107. The Preparation and Diazotisation of p-Aminomonomethylaniline.

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Hantzsch's failure to diazotise *p*-aminomonomethylaniline was apparently due to the presence of *p*-phenylenediamine in his initial material, which originated from the fission of the methyl group during the reduction of *p*-nitrosomonomethylaniline in acetic acid solution. A new method of reduction with iron and ferrous ammonium sulphate (or ferrous sulphate) in neutral solution is now described, in which the rupture of the methyl group has been avoided, and this method has proved to be of general service. The *p*-aminomonomethylaniline when treated with nitrous acid is first diazotised and subsequently nitrosated at the methylamino-group.

Hantzsch (*Ber.*, 1902, **35**, 896) stated that *p*-aminomonomethylaniline cannot be diazotised (cf. also Ayling, Gorvin, and Hinkel, J., 1941, 614), and Saunders (" The Aromatic Diazo-Compounds and their Technical Applications," E. Arnold & Co., London, 1936, p. 63) accepts this report in a discussion on the influence of substituents on the stability of diazonium compounds, concluding that a monoalkylamino-group in the para-position to the diazo-group will decrease the stability of the diazotised amine to such an extent that it decomposes as a primary aliphatic amine does when treated with nitrous acid.

In D.R.-P. 154,336 (cf. A., 1904, 1063) the diazotisation of *p*-aminomonoalkylanilines in general, and of the methyl compound in particular, was reported, but it was accompanied by nitrosation at the *p*-alkylamino-group, since 2 mols. of nitrous acid were employed per mol. of the *p*-aminomonoalkylaniline taken; the *p*-diazoderivative of the nitrosoamine formed, coupled normally with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid in the presence of sodium hydroxide, carbonate, or acetate. This patent was apparently overlooked by the above authors.

It is not stated in the patent how the *p*-aminomonomethylaniline was prepared, but Hantzsch, who made it by reduction of *p*-nitrosomonomethylaniline with zinc and acetic acid, reported that his attempted diazotisation of it only resulted in a vigorous evolution of nitrogen. When Hantzsch's directions for the preparation of *p*-aminomonomethylaniline were followed, however, a copious evolution of methyl acetate was obtained, and similar reductions by metals and acids, of both *p*-nitroso- and *p*-nitro-monomethylaniline, always resulted in a partial expulsion of the methyl group with formation of *p*-phenylenediamine. The latter compound has recently been reported as a catalyst for the decomposition of diazonium salts. Golossenki (*Chem. Zentr.*, **1937**, **108**, II, 112) determines these by decomposing them in the cold with *p*-phenylenediamine, an operation requiring 5—10 mins. This observation has been confirmed by us, and we also attribute the loss in yield of dye, when diazo-compounds are coupled with *m*-phenylenediamine containing the *o*-isomeride as impurity, to a similar catalytic decomposition.

We find that fission of the methyl group may be avoided by reducing *p*-nitroso- or *p*-nitro-monomethylaniline in neutral suspension in boiling water with iron powder (preferably as pin dust), and with a small amount of ferrous ammonium sulphate (or ferrous sulphate) present; reduction takes place smoothly with passage of *p*-aminomonomethylaniline into solution, where, when it is treated with nitrous acid, none of the frothing and decomposition described by Hantzsch is experienced.

In the patent (*loc. cit.*) no indication is given as to whether diazotisation precedes nitrosation or *vice versa*, or whether both occur simultaneously, and it is now established that diazotisation precedes nitrosation, since when less than 1 equiv. of sodium nitrite is employed only diazotisation occurs. This fact was established by adding the diazo-mixture to excess of dilute sodium hydroxide, filtering off the precipitated excess of *p*-aminomonomethylaniline, and then coupling the diazo-hydroxide left in the filtrate with β-naphthol to form p-N-*methylaminobenzeneazo-β-naphthol*, which was shown to be identical with the compound prepared by hydrolysis of authentic *p*-*N*-acetomethylamidobenzeneazo-β-naphthol. Also, when the solution of *p*-aminomonomethylaniline in dilute sulphuric acid was treated with less than 1 equiv. of sodium nitrite, followed by potassium iodide, *p*-iodomonomethylaniline was formed, but owing to difficulties of crystallisation it was converted by treatment with nitrous acid into the readily crystallisable p-*iodo*-N-*nitrosomethylaniline*. Similarly, when deficiency diazotisation was carried out in hydrochloric or hydrobromic acid and followed by the corresponding Sandmeyer reaction, *p*-chloro- and *p*-bromo-monomethylanilines were formed, respectively, and, being liquids, were converted into the solid *N*-nitroso-compounds for identification. Generally, the *N*-nitrosated unlike the free *N*-methylamino-compounds crystallise well from the ordinary solvents.

Since *p*-aminomonomethylaniline can be diazotised independently of attendant nitrosation, the theoretical arguments developed by Saunders *et al.* (*loc. cit.*) based on *non*-diazotisation become invalid. It was to be anticipated that diazotisation would precede nitrosation, since both processes can be regarded from one standpoint as involving condensation of the hydroxyl group of the nitrous acid with hydrogen, and the electron-repelling methyl group would tend to bind the condensing hydrogen of the methylamino-group more firmly than the corresponding hydrogen in the unsubstituted amino-group.

The reduction method referred to above is to be preferred for general purposes to the ordinary Béchamp process with iron and dilute acid, especially as the very objectionable odours inseparable from the latter procedure are avoided.

EXPERIMENTAL.

Reduction of p-*Nitromonomethylaniline.*—A mixture of the nitro-compound (3 g.), pin dust (10 g.), and ferrous ammonium or ferrous sulphate (1 g.) was boiled with water (100 c.c.) under reflux for one hour, ammonia (1 c.c., *d* 0·88) added to precipitate iron, and the solution filtered. The almost colourless hot filtrate darkens on exposure to air, but deposits leaves of white *p*-aminomonomethylaniline in an atmosphere of carbon dioxide, m. p. 35·5° (Willstätter and Pfannenstiehl, *Ber.*, 1905, **38**, 2269, give m. p. 35·5°) (Found : N, 23·1. Calc. : N, 22·95%). The solution was coloured an intense red by a trace of ferric chloride but was then decolorised by hydrochloric acid, to be subsequently turned blue by addition of hydrogen sulphide water. The *picrate* was formed when the hot solution of the base (prepared as above) was filtered into a saturated solution of picric acid in water or alcohol; it crystallised from ethyl alcohol in long, slender, yellow parallelepipeds, m. p. 206° (Found : N, 20·1. $C_{13}H_{13}O_7N_5$ requires N, 19·9%). The period of one hour required for complete reduction in this example may have to be altered for other nitro-compounds.

Preparation of p-N-*Methylaminobenzeneazo-β-naphthol.*—*p*-Nitro-*N*-methylacetanilide (4 g.) was reduced as above, and the filtered solution of the *p*-amino-*N*-methylacetanilide acidified with hydrochloric acid (20 c.c., *d* 1·16), diazotised, the solution of the diazonium compound run into alkaline β-naphthol, and the precipitated *p*-*N*-acetomethylamidobenzeneazo-β-naphthol removed; it crystallised from 50% aqueous pyridine in red plates, m. p. 139° (Morgan and Grist, J., 1918, **113**, 691, give m. p. 139°) (Found : N, 13·1. Calc. : N, 13·1%), which gave a blue-red colour with concentrated sulphuric acid that changed to a reddish-scarlet on dilution with water. This acetyl compound was hydrolysed by 2 hours' boiling with a solution of hydrochloric acid (1 part, *d* 1·16) and ethyl alcohol (2 parts), then filtering it hot; the filtrate on cooling deposited the *hydrochloride* of p-N-*methylaminobenzeneazo-β-naphthol* in red micro-plates, m. p. 197—202° (Found : N, 13·6; HCl, 11·6. $C_{17}H_{15}ON_3$,HCl requires N, 13·4; HCl, 11·6%). This salt on boiling with 50% aqueous pyridine gave the *base*, which separated from the filtered solution on cooling in deep blue-black, spear-like crystals, m. p. 123° (Found : N, 15·3. $C_{17}H_{15}ON_3$ requires N, 15·2%), and gave a bluish-red colour with concentrated sulphuric acid which changed through scarlet and orange to yellow on dilution with water.

Preparation of p-N-*Nitrosomethylaminobenzeneazo-β-naphthol.*—A solution of *p*-aminomonomethylaniline (prepared as above) was acidified by either hydrochloric or sulphuric acid and then treated with just more than 2 equivs. of sodium nitrite; the excess nitrous acid was removed by urea, and the mixture then stirred into alkaline β-naphthol; p-N-*nitroso*-

methylaminobenzeneazo-β-naphthol was precipitated, removed, and dissolved in boiling pyridine, from which it separated on cooling in red, spearlike needles, m. p. 178° (Found: N, 18·5. $C_{17}H_{14}O_2N_4$ requires N, 18·3%), which gave a brilliant red-violet colour with concentrated sulphuric acid, changing through reddish-yellow to pink on dilution with water.

Experimental Proof that p-*Aminomonomethylaniline when treated with Nitrous Acid was diazotised before being nitrosated.*—The aqueous solution obtained by the reduction (as above) of *p*-nitromonomethylaniline (6 g.) was added to iced hydrochloric acid (20 c.c., *d* 1·16), and the mixture treated gradually at 0° with an aqueous solution of sodium nitrite (1·0 g.). The nitrite (now much less than 1 equiv.) reacted at once, and no positive test could be obtained with starch–potassium iodide paper. The solution was then stirred into excess of 10% aqueous sodium hydroxide and filtered immediately from the precipitated *p*-aminomonomethylaniline; the filtrate was stirred into alkaline β-naphthol, and *p*-*N*-methylaminobenzeneazo-β-naphthol was precipitated, removed, and crystallised from 50% aqueous pyridine, being obtained in deep blue-black, spearlike crystals, m. p. and mixed m. p. with the authentic compound above, 123° (Found: N, 15·3%). This precipitate was redissolved in mineral acid, treated with excess of sodium nitrite, and the solution run into alkaline β-naphthol; *p*-*N*-nitrosomethylaminobenzeneazo-β-naphthol separated and crystallised as above, m. p. and mixed m. p. with previous specimen, 178° (Found: N, 18·4%).

Three separate solutions (a), (b), and (c) were prepared as above by deficiency diazotisation and removal of unreacted *p*-aminomonomethylaniline; (a) and (b) were given Sandmeyer treatment to obtain the steam-volatile *p*-chloro- and *p*-bromo-monomethylanilines respectively; (c) was acidified with the necessary amount of sulphuric acid and the solution treated with aqueous potassium iodide, whereupon crude *p*-iodomonomethylaniline was precipitated, but as it proved difficult to crystallise owing to the separation of iodine, it was converted by nitrous acid into p-*iodo*-N-*nitrosomethylaniline*, which readily crystallised from 50% aqueous pyridine or light petroleum in long, colourless needles, m. p. 112° (Found: N, 10·8; I, 48·3. $C_7H_7ON_2I$ requires N, 10·7; I, 48·4%), and gave the Liebermann nitroso-reaction.

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