425. *Decomposition Reactions of the Aromatic Diazo-compounds. Part III. Some Non-ionic Reactions of Diazobenzene Hydroxide.*

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Experimental evidence is brought forward to support the view that diazobenzene hydroxide, Ph·N:N·OH, which is formed by the hydrolysis of sodium benzenediazotate, undergoes decomposition with elimination of nitrogen and the production of the free neutral phenyl, Ph·, and hydroxyl, ·OH, radical.

For example, diazobenzene hydroxide decomposes in carbon disulphide to yield diphenyl disulphide, Ph·S·SPh, and in *cyclo*hexane to yield benzene, together with more complex products. In the absence of any other organic substance an aqueous solution of sodium benzenediazotate decomposes with the formation of a trace of benzene.

According to the hypothesis of non-ionic fission of diazobenzene hydroxide there should be produced two electrophilic groups, Ph· and ·OH, and in consequence one should observe an oxidising action similar in character to that of iodine. Oxidising reactions of alkaline diazo-solutions have already been commented on by Angeli, and it is now possible to explain the occurrence of these reactions without recourse to his special structure for the normal diazotates. The Bart synthesis of phenylarsonic acids is also thought to include a non-ionic reaction.

Whilst studying the preparation of diphenyl derivatives by Gomberg's method, Grieve and Hey (J., 1934, 1797) came to the conclusion that the active reagent was the diazoaryl hydroxide, Ar·N:N·OH, which decomposed to give free neutral aryl radicals. These then reacted with an aromatic compound, C_6H_5R, to yield a *p*-substituted diphenyl derivative, *p*-Ar·C_6H_4R, irrespective of the polar character of R. A similar non-ionic fission was considered to take place in diazobenzene acetate (nitrosoacetanilide), since it was another phenylating agent of the same non-polar character.

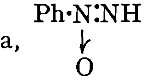
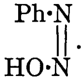
In Part I (this vol., p. 113) it was shown that diazobenzene acetate reacted with a number of organic liquids such as carbon tetrachloride, carbon disulphide, hexane, and *cyclo*hexane to yield products which could have been produced only if a highly active phenyl radical had been present during the reaction. It was therefore of interest to examine the reaction between diazobenzene hydroxide and the stable non-aromatic liquids carbon disulphide and *cyclo*hexane, the procedure of Hey being adopted.

Aniline in dilute sulphuric acid was diazotised, and the organic solvent added to the filtered diazonium salt solution. The cold mixture was made alkaline and allowed to decompose slowly. From the reaction with carbon disulphide, diphenyl disulphide was isolated, and from the reaction with *cyclo*hexane conclusive evidence was obtained of the production of benzene. Further Hey (private communication) has found that, if carbon tetrachloride is used, chlorobenzene is obtained. Thus a complete analogy can be traced between the reactions of diazobenzene hydroxide and of diazobenzene acetate. The general course of the reactions described in the experimental section of this paper leaves little doubt that the reactions occur in the organic liquid and not in the aqueous phase, and, in earlier discussions of the mechanism of the diphenyl synthesis, it has already been suggested that organic solvents extract diazobenzene hydroxide from alkaline solutions of the readily hydrolysed sodium benzenediazotate (Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1373).

Non-ionic reactions involving free neutral radicals such as Ph· and ·OH are inevitably complex, since the neutral radicals are extremely reactive entities which interact with practically the first molecule they encounter. Consequently a large amount of a complex tar is produced during the decomposition of alkaline diazo-solutions. This, as Hey and others have already shown, contains complex polyphenyls, which result from reactions between aryl radicals and some of the molecules of simpler reaction products formed at early stages of the decomposition of the diazo-compound.

Since the reaction between diazobenzene hydroxide and *cyclo*hexane substantiated the occurrence of the reaction $\mathrm{Ph\cdot + HR \longrightarrow PhH}$, it was of interest to determine whether benzene might also result from the complex intermolecular decomposition of diazobenzene hydroxide in absence of other molecules except water molecules. Consequently a benzenediazonium sulphate solution was made alkaline and allowed to decompose gradually. It gave a considerable quantity of a tar insoluble in alkali, which, by extraction with hexane, was shown to contain a trace of benzene. Hence the intermolecular decomposition of diazobenzene hydroxide 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, a process which is the reverse of the usual breakdown of aqueous solutions of diazonium compounds to give phenols.

These experiments, therefore, supporting those of Grieve and Hey, show that it is quite justifiable to interpret a number of reactions of aromatic diazo-compounds occurring in neutral or alkaline conditions as reactions involving neutral radicals. Some other reactions which may be of this type receive mention below.

In the preceding paper (Part II) it has been pointed out that substances which dissociate to give a pair of neutral radicals are oxidising agents. Hence one should find that diazobenzene hydroxide solutions are, like iodine solutions, oxidising agents. Angeli (*Ber.*, 1930, **63**, 1977) brought forward a good deal of experimental evidence to show that diazotates were strong oxidisers in order to justify his structural formula,  $\mathrm{Ph{\cdot}}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{N}}\mathrm{{:}NH}$ for *normal* diazobenzene hydroxide, to which Hantzsch had assigned the *syn*-diazo-structure  $\begin{matrix}\mathrm{Ph{\cdot}N}\\ \|\\ \mathrm{HO{\cdot}N}\end{matrix}$.

The experimental fact that diazo-compounds are oxidising agents is not generally appreciated, since when one makes a diazonium salt solution by the use of a nitrite the resulting mixture generally contains a little free nitrous acid. If, however, one adds pure benzenediazonium sulphate solution to a cold aqueous solution of leucomethylene-blue, nitrogen is evolved and the blue colour is at once restored. Sodium benzenediazotate will oxidise quinol (Orton and Everatt, J., 1908, **93**, 1010), sodium arsenite, ammonium sulphide, potassium ferrocyanide, and other substances under conditions in which nitrogen is evolved and either benzene or diphenyl is formed. Reagents which reduce diazonium salts to phenylhydrazine undoubtedly act in another manner. Hantzsch and Strasser (*Ber.*, 1931, **64**, 655) have shown that there are serious objections to the structural formula of Angeli, which represents a substance which should hydrolyse at once to a mixture of nitrobenzene and ammonia, but nevertheless they have not been able to explain the oxidising power of the diazotates by means of the older formulæ. The hypothesis of non-ionic fission of diazobenzene hydroxide will, however, suffice to explain this property of the diazotates.

Another reaction of diazobenzene hydroxide which illustrates its similarity in oxidising properties to iodine is the Bart synthesis of arylarsonic acids, in which an arsenite is

$$\mathrm{Ar{\cdot}N{:}N{\cdot}OH} + \mathrm{Na_2HAsO_3} \longrightarrow \mathrm{N_2} + \mathrm{Ar{\cdot}AsO(ONa)_2} + \mathrm{H_2O}$$

converted into a derivative of quinquevalent arsenic. This reaction occurs spontaneously in a cold neutral solution, without recourse to any copper derivative as catalyst, and it has been noticed (Schmidt, *Annalen*, 1920, **421**, 159; Bart, *ibid.*, 1922, **429**, 55) that diphenyl derivatives are regular by-products, as would be expected if free aryl radicals were present during the course of the reaction. The formation of covalent organo-metallic compounds (preceding paper) is also of obvious significance in connection with the mechanism of the Bart reaction.

The production of diaryl disulphides in interactions between diazo-solutions and neutral or alkaline solutions of sulphides or thiosulphates may again be due to the transient presence of neutral radicals. Further extensions of this hypothesis suggest themselves and perhaps a reinvestigation of the Sandmeyer reaction may reveal that cuprous salts operate as catalysts by favouring the non-ionic decomposition process.

EXPERIMENTAL.

The Reaction of Diazobenzene Hydroxide.—With carbon disulphide. 20 G. of aniline sulphate in 200 c.c. of N-sulphuric acid were diazotised with sodium nitrite (7 g.) and 100 c.c. of carbon disulphide were added to the filtered diazo-solution at 0°. The carbon disulphide layer remained colourless. 100 C.c. of 2N-sodium hydroxide were then added slowly with shaking. The mixture had an alkaline reaction, the carbon disulphide layer became dark brown, and the aqueous layer was practically colourless. When the mixture was allowed to warm, nitrogen was evolved from the carbon disulphide layer. The reaction was completed by heating for 1 hour on the water-bath and the carbon disulphide was then distilled off. The aqueous residue was decanted from an insoluble tarry red mass, which on treatment with acetic acid yielded a solid product. This, by repeated crystallisation from acetic acid and from methyl alcohol, gave colourless crystalline diphenyl disulphide (3·8 g.), m. p. and mixed m. p. 61·5°.

With cyclo*hexane.* 20 G. of aniline sulphate, diazotised in 200 c.c. of N-sulphuric acid as before, were mixed with 100 c.c. of benzene-free *cyclo*hexane and made alkaline at 0° with 100 c.c. of 2N-sodium hydroxide. Tar was formed in the dark *cyclo*hexane layer and nitrogen was at once evolved. The reaction was completed by 1 hour's heating on the water-bath. After cooling, the *cyclo*hexane layer was separated, washed successively with acid and alkali, and distilled from a water-bath. 1 C.c., tested by the iodic acid method of Masson and Race (this vol., p. 1718), gave a positive reaction for benzene. The remainder of the distillate was therefore nitrated, 30 c.c. each of fuming nitric and concentrated sulphuric acid being used, and, after pouring into water, the nitrated product was extracted with ether. The extract, after being washed with alkali, was concentrated and then gave *m*-dinitrobenzene (1·8 g.), m. p. (after recrystallisation from alcohol) and mixed m. p. 91°.

The reaction without added solvent. Another diazo-solution, prepared as before from 20 g. of aniline sulphate, was made alkaline at 0° with 100 c.c. of 2N-sodium hydroxide, under an efficient reflux condenser, and allowed to decompose slowly, the reaction finally being completed by 1 hour's heating on the water-bath. After slight cooling, 25 c.c. of hexane (B.D.H. " pure for spectroscopy ") were added, as a vehicle for the collection of any benzene, and the mixture was distilled from a water-bath. There remained a considerable quantity of a hardish tar, insoluble in alkali and smelling noticeably of phenyl *iso*cyanide. Phenol, therefore, is not a major product of the decomposition. The hexane distillate, after being washed with acid and with alkali, gave a positive test for benzene by the iodic acid method, and on nitration a few mg. of *m*-dinitrobenzene, m. p. 90—91° (after crystallisation from dilute methyl alcohol), were obtained in needles.

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