237. *The Decomposition of Aniline Nitrite.*

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The nitrites of some aliphatic and alicyclic amines are remarkably stable substances and can be recrystallised from hot water without undergoing decomposition (cf. among others, Wallach, *Annalen*, 1907, **353**, 318). On heating in the dry state, decomposition usually takes place, but under reduced pressure certain amine nitrites may sublime in part unchanged (Ray and Datta, J., 1911, **99**, 1475).

The nitrites of aromatic amines are almost unknown, either in solution or in the solid state. Wallach prepared *as.-m*-xylidine nitrite and crystallised it from water : it was an unstable substance and soon changed into a red oil, the nature of which was not determined (*Annalen*, 1907, **353**, 321). Aniline nitrite was prepared by Earl and Hall (*J. and Proc. Roy. Soc. N.S.W.*, 1932, **66**, 453), and its identity established by its quantitative conversion into aniline and sodium nitrite on treatment immediately after preparation with sodium hydroxide solution.

Whether the amine nitrites as such play any part in the characteristic nitrous acid–amine reactions is not known with certainty, although Schmid (*Ber.*, 1937, **70**, 421) assigns a rôle to undissociated aniline nitrite in the diazotisation process. With a view to throwing light on this question a study has been undertaken of the changes undergone by aniline nitrite in the dry state on keeping.

When first prepared by evaporation under reduced pressure of its ethereal solution, aniline nitrite is obtained in colourless needles, which very soon become yellow. At this stage the product is entirely soluble in water and from the aqueous solution a brownish-yellow precipitate, consisting principally of diazoaminobenzene, almost immediately commences to separate. When the dry nitrite is kept under reduced pressure in an atmosphere of nitrogen at —6° to —8° for one hour, it becomes orange to brown and only partly soluble in water. The insoluble part is principally diazoaminobenzene with small amounts of associated substances, probably bisdiazoaminobenzene and benzenediazoaminoazobenzene. The soluble part contains a relatively stable diazo-compound which couples readily with alkaline β-naphthol and reacts with aniline to give diazoaminobenzene. An approximately $N/30$-solution retains 88% of its content of diazo-compound after standing at room temperature (19°) for two hours. The compound is therefore much more stable than benzenediazonium hydroxide (Hantzsch, *Ber.*, 1898, **31**, 340), and the readiness with which it couples excludes the possibility of its being of the nitrosoamine type (Hantzsch and Pohl, *Ber.*, 1900, **35**, 2964) : the *anti*-diazohydroxide structure seems the most probable.

A separation of the diazo-compound from diazoaminobenzene can be effected by treatment of the reaction mixture with chloroform instead of with water. Most of the material is dissolved by the chloroform, but a small amount of a yellow liquid floats on the surface of the solution and is easily separated. This product is readily soluble in water or methanol but is insoluble in ether. A drop of it introduced into alkaline β-naphthol solution gives an immediate red precipitate, and when approximately equal volumes of aniline and the liquid are mixed a solid mass of diazoaminobenzene is obtained after a few seconds. The liquid decomposes at room temperature with the evolution of gas, but not violently. The customary methods of analysis are inapplicable, but estimations of the content of diazo-compound (see p. 1131) were uniformly in the neighbourhood of 41% of diazobenzene hydroxide. The liquid product, therefore, does not represent a pure diazohydroxide. The contaminant most likely to be present is water, although the sample used for analysis was repeatedly washed with dry ether and subsequently kept at 50 mm. pressure for over an hour. If water is present, it appears that the diazo-compound is extremely soluble in it and is difficult to dehydrate. On the other hand the liquid product may be a complex substance which readily yields 41% of diazo-compound when treated with appropriate reagents. A further investigation of this substance and of the corresponding products from other amines is being made.

It is clear that even in the solid state aniline nitrite changes into a diazo-compound. Part of the latter then undergoes a secondary reaction with part of the unchanged aniline nitrite with the liberation of nitrous acid and the formation of diazoaminobenzene, a reaction which proceeds with even greater ease in aqueous solution. In view of the fact that nitrous acid and possibly its decomposition products are present, it cannot be claimed that the evidence points convincingly to the formation of diazo-compound solely by intramolecular change of the nitrite. Again, traces of water are probably present, since the rapidity of manipulation necessary during the preparation of the nitrite militates against a thorough drying of the ethereal solution. Nevertheless the most marked changes do take place when the aniline nitrite is most likely to be dry, that is, after evaporation is complete and when kept under greatly reduced pressure in a slow stream of dry nitrogen.

EXPERIMENTAL.

Preparation of Aniline Nitrite.—The conditions described by Earl and Hall (*loc. cit.*) were as follows : A concentrated solution of sodium nitrite (1·5 g. in 3 ml. of water) was covered with pure ether (20 ml.) and cooled to about —15°. A solution of pure aniline hydrochloride (2 g. in 5 ml. of water) was prepared and cooled to —8°. Water free from carbon dioxide was used in the preparation of the solutions. The aniline hydrochloride solution was poured rapidly into the nitrite solution with vigorous stirring, care being taken that none of the former touched the sides of the flask. The decomposition that occurred during mixing was minimised by using a considerable excess of nitrite (up to 1·5 mols.) and making the nitrite solution faintly alkaline to litmus. (Very concentrated solutions of the reactants are advisable, since an excess of water favours the precipitation of diazoaminobenzene.) A white precipitate formed almost immediately and, on further stirring, dissolved in the ether. The ethereal solution was decanted on to anhydrous sodium sulphate cooled to −15°. The extraction with ether was repeated. After drying for a few minutes, the ethereal solution was decanted into a small filter-flask fitted with a capillary tube (to admit a fine stream of air, previously cooled and dried), and the ether removed under reduced pressure. After 20—60 minutes, a mass of white needles, soluble in water, ether or alcohol, remained.

One modification since found to be advantageous is to evaporate the ethereal solution under reduced pressure in an atmosphere of dry cooled nitrogen instead of air: the colouring of the product appears to be retarded and the possibility of oxidation diminished.

Change of Aniline Nitrite on Keeping.—After the evaporation of the ethereal solution was complete the dry material was kept at −6° to −8°/60 mm., a slow current of dry nitrogen being continuously admitted. After 1 hour, 50 ml. of water cooled to 0° were added, and the undissolved material filtered off and washed repeatedly with cold water. The filtrate and washings were united (total vol., 76·5 ml.) and 20 ml. were run immediately into an alkaline β-naphthol solution (1 g. of β-naphthol, 15 ml. of water, 3 ml. of 33% sodium hydroxide solution), and 20 ml. were kept at room temperature (19°) for 2 hours before being added to a similar β-naphthol solution. The weights of benzeneazo-β-naphthol (m. p. 127—128°; pure benzeneazo-β-naphthol, 132°) collected on Gooch crucibles and dried to constant weight were 0·1518 and 0·1339 g. respectively. No precipitate had separated from the part of the solution which had been kept before addition to β-naphthol; therefore no aniline nitrite was present.

The water-insoluble part of the reaction product was dissolved in a small quantity of boiling alkaline alcohol. Water was added until slight precipitation commenced, and the solution then cooled in a freezing mixture. The crystalline diazoaminobenzene was filtered off, washed with a little aqueous alcohol, and dried in air. Yield, 0·75 g.; m. p. 94—95°.

The yields of benzeneazo-β-naphthol and diazoaminobenzene correspond to 0·30 and 0·98 g. of aniline hydrochloride respectively, and together account for approximately 65% of the aniline hydrochloride (2 g.) used in the preparation.

Separation of the Diazo-compound.—In another experiment, instead of the reaction product being treated with water, 10 ml. of dry chloroform cooled to −6° were added. The pale yellow liquid diazo-compound floating on the surface was separated and washed with more chloroform at −6°. It gave the characteristic reactions of a diazo-compound with alkaline β-naphthol and with aniline. Before analysis the product was washed three times with cooled ether (dried over sodium) and was then kept at 50 mm. pressure for over an hour.

A corked flask containing 20 ml. of an alkaline β-naphthol solution (3 g. of β-naphthol dissolved in 20 ml. of 10% sodium hydroxide solution and made up to 200 ml. with water) was weighed and then cooled in a freezing mixture for some minutes; about 0·1 ml. of the diazo-compound was introduced with thorough shaking, and the flask again closed, allowed to attain room temperature, and weighed. The benzeneazo-β-naphthol was collected on a weighed Gooch crucible, washed thoroughly, and dried to constant weight. The amount of diazohydroxide was then calculated and in duplicate determinations found to be 41·8 and 41·4%. Another determination on the same product with a more dilute β-naphthol solution gave 42·0%. The m. p. of the dry benzeneazo-β-naphthol was in no case below 129°, and the pure recrystallised substance melted at 132°.

Addendum. Further examination showed that the aqueous solution of the diazo-compound was neutral and liberated iodine extremely easily from a solution of potassium iodide acidified with dilute acetic acid but not from a neutral solution. It gave the brown-ring test characteristic of nitrates and nitrites, but formed only a very slight precipitate with an acetic acid solution of "nitron" after long standing. This behaviour points to the probable presence of benzenediazonium nitrite as the principal constituent of the "diazo-compound."

The author's thanks are due to Professor Sir William Pope for the provision of facilities for carrying out this work.

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[*Received, May 24th,* 1937.]