113. *The Decomposition Reactions of Sodium Aryldiazoates. Part I. Replacement of the Diazo- by the Nitro-group in Alkaline Solution with Sodium Nitrite.*

By HERBERT H. HODGSON and EDWARD R. WARD.

A general reaction is described in which a diazotised amine reacts in alkaline solution with sodium nitrite to give the corresponding nitro-compound, thereby involving replacement of the diazo- by the nitro-group. Examples given are: aniline, *p*-toluidine, *p*-chloroaniline, *o*-nitroaniline, sodium *p*-nitrophenylnitrosoamine, β-naphthylamine, and 4-nitro-1-naphthylamine.

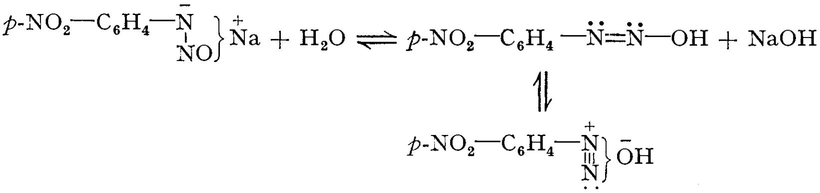
A NUMBER of reactions of aromatic diazo-compounds under aqueous neutral or alkaline conditions have been recently described, and their interpretation based on the occurrence of neutral radicals. The present authors believe, however, that the results can generally be satisfactorily explained on simple polar conceptions. In particular, reference is made to the paper " Some non-ionic Reactions of Diazobenzene Hydroxide " (Waters, *J.*, 1937, 201) in which it was claimed that when an alkaline solution of benzenediazonium sulphate was allowed to decompose slowly a trace of benzene was obtained. This production of benzene was explained as follows: " Hence the intermolecular decomposition of diazobenzenehydroxide possibly does include the hydrogenation of some of the free radicals by other of the aromatic molecules, though as an alternative it may be suggested that free phenyl radicals can abstract hydrogen from water molecules, $Ph^* + H_2O \longrightarrow Ph{:}H + {}^*OH$, a process which is the reverse of the usual breakdown of aqueous solutions of diazonium compounds to give phenols."

If the observation of the trace of benzene were correct, it indicates, on an alternative viewpoint, the presence of a reducing agent at some stage of the complex reaction. Now the only substance of this character appears to be sodium nitrite, which may have been formed by hydrolysis of the sodium phenylnitrosoamine, $\left.\begin{matrix}C_6H_5\cdot\bar{N}\\ \quad\ |\\ \quad NO\end{matrix}\right\}\overset{+}{Na}$, present in the alkaline solution, or been present from the start, since no reference is made in the experiment to removal of the slight excess of nitrous acid after diazotisation. The nitrosoamine ion might also have been concerned in the reduction. Further, if benzene had been produced in the manner suggested by the attack of the phenyl radical on water, a much larger amount than a trace might have been anticipated. To ascertain whether sodium nitrite had any effect *per se*, a large amount of it was dissolved in the alkaline diazoate solution, and, after being kept overnight, the mixture was steam distilled, and about 11% of nitrobenzene was obtained. The experiment was then repeated without further addition of sodium nitrite other than the amount required for complete diazotisation, and, after being kept overnight, the mixture was heated for 1 hour on the waterbath (*vide* Waters, *loc. cit.*) and then (*a*) steam distilled, (*b*) solvent-extracted in a second experiment. In both cases nitrobenzene was formed, and since it gives the same tests as those recorded by Waters for benzene (*loc. cit.*), it was necessary to remove it before testing for benzene (by acid reduction to aniline). Repeated experiments have failed to establish the presence of benzene. Furthermore, experiments in which insufficient nitrous acid was used, thereby entailing the formation of some diazoaminobenzene on making the diazotisation mixture alkaline, failed to give any benzene. In the circumstances we believe that the " benzene " of the Waters experiment was, in fact, nitrobenzene.

Phenol is stated by Waters not to be a major product of the decomposition, but in experiments carried out by Hodgson and Marsden (*J. Soc. Dyers and Col.*, 1945, **61**, 20) on the decomposition of diazotised aniline at the six approximate pH values of 10·5, 8·8, 6·7, 5·3, 5·2 and 4·2, phenol is not only the major product of the decomposition but at the time of formation it has coupled in varying amounts with any unchanged benzenediazohydroxide to give benzeneazo-, -bisazo-, and -trisazo-phenol. These experiments were carried out at pH values lower than that of Waters's experiment (by calculation on the assumption that his aniline sulphate had the formula $C_6H_5{\cdot}NH_2,H_2SO_4$), and therefore were nearer the conditions for obtaining the maximum amount of benzenediazohydroxide.

To ascertain whether the sodium nitrite reaction was a general one, the experiments, with suitable modifications for the amines concerned, were carried out with *p*-toluidine, *p*-chloroaniline, *o*-nitroaniline, β-naphthylamine, and 4-nitro-1-naphthylamine. In each case, nitro-compounds were obtained which indicated replacement of the diazo- by the nitro-group. To avoid auto-coupling in the experiments with β-naphthylamine and 4-nitro-1-naphthylamine, the diazo-solution was dropped gradually into a boiling solution of sodium nitrite containing sodium hydroxide through which a current of steam was passing, whereby the slowly volatile 2-nitro- and 1 : 4-dinitro-naphthalene were removed in sufficient amounts to show that some replacement had occurred.

For the case of *p*-nitroaniline, the sodium salt of *p*-nitrophenylnitrosoamine, $NO_2{\cdot}C_6H_4{\cdot}\left.\begin{matrix}N\\ NO\end{matrix}\right\}\overset{+}{Na}$, was isolated and steam distilled with sodium nitrite. At first *p*-dinitrobenzene came over, but after a time the reaction slackened and then ceased altogether; this inhibition was traced to the increased alkalinity of the flask liquor whereby the sodium nitrosoamine had been stabilised, *i.e.*, prevented from hydrolysing according to the scheme :



$$p\text{-}NO_2\text{—}C_6H_4\text{—}\left.\begin{matrix}\bar{N}\\ |\\ NO\end{matrix}\right\}\overset{+}{Na} + H_2O \rightleftharpoons p\text{-}NO_2\text{—}C_6H_4\text{—}\ddot{N}{=}\ddot{N}\text{—}OH + NaOH$$
$$\updownarrow$$
$$p\text{-}NO_2\text{—}C_6H_4\text{—}\left.\begin{matrix}\overset{+}{N}\\ |||\\ \underset{\cdot\cdot}{N}\end{matrix}\right\}\overset{-}{OH}$$

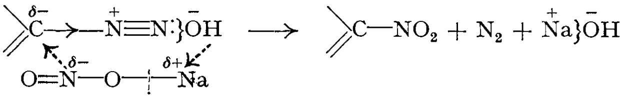
This increased alkalinity is due to the development of sodium hydroxide during the replacement :

$$p\text{-}NO_2\text{—}C_6H_4\text{—}\overset{+}{N}{\equiv}N{:}\}\overset{-}{O}H + NaNO_2 \longrightarrow p\text{-}NO_2\text{—}C_6H_4\text{—}NO_2 + N_2 + NaOH$$

The experiment with diazotised *o*-nitroaniline made slightly alkaline after diazotisation and steam distilled with sodium nitrite, gave a similar cessation of reaction due to the same cause, *viz.*, development of free alkali.

In all the experiments recorded, the respective reduction products, *viz.*, toluene, chlorobenzene, nitrobenzene, naphthalene, and α-nitronaphthalene were never detected despite close search for them, thereby supporting our belief that nitrobenzene and not benzene was the compound obtained in the original experiment by Waters (*loc. cit.*).

The reaction between sodium nitrite and a diazo-compound in dilute sodium hydroxide solution is thus similar to that of the replacement of a diazo- by a nitro-group in a diazonium cobaltinitrite (Hodgson and Marsden, *J.*, 1944, 22), *viz.*, attack at the significant carbon atom of the diazonium ion by the anionoid O—N=O group :

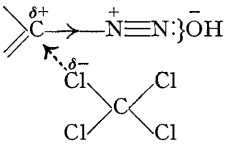


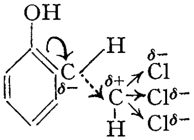
$$\underset{\underset{O=\overset{\delta-}{N}\text{—}O\text{—}\vdots\text{—}\overset{\delta+}{Na}}{\nwarrow\qquad\swarrow}}{>\overset{\delta-}{C}\rightarrow\text{—}\overset{+}{N}{\equiv}N{:}\}\overset{-}{O}H} \longrightarrow\ >C\text{—}NO_2 + N_2 + \overset{+}{Na}\}\overset{-}{O}H$$

and appears to be a general one. There is no need to keep the alkaline diazo-solution, and steam distillation can be carried out immediately the reactants are mixed.

The work of Bamberger and Storch (*Ber.*, 1893, **26**, 471, 476) on the oxidation of diazo-compounds in alkaline solution includes examples of the formation of nitrobenzene from diazotised aniline which can be ascribed to direct oxidation, since overwhelming amounts of oxidising agents—*e.g.*, for 10 g. of aniline, 71 g. of potassium ferricyanide or *ca.* 100 g. of potassium permanganate—were used and left in contact with the alkaline diazoate for periods of at least 4 days, after which only a trace of nitrobenzene was recorded. This is in striking contrast to the immediate formation of substantial amounts of nitrobenzene and of other nitro-compounds in the present experiments. Any idea of oxidation of the diazo-compounds to nitro-compounds by the sodium nitrite can therefore be eliminated as an alternative mechanism in the experiments now recorded.

The reaction of sodium benzenediazoate with carbon tetrachloride to give chlorobenzene as reported by Hey for Waters's paper (*loc. cit.*, p. 2015) can be simply interpreted in like manner, *viz.*, attack by anionoid chlorine at the carbon atom to which the diazonium group is attached (cf. the converse Reimer–Tiemann reaction, where kationoid carbon attacks the anionoid ortho–para positions in a phenol); there is no need to invoke any free radical hypothesis to explain these various reactions.





(Reimer–Tiemann reaction.)

In the aniline experiment with excess of sodium nitrite, *ca.* 6% of diphenyl was isolated; this would seem to indicate that acceptance of an electron by the diazonium ion was taking place to some extent without resultant combination of the radical so formed with the donor, and that, in the subsequent elimination of nitrogen from the diazo-radical to give the phenyl radical, two of these combine to give diphenyl.

EXPERIMENTAL.

Aniline Decompositions.—(a) *With excess sodium nitrite.* Aniline (0·1 g.-mol.) dissolved in a mixture of sulphuric acid (0·15 g.-mol.; *d* 1·84) and ice-water (200 g.) was diazotised by the gradual addition of sodium nitrite (0·1 g.-mol.) dissolved in the least amount of water until the positive test with starch–potassium iodide paper was obtained. After filtration, the filtrate was made just alkaline to Congo-red by careful addition at 0° of 10% aqueous sodium hydroxide, at which stage sodium nitrite (50 g.) was dissolved in the mixture. Decomposition was rapid even at 0°, and, after keeping overnight, the volatile reaction products were removed by steam distillation. The cooled steam distillate was extracted with ether, and the ether removed from the extract. On subsequent fractionation of the residue, pure nitrobenzene (1·35 g.; *ca.* 11% yield) and diphenyl (0·5 g.; *ca.* 6% yield) were obtained, leaving a small amount which boiled above 260°.

(b) *Without addition of excess sodium nitrite.* A trace of nitrobenzene was obtained both by steam distillation and also by solvent-extraction following the procedure of Waters (*loc. cit.*); it was identified by acid reduction to aniline and subsequent conversion into benzeneazo-β-naphthol. After removal of nitrobenzene as aniline from the solvent extract, no benzene could be detected by nitration or other methods.

Similar Decompositions afforded by other Amines.—(*a*) *p*-Toluidine (3·6 g.) was diazotised as for aniline, with corresponding quantities, and the alkaline solution treated with sodium nitrite (20 g.). Decomposition was rapid even in the cold, and, after 3 hours, the mixture was steam distilled, and a solid (0·4 g.) passed over. This was reduced with tin and hydrochloric acid; most of the solid dissolved, and on steam distillation of the mixture there passed over a small amount of a strong-smelling white solid which was probably *pp'*-ditolyl; on the flask liquor being made alkaline and then steam distilled, *p*-toluidine passed over and was identified by m. p. and conversion into *p*-tolueneazo-β-naphthol. The main product of the reaction was thus *p*-nitrotoluene in *ca.* 9% yield.

(*b*) *p*-Chloroaniline (4·3 g.) in like manner afforded *p*-chloronitrobenzene (0·5 g., *ca.* 9% yield).

(*c*) *o*-Nitroaniline (7 g.), when treated as above, gave an alkaline solution which only decomposed slowly in the cold, and on steam distillation after 1 hour afforded *o*-dinitrobenzene (0·3 g., *ca.* 4% yield). The reaction gradually ceased as the alkalinity developed.

(*d*) *p*-Nitroaniline. Sodium *p*-nitrophenylnitrosoamine (20 g.) was dissolved in water (600 c.c.) and sodium nitrite (20 g.) added; no decomposition occurred in the cold, but pure *p*-dinitrobenzene (1·8 g.; *ca.* 10% yield) was obtained on steam distillation. The reaction gradually ceased as alkalinity developed.

(*e*) β-Naphthylamine (5 g.) was mixed with sulphuric acid (5·8 g.; *d* 1·84) and ice–water (50 g.), and diazotised by rapid addition of sodium nitrite (3 g.) dissolved in the minimum of water; the filtered solution was then added dropwise to a boiling solution of sodium nitrite (25 g.) in water (100 c.c.) containing 10% aqueous sodium hydroxide (15 c.c.) through which a current of steam was passing. 10% Aqueous sodium hydroxide was added as required to maintain alkalinity. Pure β-nitronaphthalene (0·4 g.; *ca.* 7% yield) passed over, but no naphthalene was present in the distillate.

(*f*) 4-Nitro-1-naphthylamine (5 g.) was treated in similar manner, and afforded sufficient 1 : 4-dinitronaphthalene for its identification.

All the nitro-products referred to were identified by comparison with authentic specimens.

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