40. *Replacement of the Diazo-group by Hydrogen.*

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A general deamination procedure is described, which is based on the decomposition by metals, such as zinc and copper, of suspensions of a stabilised salt of the diazotised amine in alcohol and other non-aqueous solvents. Naphthalenedisulphonic acids and 2-hydroxynaphthalene-1-sulphonic acid are effective stabilisers for this purpose.

Replacement of the diazo-group by hydrogen by means of ethyl alcohol (Griess, *Phil. Trans.*, 1864, **164**, 683) leads to a diversity of products and consequent decrease in the yield of the substance required. Other methods proposed from time to time with the object of avoiding the preparation of the diazo-compounds in the dry state and the uncertainty of the reducing action of alcohol give moderate yields and the optimum conditions have to be found by experiment.

A method is now described which surmounts the former difficulties and uncertainties and consists in decomposing a diazotised amine which has been stabilised by a naphthalenedisulphonic acid or an acid such as oxy-Tobias acid. The most effective agent for the decomposition is zinc dust, reacting with the dry stabilised salt suspended in alcohol. Precipitated copper powder can be used where zinc dust might react simultaneously with other groups, *e.g.*, the nitro-group. Metals such as aluminium and magnesium do not in general exceed zinc and copper in efficiency, and sodium formate gives a somewhat inferior yield.

Saunders (" The Aromatic Diazo-compounds and their Technical Applications," p. 146) states that, when finely divided metals are used in conjunction with alcohols, it is the latter which appear to be activated in some way, the metals themselves not reacting directly on the diazo-compound. It is now found that the reaction with the stabilised compounds proceeds in methyl and ethyl alcohol, acetone, ether, nitrobenzene, benzene, chloroform, and carbon tetrachloride; it is sluggish in the last three solvents, which must be used at their boiling points for efficient decomposition. The yields in all the cases investigated (see below) are high and with zinc or copper and ethyl alcohol approach 100%.

The decomposition appears to be a simple exchange of hydrogen from one of the sulphonic acid groups *via* the agency, catalytic or otherwise, of the metal, since no aldehyde could be detected when alcohol was used. The action of ethyl alcohol alone on the stabilised salts of diazotised α-naphthylamine was to produce partly naphthalene, acetaldehyde, and a tar in which the presence of α-ethoxynaphthalene was established.

The following amines have been deaminated *via* their stabilised salts with naphthalene-1 : 5-disulphonic acid and with oxy-Tobias acid: aniline; *o*-, *m*-, and *p*-toluidine; *o*-, *m*-, and *p*-anisidine; *o*-, *m*-, and *p*-nitroaniline; *m*-phenylene- and *m*-tolylene-diamine; *p*-aminophenol; benzidine; α- and β-naphthylamines; and a large number of nitronaphthylamines and nitroaminodinaphthyls, for which the work was originally undertaken. In most cases the stabilised diazo-salts required slight variations in technique for their preparation in optimum yield, but in every case their deamination has been accomplished with maximum efficiency. The method is thus considered to be of general application.

EXPERIMENTAL.

Preparation of Stabilised Diazonium Salts.—(a) *From naphthalene*-1 : 5-*disulphonic acid.* The amine (0·1 g.-mol.) is diazotised in hydrochloric or sulphuric acid by customary processes, the total volume being kept at the minimum, and the solution (filtered if necessary) is stirred into a paste of naphthalene-1 : 5-disulphonic acid (0·1 g.-mol.) and water (60 c.c.). The stabilised diazonium salt, which is usually precipitated within 30 minutes, is filtered off (the filtrate is treated with sodium chloride for augmentation of the yield) and dried at 30—40°. The yield usually exceeds 90%.

(b) *From oxy-Tobias acid* (2-*naphthol*-1-*sulphonic acid*). The solution of the diazotised amine (0·1 g.-mol.) is treated with sodium acetate for removal of mineral acid and stirred into a paste of oxy-Tobias acid (0·1 g.-mol.) and water (60 c.c.). Sodium chloride is added to complete the precipitation of the stabilised diazonium compound, which is filtered off and dried at 30—40°. The products are often coloured by a small quantity of dye, but even when somewhat tarry they can be used in the deamination process.

Decomposition of the Stabilised Diazonium Salts.—(1) *By zinc dust and ethyl alcohol.* The dry salt (20 g.), suspended in ethyl alcohol (80 c.c.), is treated gradually at room temperature with zinc dust until the initial vigorous evolution of nitrogen subsides (*ca.* 30 g. necessary). The deaminated products are isolated and weighed. The yields in all cases are almost theoretical.

(2) *By zinc dust and acetone.* The procedure is as that described in (1); the yields are *ca.* 5% lower.

(3) *By copper powder and ethyl alcohol.* The copper powder is precipitated from copper sulphate solution by zinc dust. It is more sluggish in its action than zinc dust and in some cases a temperature of 30—35° is necessary before the evolution of nitrogen commences.

The authors thank the Department of Scientific and Industrial Research for a grant which enabled one of them (E. M.) to take part in this research, and Imperial Chemical Industries Ltd. (Dyestuffs Group) for various gifts.

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