60. *The Replacement of Bromine in Bromophenols by the Nitro-group. Part III. 2 : 3 : 4 : 6-Tetrabromophenol and 2 : 4 : 6-Tribromo-3-iodophenol. A Review of the Halogen Effect in Position* 3.

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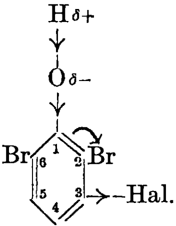
OF the four halogeno-analogues, only 3-iodo-2 : 4 : 6-tribromophenol reacts with nitric acid in accordance with the general rule of bromine displacement in the *p*-position to the hydroxyl group (compare Hodgson and Smith, J., 1931, 2268), the 3-fluoro- (Hodgson and Nixon, this vol., p. 273), 3-chloro- (Hodgson and Smith, *loc. cit.*), and 3-bromo-2 : 4 : 6-tribromophenols having respectively their 6-, 2-, and 6- and 2-bromine atoms replaced by the nitro-group.

Ionisation of the respective 3-halogeno-2 : 4 : 6-tribromophenols, due to the combined inductive (— *I*) effects (Ingold and Shaw, J., 1926, 2918), will be in the order F>Cl>Br>I, but the resultant *T* — *I* effect of the 3-halogeno-atom will be in the reversed order, and in the case of the 3-iodo-analogue, where *T* is large and *I* small, the resultant effect co-operates in the general scheme of activation, so that the 4-carbon, which is more frequently activated than the 2- and 6-carbons (Lapworth and Robinson, *Mem. Manchester Phil. Soc.*, 1928, **72**, 47) and is now reinforced by the 3-iodine effect, should still more readily admit of attack by the kationoid nitric acid than the 4-carbon in 2 : 4 : 6-tribromophenol.

In the cases of the 3-fluoro- and 3-chloro-analogues, the more powerful combined inductive effect will probably impose configuration (I) more frequently than its alternative, so that the 2-carbon atom will be the most strongly activated by the anionoid oxygen, and should be preferentially attacked. This occurs with the 3-chloro-analogue, but not with the 3-fluoro-compound, which has its 6-bromine replaced. The greater activation of the 6-carbon in the fluoro-analogue would appear to be due to the far greater deactivating effect of the 3-fluorine atom compared with the other halogens, with the result that, on the one hand, its *T* — *I* effect is exerted almost entirely at the 6-carbon, and, on the other, there is a powerful deactivating direct (— *D*) effect (Ingold and Vass, J., 1928, 417) through space upon the 2- and 4-carbon atoms.



(I.)

In the case of a 3-nitro-group being present (Hodgson and Smith, *loc. cit.*), which in some respects might be compared with fluorine, both the *T* and the *I* effect are negative with the consequence that, 2-, 4-, and 6-carbons being almost equally deactivated, the general para-displacement rule operates and 4-bromine is replaced, the reaction being assisted by the special ortho-effect during further nitration when one nitro-group is already present (Lapworth and Robinson, *loc. cit.*, p. 48).

In the remaining case of 3-bromo-2 : 4 : 6-tribromophenol where conditions are similar but more evenly balanced than in the 3-chloro-analogue, replacement occurs at both the 2- and the 6-position.

EXPERIMENTAL.

The Action of Nitric Acid on 2 : 3 : 4 : 6-*Tetrabromophenol.*—The phenol (5 g.) was stirred into a solution of nitric acid (18 c.c.; *d* 1·42) in water (16 c.c.) during one hour, and the mixture kept at room temperature for 20 hours; it was then diluted with water, and the precipitated solid filtered off and steam-distilled. The steam-volatile 2 : 3 : 4-tribromo-6-nitrophenol, which crystallised from 80% alcohol in yellow rectangular prisms, m. p. 123° (Jackson and Fiske, *Amer. Chem. J.*, 1903, **30**, 71, give m. p. 120—121°; Kohn and Sussmann, *Monatsh.*, 1926, **46**, 575, give m. p. 121°) (Found : N, 3·7. Calc. : N, 3·7%), was accompanied by a small amount of the more water-soluble 3 : 4 : 6-tribromo-2-nitrophenol, which crystallises from alcohol in yellow needles, m. p. 109° (Hodgson and Nixon, J., 1929, 2424) (Found : Br, 63·6. Calc. : Br, 63·8%): These products give identical m. p. and mixed m. p. with dibrominated 3-bromo-6-nitrophenol and 3-bromo-2-nitrophenol respectively.

Bromination of 3-*Bromo*-4-*nitrophenol*.—The phenol (2 g.), dissolved in alcohol (10 c.c.), was treated with bromine (2 c.c.), the mixture kept for 30 minutes and then diluted with water (20 c.c.), and the precipitated 2 : 3 : 6-*tribromo*-4-*nitrophenol* crystallised from hot water, forming very pale yellow needles, m. p. 151° (decomp.) (Found : Br, 63·5. $C_6H_2O_3NBr_3$ requires Br, 63·8%).

Tribromination of 3-*Iodophenol*.—5G., dissolved in alcohol (15 c.c.), were gradually treated with bromine (3·5 c.c.). The 2 : 4 : 6-*tribromo*-3-*iodophenol* was steam-distilled and then crystallised from 70% alcohol, forming colourless needles, m. p. 91°, which, being somewhat hygroscopic, were dried at 70° prior to analysis (Found : Br + I, 80·0. $C_6H_2OBr_3I$ requires Br + I, 80·3%).

The Action of Nitric Acid on 2 : 4 : 6-*Tribromo*-3-*iodophenol*.—The phenol (1 g.) was added gradually to a solution of nitric acid (7 c.c.; *d* 1·42) and water (3 c.c.) during ½ hour, the mixture kept at room temperature for 6 hours and then diluted with water, and the precipitated non-volatile 2 : 6-*dibromo*-3-*iodo*-4-*nitrophenol* freed from unchanged initial material by steam-distillation and crystallised from water, forming short colourless prisms, m. p. 145° (Found : Br + I, 67·4. $C_6H_2O_3NBr_2I$ requires Br + I, 67·8%), identical (mixed m. p.) with the product formed by the dibromination of 3-iodo-4-nitrophenol.

Bromination of 3-*Iodo*-6-*nitrophenol in Alcoholic Solution with Excess of Bromine*.—This afforded 2 : 4-*dibromo*-3-*iodo*-6-*nitrophenol*, which crystallised from alcohol in pale yellow needles, m. p. 173° (Found : Br + I, 67·5. $C_6H_2O_3NBr_2I$ requires Br + I, 67·8%).

The authors desire to thank the Department of Scientific and Industrial Research for a grant to one of them (E. W. S.) and the Imperial Chemical Industries Ltd. for their various gifts. They also wish to acknowledge the valuable assistance of Mr. R. J. H. Dyson in the preparative work.

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