

62. A General Method for the Preparation of Solid Aryldiazonium Sulphates.

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The general diazotisation procedure of Hodgson and Walker (*J.*, 1933, 1620), or the inverted variation of it for amines which are sparingly soluble in glacial acetic acid (Hodgson and Turner, *J.*, 1943, 86), is applicable to all amines capable of diazotisation, and solid diazonium sulphates are precipitated from their solutions by addition of ether, or other suitable solvent, in solid crystalline condition. This process has been applied to α -naphthylamine, *m*-toluidine, and *m*-anisidine, hitherto reported as not diazotised but nitrosated by nitrosylsulphuric acid.

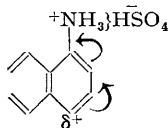
KNOEVENAGEL'S generalised method (*Ber.*, 1890, 23, 2995) for obtaining solid diazonium salts by suspending the dry amine salt in ethyl alcohol and treating it with an alkyl nitrite (originally employed by Schmitt, *Ber.*, 1868, 1, 67, for obtaining the diazonium chlorides of the aminophenols; cf. also Meyer and Stuber, *Annalen*, 1873, 165, 187; Cameron, *Amer. Chem. J.*, 1898, 20, 229) is valuable as a laboratory means for diazotising amines which are not easily dealt with by the direct method (cf. Kaufler, *Z. Farb.-Ind.*, 1903, 2, 469) but is stated (Saunders "The Aromatic Diazo-compounds and their Technical Applications", Edward Arnold & Co., London, 1936, p. 15) to be unlikely to compel an amine of low reactivity to yield its diazo-derivative; *e.g.*, only monodiazotisation results with 2:7-naphthylenediamine (Kaufler and Karrer, *Ber.*, 1907, 40, 3263). Hantzsch and Jochem (*Ber.*, 1901, 34, 3337) found it better to use glacial acetic acid in place of alcohol (cf. also Schoutissen, *Rec. Trav. chim.*, 1921, 40, 763, who carries out the operation more expeditiously by dissolving the amine in alcohol and preparing the salt immediately before adding the alkyl nitrite). The molecule of water produced in the reaction causes some difficulty, since ether is generally used to precipitate the diazonium salts from hydroxylic solvents, and the salts are prone to be sticky if a solvent should be employed in which the reaction water is not miscible; consequently, attempts have been made (S.C.I., D.R.-P. 575,832; F.P. 727,293; Sw.P. 152,611) to use non-hydroxylic solvents, *e.g.*, carbon tetrachloride, acetic ester, or benzene, and to bind the water produced in

the reaction by adding a desiccating agent such as calcined sodium sulphate. The diazonium sulphates are the most satisfactory for general use on account of their stability, some, such as *p*-nitrobenzenediazonium and dianisidinetetrazonium sulphates, having been in commerce for years with no other stabiliser than free mineral acid, and considerable additions have recently been made to this class since easily isolated stable diazonium salts are attractive because the cost of stabilisers is saved, the solubility is good, and there is minimum of complication. Further, many aryldiazonium sulphates formerly thought to be dangerously unstable have been prepared by diazotisation in *ca.* 85% sulphuric acid with nitrosylsulphuric acid and precipitated therefrom by organic liquids miscible with the acid such as the lower aliphatic alcohols at temperatures well below 0°. Among the amines claimed (I.G., E.P. 441,085; Anm., I. 47,579; F.P.P. 776,009, 775,963; Sw.P. 177,263; D.R.-P. 622,306) as being suitable for this process are the nitroanilines, and the mono-, di-, and poly-halogenoaminophenol ethers. In this connection, Hantzsch and Borghaus (*Ber.*, 1897, **30**, 93) have shown that the solid tetrazosulphate is much more stable than the chloride in the case of both *m*- and *p*-tetrazobenzene. In the various processes referred to above, diazotisation can be brought about not only with alkyl nitrites in such solvents as those mentioned, but also with liquid nitrogen trioxide (cf. Bamberger, *Ber.*, 1894, **27**, 1948; Morgan and Upton, *J.*, 1917, **111**, 187), nitrosyl chloride, or nitrosylsulphuric acid.

The importance of the solid aryldiazonium sulphates may thus be realised from the variety of methods devised to obtain them, and of these the most general is that involving the use of nitrosylsulphuric acid. This method, however, fails when diazo-oxide formation occurs, as in the cases of the 2-nitro-1- and 1-nitro-2-naphthylamines, 2:4-dinitro-1-naphthylamine, 2:4-dibromo-1-naphthylamine, and 1:4-dibromo-2-naphthylamine; or when nitrous acid attacks some other part of the molecule in preference to the amino-group to form nitroso-compounds, as in the cases of *m*-toluidine or *m*-anisidine (I.G., D.R.-P. 561,425) and α -naphthylamine (I.G., E.P. 355,970; D.R.-P. 519,729) (cf. also Blangey, *Helv. Chim. Acta*, 1938, **21**, 1579).

Since it was especially for those amines mentioned above as prone to form diazo-oxides that Hodgson and Walker's method (*loc. cit.*) was devised, it appeared of interest to examine its general utility for the preparation of solid diazonium sulphates. All amines known to admit of diazotisation may be diazotised smoothly by this sulphuric acid-glacial acetic acid procedure, or when the amine is not too soluble by an inverted variant of it (Hodgson and Turner, *loc. cit.*), and the solution of the diazonium sulphate, when treated with sufficient ether for the purpose, affords the solid compound in beautiful crystalline form which can be freed from acid by first washing with a mixture of ether and glacial acetic acid and finally with ether, or by the use of a solvent such as ethyl acetate, which is soluble in the glacial acetic-sulphuric acid mixture but in which the diazonium sulphate is insoluble. Should the precipitation of the salt be made too rapidly and an oily form result by reason of admixed solvent (which seldom occurs), solidification is brought about by washing the oily precipitate with a little ethanol or by keeping it ice-cold for a short time. The yields are of the order of 70—100%.

By this means 2-nitro-, 2:4-dinitro-, and 2:4-dibromo-1-naphthalene- and 1-nitro-2-naphthalene-diazonium sulphates have been obtained in solid crystalline form, and also the diazonium sulphates of α - and β -naphthylamines, *m*-toluidine, and *m*-anisidine. The last four amines were all diazotised smoothly and almost completely by Hodgson and Walker's procedure (*loc. cit.*), and, when the glacial acetic-sulphuric acid solutions were diluted with ice, the aqueous solutions of the diazonium salts were stable and available for use. It would appear, therefore, that the nitrosation instead of diazotisation which is stated to occur (*loc. cit.*) with nitrosylsulphuric acid in 85% sulphuric acid must be connected with the presence of water in this medium, the reaction of the nitrous acid at the *p*-carbon atom being then more rapid than at the positive diazonium ionic group. This reaction would appear to support Kenner's views (*Chem. and Ind.*, 1941, **60**, 443) that nitrous acid under these conditions is a nucleophilic (anionid) reagent, since the electronic effect is to render the *p*-carbon atom positively charged (see inset), and the salt formation to protect the amine from attack. The non-diazotisation



by pure nitrosylsulphuric acid of α -naphthylamine, *m*-toluidine, and *m*-anisidine is common to other aromatic amines, so that nitrosation can occur in those amines prone to it, whereas when glacial acetic acid is added, the nitrosylsulphuric acid affords free nitrous acid which can then effect the diazotisation.

Schoutissen's technique of diazotising amines by addition of phosphoric acid to their solutions in nitrosylsulphuric acid (*J. Amer. Chem. Soc.*, 1933, **55**, 4531) is of much less utility for the

isolation of the diazonium sulphates by ether addition, because of the very limited solubility of ether in the phosphoric-sulphuric acid mixture.

Since Hodgson and Walker's method is general for all amines hitherto found to be capable of diazotisation, it follows that the preparation of solid diazonium sulphates may now be accomplished in all cases by a single procedure, and since ether is soluble in the glacial acetic-sulphuric acid mixture which retains the water formed in the diazotisation, the resulting separations of solid diazonium sulphate are not sticky.

EXPERIMENTAL.

General Procedure.—A cold solution of the amine (1 g.) in glacial acetic acid (10 c.c.) is stirred into the required amount of sodium nitrite (*ca.* 1 g. in most cases) dissolved in sulphuric acid (5 c.c., *d* 1.84) at 0°, and the mixture kept until the diazotisation is complete (usually *ca.* 10 minutes, but 30 minutes should be ample). Although the mixture is normally kept at *ca.* 0° during the addition, yet working at room temperature has never shown any decreased yield. Ether (50 c.c., or as much as required) is stirred gradually into the mixture, and the solid diazonium sulphate separates and is filtered off, the mixed acid being removed with ether-glacial acetic acid and finally with ether.

Analysis.—To determine the yield, the precipitated, washed solid is dissolved immediately in water, and the solution (filtered if necessary) is stirred into the appropriate amount of an alkaline β -naphthol solution; the insoluble azo-dye which is precipitated is removed, washed free from β -naphthol with hot 2% aqueous sodium hydroxide, and from alkali by hot water, dried, and weighed.

Typical yields of solid diazonium sulphates (% in parentheses) were as follows: Aniline (72), benzidine (98), *p*-nitroaniline (75), *m*-phenylenediamine (72.3), α -naphthylamine (67), β -naphthylamine (68), *m*-toluidine (73.3), *m*-anisidine (73.8).

Remarks.—Precipitation of diazonium sulphate was almost instantaneous with tetrazotised benzidine, very rapid with *m*-phenylenediamine, and rapid in the cases of the other diazotised amines mentioned except aniline, from whose solution the diazonium sulphate separated more gradually. All the diazonium sulphates were fairly stable.

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