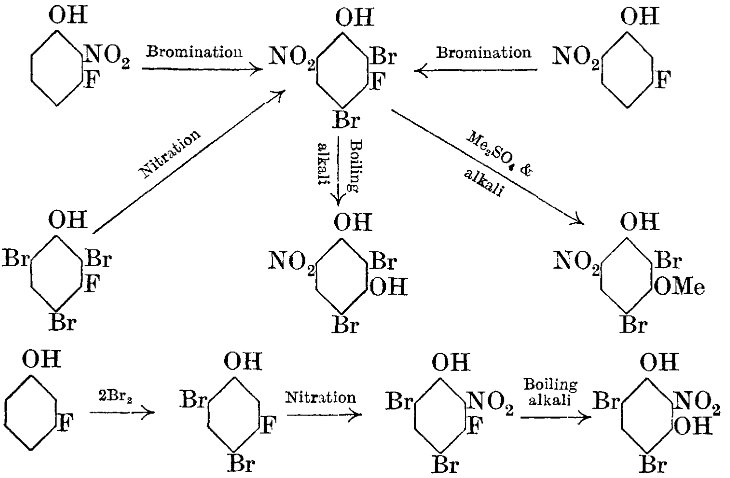
37. *The Replacement of Bromine in Bromophenols by the Nitro-group. Part II. 3-Fluoro-2 : 4 : 6-tribromophenol. Some Cases of Group Migration.*

By HERBERT HENRY HODGSON and JOSEPH NIXON.

HODGSON and SMITH have already observed (J., 1931, 2268) that previous work in this field appeared to indicate that a bromine atom in the 4-position to a hydroxyl group becomes labile in the presence of nitric acid, but that 3-chloro-2 : 4 : 6-tribromophenol was an exception in that the 2-bromine atom is replaced by a nitro-group.

It has now been found that 3-fluoro-2 : 4 : 6-tribromophenol is another exception, the 6-bromine atom being displaced by a nitro-group with production of 3-*fluoro*-2 : 4-*dibromo*-6-*nitrophenol.*

In keeping with the above behaviour, 3-fluoro-2-nitrophenol when treated with bromine yields 3-fluoro-2 : 4-dibromo-6-nitrophenol owing to migration of the nitro-group, whereas 3-fluoro-6-nitrophenol is normally dibrominated to the same product.



The constitution of 3-fluoro-2 : 4-dibromo-6-nitrophenol was established by the ready replacement of the fluorine (1) by hydroxyl by boiling alkali, 2 : 4-dibromo-6-nitroresorcinol being formed, and (2) by methoxyl by methyl sulphate and alkali, with formation of 2 : 4-*dibromo*-6-*nitroresorcinol* 3-*methyl ether*.

3-Fluorophenol is dibrominated normally in chloroform solution to give 3-*fluoro*-4 : 6-*dibromophenol* (compare Hodgson and Nixon, J., 1929, 2424, for the corresponding dibromination of 3-bromophenol), which is nitrated normally to give 3-*fluoro*-4 : 6-*dibromo*-2-*nitrophenol*; the constitution of this was established by its conversion by boiling alkali into 4 : 6-dibromo-2-nitroresorcinol.

The scheme on p. 273 depicts the results obtained.

As with their chloro-analogues, the sodium salt of 3-fluoro-2-nitrophenol is much more soluble in water than that of 5-fluoro-2-nitrophenol.

EXPERIMENTAL.

Dibromination of 3-*Fluoro*-6-*nitrophenol*.—The phenol (1·5 g.), dissolved in alcohol (10 c.c.), was treated with water (6 c.c.) and then slowly with bromine (1·2 c.c.) at room temperature. The yellow solid which separated was steam-distilled; the volatile 3-*fluoro*-2 : 4-*dibromo*-6-*nitrophenol* crystallised from 50% alcohol in long, pale yellow needles, m. p. 76° (Found : Br, 51·0. $C_6H_2O_3NFBr_2$ requires Br, 50·8%).

Dibromination of 3-*Fluoro*-2-*nitrophenol*.—The product obtained from this phenol by the above procedure was identical with 3-fluoro-2 : 4-dibromo-6-nitrophenol; m. p. and mixed m. p. 76° (Found : Br, 50·9%).

Confirmatory Identification Experiments.—(a) The above dibromo-products were separately refluxed for 2 hours with a solution of potassium hydroxide (10 g.) in water (100 c.c.). On acidification, a product was obtained in each case which, after crystallisation from 50% alcohol, melted at 151° and was identical (mixed m. p.) with the 2 : 4-dibromo-6-nitroresorcinol (m. p. 151°) obtained by dibromination of 6-nitroresorcinol (Dahmer, *Annalen*, 1904, **333**, 360, gives m. p. 149°) (Found : Br, 51·0 and 51·1. Calc. : Br, 51·1%). Qualitative tests failed to detect the presence of fluorine.

(b) *Attempted methylation of* 3-*fluoro*-2 : 4-*dibromo*-6-*nitrophenol*. This product, when treated in aqueous alkaline solution with methyl sulphate, gave 2 : 4-*dibromo*-6-*nitroresorcinol* 3-*methyl ether*, m. p. 128° (Found : Br, 48·8. $C_7H_5O_4N_2Br$ requires Br, 48·9%), identical with the product described below.

Dibromination of 6-*Nitroresorcinol* 3-*Methyl Ether*.—This substance (1 g.), dissolved in alcohol (40 c.c.), was shaken with bromine (1 c.c.), gradually added at room temperature. The yellow solid which separated was removed, steam-distilled, and crystallised from 50%

alcohol, forming yellow needles, m. p. and mixed m. p. with above product, 128° (Found: Br, 48·9%).

Action of Nitric Acid on 3-*Fluoro*-2 : 4 : 6-*tribromophenol.*—The phenol (1 g.) was added during 30 minutes to nitric acid (15 c.c.; *d* 1·42), the red solution evolving an odour of hypobromous acid. After 2 hours, the mixture was poured on ice and the precipitated solid was removed and steam-distilled; it then crystallised from 50% alcohol in yellow needles, m. p. 76° (Found: Br, 50·7%), identical with the 3-fluoro-2 : 4-dibromo-6-nitrophenol obtained by dibromination of 3-fluoro-2- and -6-nitrophenols respectively.

Dibromination of 3-*Fluorophenol.*—The substance (2·2 g.), dissolved in chloroform (20 c.c.), was treated with shaking during 10 minutes with a solution of bromine (2 c.c.) in chloroform (6 c.c.); hydrogen bromide was evolved and the solution became hot. The chloroform was distilled, and the residual oily 3-*fluoro*-4 : 6-*dibromophenol* frozen; it then crystallised from light petroleum in white needles, m. p. 45° (Found: Br, 59·0. $C_6H_3OFBr_2$ requires Br, 59·2%).

Nitration of 3-*Fluoro*-4 : 6-*dibromophenol.*—The phenol (1 g.) was gradually added to nitric acid (10 c.c.; *d* 1·42) at 0°, the mixture stirred for 15 minutes at 0° and poured on ice, and the precipitated 3-*fluoro*-4 : 6-*dibromo*-2-*nitrophenol* steam-distilled; it then crystallised from 50% alcohol in yellow needles, m. p. 74°, depressed by admixture with 3-fluoro-2 : 4-dibromo-6-nitrophenol (Found: Br, 50·7. $C_6H_2O_3NBr_2F$ requires Br, 50·8%).

Action of Aqueous Potassium Hydroxide on 3-*Fluoro*-4 : 6-*dibromo*-2-*nitrophenol.*—The substance (1 g.) was refluxed for 2 hours with a solution of potassium hydroxide (10 g.) in water (100 c.c.), and the mixture acidified and steam-distilled; 4 : 6-dibromo-2-nitroresorcinol passed over and crystallised from 50% alcohol in bright red needles, m. p. and mixed m. p. with an authentic specimen 117° (Weselsky and Benedikt, *Monatsh.*, 1880, **1**, 895, give m. p. 117°) (Found: Br, 50·9. Calc.: Br, 51·1%).

The authors desire to thank the Imperial Chemical Industries, Ltd., for the gift of various chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, November* 20*th*, 1931.]