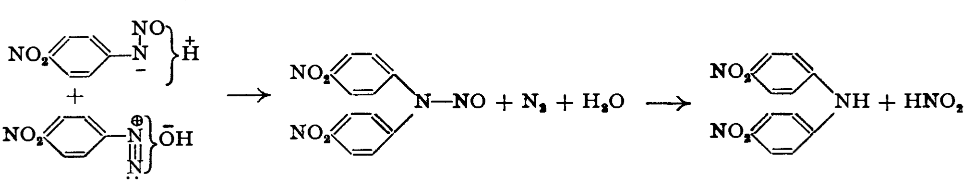
in which (*c*) is hydrolysed according to the scheme :



whereby the *p*-nitroaniline formed couples with (*b*) to give *pp'*-dinitrodiazoaminobenzene whereas (*a*) is attacked by anionoid water to give *p*-nitrophenol according to the scheme :



This then couples with (*b*) to give 4-nitro-2-*p*-nitrobenzeneazophenol. Bucherer and Wolff (*Ber.*, 1909, **42**, 881) ascribe the formation of *p*-nitroaniline to hydrolysis of (*a*), but this is erroneous in our opinion, since it is hydrolysis of diazonium salts which always leads to phenol formation. The formation of *pp'*-dinitrodiphenylamine would seem to arise from interaction of (*a*) and (*c*) according to the scheme :



Nitrous acid will thus be developed from two of the three reactions above.

Part of the tar may be formed by decomposition of the compound $NH(N{:}N\cdot C_6H_4\cdot NO_2)_2$, which is a possible product of the reaction (cf. Bucherer and Wolff, *loc. cit.*), while another possible product is the diazo-oxide, $NO_2\cdot C_6H_4\cdot O\cdot N{:}N\cdot C_6H_4\cdot NO_2$, which would undoubtedly contribute to the tar yield during the various treatments to which (D) is subjected, especially as some tar appears during two of the coupling reactions to be described between neutral diazotised *p*-nitroaniline and *p*-nitrophenol.

The results above are in accord with the experience of Atkinson and his collaborators (*J. Amer. Chem. Soc.*, 1940, **62**, 1704; 1941, **63**, 730; 1943, **65**, 476; and 1945, **67**, 1513), who found that the actual reduction of aryldiazonium salts in aqueous solution proceeded according to the general scheme:

$$R\cdot N_2X \longrightarrow R\cdot R + R\cdot N{:}N\cdot R + R\cdot O\cdot R + R\cdot NH\cdot R + RX + R\cdot OH + R\cdot NH_2 + N_2.$$

In neutral solution and by decompositions *per se*, the formation of *pp'*-dinitrodiphenyl did not appear to occur to a detectable extent, since no benzidine was isolated after reduction.

EXPERIMENTAL.

Preparation of 4-*Nitro*-2-p-*nitrobenzeneazophenol.*—(*a*) *p*-Nitroaniline (1·38 g.) was dissolved in a hot mixture of hydrochloric acid (5 c.c., *d* 1·18) and water (5 c.c.), and the solution stirred into iced water (40 c.c.); a finely divided suspension was obtained which was diazotised completely on the addition in one batch of sodium nitrite (1 g.) in water (5 c.c.). This solution was neutralised with calcium carbonate, filtered, and then stirred into one of *p*-nitrophenol (2·0 g.) in water (50 c.c.) containing either (*a*) sodium hydrogen carbonate (2·0 g.) or (*b*) sodium acetate (5 g.), maintained at 0° by ice. This cooling precaution was taken to avoid rapid unimolecular decomposition of the diazo-compound. Coupling ensued at once, but stirring was continued for 15 minutes, and the precipitates (*a*) or (*b*) were ground with a little water to solidify any small amount of tar present (crude m. p. 164—175°), and washed with warm aqueous sodium hydrogen carbonate to remove any *p*-nitrophenol, followed by a washing with cold 2% aqueous sodium hydroxide, which was found to dissolve it very gradually, since the washings on acidification afforded the azo-compound in light yellow crystalline micro-plates, m. p. 193—201°. The product was then washed with dilute hydrochloric acid and hot water before extraction 3 times with 80% ethanol; the extracts deposited the azo-compound in brown-red micro-plates, m. p.s 181—190°, 199—206°, and 199—206°, the respective residues having m. p.s 166—181°, 166—180°, and 148—156°. The crystals, m. p. 199—206°, were recrystallised from 80% ethanol and obtained in brownish-red prisms, m. p. 205—206° (Found: N, 19·6. Calc. for $C_{12}H_8O_5N_4$: N, 19·4%), and the above yellow micro-plates of m. p. 193—201° recrystallised from 80% ethanol in yellow-orange prisms, m. p. 205—207° (Found: N, 19·6%). Both chromoisomeric forms afforded a deep crimson colour with acetone–aqueous sodium hydroxide which turned to a bright scarlet on dilution with water, and dissolved in boiling aqueous hydroxide to a scarlet solution.

(*b*) The neutralised solution of *p*-nitrobenzenediazonium chloride [prepared as above from *p*-nitroaniline (1·38 g.)] was stirred into a solution of *p*-nitrophenol (2·0 g.) containing calcium carbonate (5 g.) in suspension. Coupling ensued gradually with complete absence of tar, and the solid mixture, after treatment with dilute hydrochloric acid to remove the calcium carbonate, was worked up as above for the azo-compound.

Examination of the Decomposition Products from Neutralised p-*Nitrobenzenediazonium Sulphate.*—*p*-Nitroaniline (2·76 g.) was dissolved in a mixture of sulphuric acid (6 c.c., *d* 1·84) and water (20 c.c.), and diazotised at 0° (ice) with a solution of sodium nitrite (2 g.) in the minimum amount of water added in one batch. This solution was then stirred into an iced suspension of calcium carbonate (15 g.), and filtered when it was neutral to Congo-red paper. Two such solutions were prepared, and one left to decompose spontaneously at room temperature while the other was stirred with calcium carbonate (2 g.). At the end of 7 days the products were filtered off, washed with water (and the second one treated with dilute hydrochloric acid to remove calcium carbonate), and dried; the amounts were 1·8 g. and 2·4 g. respectively. Each mixture was worked up as follows.

(1) *p*-Nitrophenol was identified in the filtrate from the mixture.

(2) 4-Nitro-2-*p*-nitrobenzeneazophenol was obtained when the mixture was first heated with water to remove any *p*-nitrophenol which might be present, and then extracted with boiling sodium carbonate or hydrogen carbonate. The hot extract contained some *pp'*-dinitrodiazoaminobenzene which crystallised out on cooling, and was identified by its colour tests (magenta with acetone–sodium hydroxide) and by crystallisation from boiling ethanol, whereby it was obtained in yellow needles which had no definite m. p. but decomposed at 220—230° (Found: N, 24·6. Calc. for $C_{12}H_9O_4N_5$: N, 24·4%). The azo-compound was precipitated from the alkaline solution on acidification, and, after several crystallisations from 80% aqueous ethanol it was obtained in yellow-orange prisms, m. p. 202°, and mixed m. p. 203—205°, with the synthetic product above (Found: N, 19·6%).

(3) The remainder of the *pp'*-dinitrodiazoaminobenzene was extracted from the residue after treatment with alkaline carbonate by boiling aqueous sodium or potassium hydroxide, and identified as under (2). About 50% of a low-melting tar remained undissolved.

(4) *Presence of* pp'-*dinitrodiphenylamine.* The above tar was extracted with boiling glacial acetic acid. A few mg. of a substance, m. p. 206—210°, were deposited on cooling (*pp'*-dinitrodiphenylamine has m. p. 212°); this substance gave a blue-violet colour with acetone–sodium hydroxide similar to that afforded by an authentic specimen (cf. Hantzsch, Hein, and Hurdtmann, *Ber.*, 1919, **52**, 498) but much bluer than the magenta afforded by *pp'*-dinitrodiazoaminobenzene (Found: N, 16·6. Calc. for $C_{12}H_9O_4N_3$: N, 16·2%). Since *pp'*-dinitrodiphenylamine is sparingly soluble in boiling concentrated

hydrochloric acid to give a deep yellow fluorescent solution from which it separates on cooling, and is also soluble in boiling alcoholic potassium hydroxide from which it separates in crystalline form when the cold solution is cautiously diluted with water, whereas the similarly treated *pp'*-dinitrodiazoaminobenzene remains dissolved, the original reaction mixture was submitted to each of these extractions; only a few mg. of a solid resulted in each case, but these gave the blue-violet colour test above with acetone–sodium hydroxide, and when reduced they afforded a solution which gave a bright blue colour with chromic acid.

(5) *Absence of* pp'*-dinitrodiphenyl.* The original mixture on reduction, either by iron and stannous chloride with hydrochloric acid or by zinc in glacial acetic acid, afforded solutions which gave no precipitate of benzidine sulphate on addition of sulphuric acid or of sodium sulphate, but when oxidised with ferric chloride or chromic acid gave *p*-benzoquinone from the *p*-phenylenediamine present.

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