

CCCIX.—*The Replacement of Bromine in Bromophenols by the Nitro-group. Part I. 2:4:6-Tribromo-3-nitrophenol and -3-chlorophenol. Some Cases of Group Migration.*

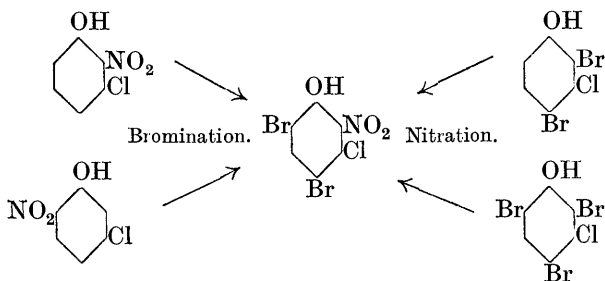
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NUMEROUS cases of the displacement of bromine by the action of nitric acid on bromophenols are on record, *e.g.*, the formation of 6-bromo-2:4-dinitrophenol from 4-bromophenol (Meldola and Streatfeild, *J.*, 1898, **73**, 683), of 2:6-dibromo-4-nitrophenol from 2:4:6-tribromophenol (Armstrong and Harrow, *J.*, 1876, **29**, 477), of 2:6-dichloro-4-nitro- and 6-chloro-2:4-dinitro-phenol from 2:6-dichloro-4-bromophenol (Ling, *J.*, 1892, **61**, 560), and of 2:6-dibromo-4-nitro-*m*-cresol from 2:4:6-tribromo-*m*-cresol (Claus and Hirsch, *J. pr. Chem.*, 1882, **39**, 59). Further, although 2:6-dibromo-4-nitroresorcinol is formed by the action of nitrous acid on 2:4:6-tribromoresorcinol (Dahmer, *Annalen*, 1904, **333**, 360), yet nitric acid produces 2-bromo-4:6-dinitroresorcinol (Jackson and Dunlap, *Amer. Chem J.*, 1896, **18**, 130). All these observations, together with those of Hodgson and Smith (this vol., p. 1550) on the nitration

of various bromo-3-hydroxybenzaldehydes, indicate that a bromine atom in the *p*-position to a hydroxyl group becomes labile in the presence of nitric acid and is frequently displaced; it re-enters the molecule, however, should an activated position be available.

It is now shown that 2 : 4 : 6-tribromo-3-nitrophenol behaves in accordance with the above generalisation, but 3-chloro-2 : 4 : 6-tribromophenol is an exception, the 2-bromine atom being replaced by a nitro-group.

Remarkable group migrations occur during the dibromination of 5-chloro-2-nitrophenol and the nitration of 3-chloro-2 : 4-dibromophenol, in both cases 3-chloro-4 : 6-dibromo-2-nitrophenol being formed (compare Hodgson and Kershaw, J., 1930, 1419, where the last-named product so prepared is regarded as 3-chloro-2 : 4-dibromo-6-nitrophenol). The following scheme depicts the results obtained :



The proof of the constitution of 3-chloro-4 : 6-dibromo-2-nitrophenol follows from its reduction and subsequent conversion into 2 : 3-dichloro-4 : 6-dibromophenol or 3-chloro-4 : 6-dibromo-2-iodophenol. These products, and their isomerides 3 : 6-dichloro-2 : 4-dibromophenol, 3-chloro-2 : 4-dibromo-6-iodophenol, and 3-chloro-2 : 6-dibromo-4-iodophenol, have been prepared synthetically for comparison. Further, the fact that the sodium salt of 3-chloro-4 : 6-dibromo-2-nitrophenol is red is strong evidence in favour of an *o*-nitrophenolic configuration.

The sodium salt of 3-chloro-2-nitrophenol is much more soluble in water than that of 5-chloro-2-nitrophenol, doubtless owing to the fact that the chlorine atom has a greater ionising power (general effect) in the ortho-position than in the para-position to the nitro-group in the generally accepted quinonoid forms.

The reactions described were effected with nitric acid of various concentrations but weaker than fuming nitric acid (*d* 1.5), which converts 3-chloro-2 : 4 : 6-tribromophenol into 3-chloro-2 : 6-dibromobenzoquinone (Kohn and Zandman, *Monatsh.*, 1926, 47, 357).

EXPERIMENTAL.

The Action of Nitric Acid on 2 : 4 : 6-Tribromo-3-nitrophenol.—The phenol (2 g.) was added gradually to nitric acid (10 c.c.; d 1.42) with stirring (3 hours) at 12° ; there was an odour of hypobromous acid, and the solution gradually deepened in colour from yellow to red with liberation of bromine. 2 : 6-Dibromo-3 : 4-dinitrophenol, precipitated from the mixture by dilution with water, crystallised from hot water in very pale yellow, stout needles, m. p. 142° (Found : Br, 46.6. $C_6H_2O_5N_2Br_2$ requires Br, 46.8%), identical (mixed m. p.) with the dibrominated product from 3 : 4-dinitrophenol (see below).

Nitration of m-Nitrophenol.—The following new procedure, which gives very satisfactory results, depends on the circumstance that a mixture of nitric acid (8.5 c.c.; d 1.42) and water (1.5 c.c.) has no action on *m*-nitrophenol (3 g.) below 25° ; a vigorous reaction then ensues, the phenol dissolves, and the temperature rises to 45° : if, however, a very small amount (0.1 g.) of sodium nitrite is added initially, reaction begins at 18° with similar exothermic effects. *m*-Nitrophenol (10 g.) was therefore stirred gradually into a mixture of nitric acid (30 c.c.; d 1.42) and water (15 c.c.) at 18° . On addition of sodium nitrite (0.1 g.), nitration ensued with rise of temperature to 26° , and after being kept for 2 hours, the mixture was diluted with water, the isomeric 2 : 5- and 3 : 4-dinitrophenols being then separated by the method of Holleman and Wilhelmy (*Rec. trav. chim.*, 1902, **21**, 434).

Dibromination of 2 : 5- and 3 : 4-dinitrophenols in 25% aqueous-alcoholic solution with excess of bromine gives respectively 2 : 4-dibromo-3 : 6-dinitrophenol, very pale yellow, fine needles, m. p. 137° (Found : Br, 46.7. $C_6H_2O_5N_2Br_2$ requires Br, 46.8%), from water or dilute alcohol, and 2 : 6-dibromo-3 : 4-dinitrophenol, very pale yellow, stout needles, m. p. 142° (depressed by above isomeride) (Found : Br, 46.7%), from the same solvents.

Action of Nitric Acid on 2 : 4 : 6-Tribromo-3-chlorophenol.—The phenol (1 g.) was stirred into a solution of nitric acid (6 c.c.; d 1.42) and water (4 c.c.) during $\frac{1}{2}$ hour, kept at room temperature for 11 days, and then diluted with water; the solid was filtered off and steam-distilled. [The same product is obtained at once when 2 : 4 : 6-tribromo-3-chlorophenol is stirred into a mixture of nitric acid (7 c.c.; d 1.42) and water (3 c.c.) at 18° .] The volatile 3-chloro-4 : 6-dibromo-2-nitrophenol crystallised from alcohol in pale yellow needles, m. p. 90° (Found : Cl + Br, 58.6. $C_6H_2O_3NClBr_2$ requires Cl + Br, 58.9%); it was identical (mixed m. p.) with the products obtained by the bromination as above of 3-chloro-2-nitrophenol and of 5-chloro-2-nitrophenol.

Reactions of 3-Chloro-4 : 6-dibromo-2-nitrophenol.—The phenol (2 g.) in 7% aqueous sodium hydroxide (60 c.c.) was reduced with sodium hyposulphite (10 g.), and 3-chloro-4 : 6-dibromo-2-aminophenol precipitated from the colourless solution by carbon dioxide. The white solid, m. p. 148°, turned brown on filtration, and was therefore dissolved immediately in cold concentrated hydrochloric acid (15 c.c.), diazotised at 0–5° with 10% aqueous sodium nitrite, and added to cuprous chloride (5 g.) in hot concentrated hydrochloric acid (20 c.c.); 2 : 3-dichloro-4 : 6-dibromophenol, isolated by steam-distillation, crystallised from alcohol in colourless feathery needles, m. p. 90° (Found : Cl + Br, 71·7. Calc. : Cl + Br, 71·9%), identical (mixed m. p.) with an authentic specimen obtained by the dibromination of 2 : 3-dichlorophenol (compare Hodgson and Kershaw, *loc. cit.*).

When the above amine was diazotised in dilute sulphuric acid solution, and the diazo-salt decomposed with aqueous potassium iodide, 3-chloro-4 : 6-dibromo-2-iodophenol was obtained; it was removed by steam-distillation and crystallised from alcohol, forming colourless needles, m. p. 105° (Found : Cl + Br + I, 78·0. $C_6H_2OClBr_2I$ requires Cl + Br + I, 78·2%).

Alternative Preparation of 2 : 3-Dichloro-4 : 6-dibromophenol.—3-Chloro-2-nitrophenol (5 g.), dissolved in 20% aqueous sodium hydroxide (50 c.c.), was treated with sodium hyposulphite (20 g.) during one hour, the alkalinity being maintained throughout. The 3-chloro-2-aminophenol was precipitated from the solution when colourless by means of carbon dioxide. The Sandmeyer procedure (as above) then converted one portion into 2 : 3-dichlorophenol and another into 3-chloro-2-iodophenol, which, treated in aqueous suspension with excess of bromine, afforded 2 : 3-dichloro-4 : 6-dibromophenol and 3-chloro-4 : 6-dibromo-2-iodophenol respectively, identical (mixed m. p.) with the previously described products.

The preparation of 3 : 6-dichloro- and 3-chloro-6-iodo-2 : 4-dibromophenols from 5-chloro-2-nitrophenol was effected as above, except that, owing to the insoluble character of its sodium salt, the reduction mixture required heating. Both phenols crystallised from alcohol in colourless needles, the former of m. p. 98° (Found : Cl + Br, 71·6. $C_6H_2OCl_2Br_2$ requires Cl + Br, 71·9%), and the latter of m. p. 93° (Found : Cl + Br + I, 77·9. $C_6H_2OClBr_2I$ requires Cl + Br + I, 78·2%).

Preparation of 3-Chloro-2 : 6-dibromo-4-iodophenol.—3-Chloro-2 : 6-dibromo-4-nitrophenol (0·75 g.) was dissolved in 20% aqueous sodium hydroxide (15 c.c.) and reduced as above with sodium hyposulphite to 3-chloro-2 : 6-dibromo-4-aminophenol, which crystallised from alcohol in colourless needles, m. p. 168° (Found : Cl + Br, 64·5.

$C_6H_4ONClBr_2$ requires Cl + Br, 64.8%), and was converted by the Sandmeyer procedure into 3-chloro-2 : 6-dibromo-4-iodophenol, colourless needles, m. p. 102° (Found : Cl + Br + I, 77.9. $C_6H_2OClBr_2I$ requires Cl + Br + I, 78.2%), from 50% aqueous alcohol. Alternatively, this product was obtained from 3-chloro-4-nitrophenol by reduction, replacement of the amino-group by iodine, and dibromination.

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