

42. *An Interpretation of the Sandmeyer Reaction. Part IX. The Behaviour of Diazotised 2:4:6-Trichloro- and 2:4:6-Tribromo-aniline towards the Sandmeyer Reagent.*

By HERBERT H. HODGSON and A. P. MAHADEVAN.

2:4:6-Trichloro- and 2:4:6-tribromo-anilines are smoothly diazotised by the nitrosyl-sulphuric-glacial acetic acid procedure (Hodgson and Walker, *J.*, 1933, 1620) and behave normally towards the Sandmeyer reagent in concentrated mineral acid solution; in dilute acid (3—4%), reduction takes place to 1:3:5-trichloro- and 1:3:5-tribromo-benzene, respectively. In boiling dilute sulphuric acid solutions containing copper sulphate, 2:4:6-trichloro- and 2:4:6-tribromo-benzenediazonium sulphates also give large yields of the respective trihalogenobenzene.

If the mineral acid character of solutions of diazotised 2:4:6-trichloro- and 2:4:6-tribromo-aniline is maintained, the halogens are stabilised and diazo-formation is prevented (cf. also Orton, *Proc. Roy. Soc.*, 1902, **71**, 153; *J.*, 1903, **84**, 796; 1905, **87**, 99; 1907, **91**, 1554; E.P. 15,438, 1911; D.R.-P. 243,648); the behaviour, however, of the diazonium group towards the Sandmeyer reagent is now found to be determined by the acid concentration as follows. When the 2:4:6-trichloro- or -tribromo-aniline is diazotised by the direct or the inverted Hodgson and Walker method (*J.*, 1933, 1620; cf. Hodgson and Turner, *J.*, 1943, 86) and then treated with a solution of cuprous chloride or bromide in the relevant concentrated acid, replacement of the diazonium group takes place normally and smoothly with formation of 1:2:3:5-tetrachloro- or -tetrabromo-benzene, respectively. If, however, the concentrated acid solution of the diazonium salt is diluted with water, no diazo-oxide formation occurs (cf. the ease of diazo-oxide formation in the case of 2:4-dinitro-1-naphthalenediazonium sulphate), but on subsequent treatment with acid cuprous chloride or bromide as above, the diazonium group is replaced by hydrogen and 1:3:5-trichloro- or -tribromo-benzene results. In these cases the cuprous halides react as reducing agents and not as catalysts, and cupric chloride or bromide respectively is found in the ultimate reaction mixture.

This reducing behaviour of cuprous salts recalls the conversion of 2-nitro-1-naphthalenediazonium sulphate by cuprous hydroxide in glacial acetic-sulphuric acid (Hodgson, Leigh, and G. Turner, *J.*, 1942, 744) into β -nitronaphthalene. With potassium iodide, however, both 2:4:6-trichloro- and -tribromo-benzenediazonium sulphates gave normal replacement of the diazo-group by iodine, whether in concentrated or dilute mineral acid or in neutral solution; Chattaway's observation (*J.*, 1909, **95**, 869), that potassium perbromide gives 2:4:6-tribromobenzenediazonium perbromide which on heating with glacial acetic acid gives 1:2:3:5-tetrabromobenzene, has been confirmed.

Replacement of the diazonium group by hydrogen instead of by hydroxyl has been reported by Wroblewski (*Ber.*, 1874, **7**, 1061), who obtained some *m*-chloro- and *m*-bromo-toluene by boiling the aqueous diazonium salts of *m*-chloro- and *m*-bromo-*p*-toluidine; whereas, however, Wroblewski ascribed his results to the presence of some of the alcohol used in the preparation of the diazonium salts, an explanation endorsed by Cain (*J.*, 1906, **89**, 19) who obtained the expected halogeno-cresols in the absence of alcohol, yet the formation of 1:3:5-trichloro- and -tribromo-benzene took place at room temperature and must be ascribed to the reducing action of the cuprous salts on the very strongly electrophilic carbon atom to which the diazonium group is attached.

The great difficulty of replacing the diazonium group by hydroxyl in these trihalogeno-diazonium salts has been emphasised by Cain (*loc. cit.*), Cain and Norman (*J.*, 1906, **89**, 24),

and others (cf. E.P. 7233, 1897), who obtained only small amounts of the 2 : 4 : 6-trichloro- and -tribromo-phenols by the drastic method of dropping the diazonium solutions into mixtures of concentrated sulphuric acid and sodium sulphate at 135—145°. We have found that boiling aqueous sulphuric acid solutions of these diazonium salts with copper sulphate gave *ca.* 75% yields of 1 : 3 : 5-trichloro- and -tribromo-benzene, respectively, and we ascribe the inhibition of entry of the hydroxyl group to steric hindrance since 2 : 4 : 6-trichloro- and -tribromo-phenols are very stable substances.

Although Hantzsch and Jochem (*Ber.*, 1901, **34**, 3337) found it necessary to use an alkyl nitrite in glacial acetic acid for the diazotisation of 2 : 4 : 6-tribromoaniline sulphate, yet the diazotisation of 2 : 4 : 6-trichloro- and -tribromo-aniline proceeded smoothly by Hodgson and Walker's method (*loc. cit.*), and the respective diazonium sulphates were precipitated as clean solids on addition of ether.

EXPERIMENTAL.

Decomposition of 2 : 4 : 6-Tribromobenzenediazonium Sulphate.—(a) *In concentrated acid.* 2 : 4 : 6-Tribromoaniline (5 g.), dissolved in sulphuric acid (9.5 c.c., *d* 1.84), is treated at 0° with a solution of sodium nitrite (2 g.) in concentrated sulphuric acid (10 c.c.), and the mixture stirred into glacial acetic acid (20 c.c.), the whole being ice-cooled externally. After 45 minutes' keeping, a sample gave no precipitate on dilution with water (absence of diazo-oxide and undiazotised amine), and the solution was then rapidly stirred into one of cuprous chloride (5 g.) in hydrochloric acid (25 c.c., *d* 1.18). After the vigorous evolution of nitrogen had subsided, the mixture was gradually heated to the boil, diluted with water, and filtered; the solid was washed with hot dilute hydrochloric acid and water, and then crystallised from aqueous ethyl alcohol, 1-chloro-2 : 4 : 6-tribromobenzene being obtained in colourless needles, *m. p.* 91° (Jackson and Carlton, *Amer. Chem. J.*, 1904, **31**, 374, give *m. p.* 90—91°). When a solution of 2 : 4 : 6-tribromobenzenediazonium sulphate, obtained as above, was stirred with ether (200 c.c.) the solid diazonium compound was precipitated in glistening white crystals; alternatively, if it was treated with a solution of cuprous bromide (5 g.) in hydrobromic acid (25 c.c., *d* 1.7), 1 : 2 : 3 : 5-tetrabromobenzene (5.0 g.) was obtained; this crystallised from aqueous alcohol in colourless needles, *m. p.* 98° (Mayer, *Annalen*, 1866, **137**, 227, gives *m. p.* 98.5°) (Found: Br, 81.0. Calc. for C₆H₂Br₄: Br, 81.2%). Similarly, when finely powdered potassium iodide was stirred into the solution of the diazonium salt, 2 : 4 : 6-tribromiodobenzene (6.0 g.) was obtained; it was isolated from the acid mixture by pouring it on ice, and washing the collected precipitate with saturated aqueous iodide and water, and it separated from hot ethyl alcohol in colourless needles, *m. p.* 105° (McCrae, *J.*, 1898, **73**, 692, gives *m. p.* 105.5°).

(b) *In dilute mineral acid.* 2 : 4 : 6-Tribromoaniline (5 g.) was diazotised as in (a) but the solution was poured on ice, no precipitation occurring, and then neutralised with calcium carbonate and filtered. The total volume of the solution was 300 c.c., and into it was rapidly stirred a solution of cuprous chloride (5 g.) (free from cupric salt) in hydrochloric acid (25 c.c., *d* 1.18); a vigorous evolution of nitrogen occurred, a precipitate was formed, and decomposition was completed at the boil. The precipitated 1 : 3 : 5-tribromobenzene was removed (3.2 g.) and crystallised from aqueous ethyl alcohol in colourless needles, *m. p.* 120° (*lit.* 120°) (Found: Br, 76.0. Calc. for C₆H₃Br₃: Br, 76.2%); alternatively, it was removed by steam-distillation. The same result was obtained when the diluted diazonium salt solution was treated with a solution of cuprous bromide (5 g.) in hydrobromic acid (25 c.c., *d* 1.7), but when it was treated with a solution of potassium iodide (5 g.) in water (25 c.c.), 2 : 4 : 6-tribromiodobenzene was precipitated (6.0 g.); after purification and crystallisation as above, it had *m. p.* 105°. In both these cases, cupric chloride and cupric bromide were found in their respective solutions.

(c) *In boiling neutral solution.* 2 : 4 : 6-Tribromoaniline (1 g.) was diazotised, the solution diluted, neutralised with calcium carbonate, filtered, and boiled; a red colour developed (probably of an azo-compound) with formation of tar and only traces of steam-volatile 1 : 3 : 5-tribromobenzene.

(d) *In neutral solution with copper sulphate and cuprous oxide.* 2 : 4 : 6-Tribromoaniline (2.5 g.) was diazotised, and the solution diluted and neutralised as in (c), after which it was stirred with an aqueous solution of crystallised copper sulphate (2 g.) and admixed red cuprous oxide (1 g.) in the cold; a slight effervescence occurred which increased when the solution was heated and was completed at the boil; on steam-distillation, 1 : 3 : 5-tribromobenzene (1.5 g.) passed over.

(e) *In dilute sulphuric acid with copper sulphate.* 2 : 4 : 6-Tribromoaniline (2.5 g.) was diazotised, diluted, and neutralised as above, and to the filtered solution (150 c.c.), sulphuric acid (5 c.c., *d* 1.84) and crystallised copper sulphate (2 g.) were added; when the mixture was gradually heated to the boil, a vigorous evolution of nitrogen occurred, and 1 : 3 : 5-tribromobenzene (1.8 g.) separated; it was purified by steam-distillation.

Decomposition of 2 : 4 : 6-Trichlorobenzenediazonium Sulphate.—Owing to the ease of preparation of 2 : 4 : 6-tribromoaniline compared with that of 2 : 4 : 6-trichloroaniline, the above experiments were made the standards, but exactly parallel experiments were carried out with 2 : 4 : 6-trichloroaniline (0.5 g.), analogous halogeno-compounds being formed as follows: (a) 1 : 2 : 3 : 5-Tetrachlorobenzene, *m. p.* 51° (Willgerodt and Wilcke, *Ber.*, 1910, **43**, 51, give *m. p.* 51°); 2 : 4 : 6-trichloriodobenzene, *m. p.* 54° (*lit.* 54°). (b) 1 : 3 : 5-Trichlorobenzene, *m. p.* 63—64° (Beilstein and Kurbatov, *Annalen*, 1878, **192**, 333, give *m. p.* 63.5°); 2 : 4 : 6-trichloriodobenzene, *m. p.* 54°. (c) Traces of 1 : 3 : 5-trichlorobenzene. (d) and (e) 1 : 3 : 5-Trichlorobenzene.

The authors thank the Government of Madras for a Research Scholarship to one of them (A. P. M.), and Imperial Chemical Industries Ltd. (Dyestuffs Division) for gifts of chemicals.