CCXLII.—*Studies in Aromatic Substitution. Part III. The Action of Fuming Nitric Acid on the 3-Fluoro-2 : 4 : 6-trihalogeno-phenols and -anisoles.*

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WHEN treated with ice-cold fuming nitric acid, the 3-fluoro-2 : 4 : 6-trihalogenophenols all give 3-fluoro-2 : 6-dihalogeno-*p*-benzoquinones, thus resembling the various 2 : 4 : 6-trihalogenophenols already investigated (this vol., p. 1085, and preceding paper), and a like theoretical explanation would appear to be valid.

Very remarkable differences, however, were found in the reactivity of the anisoles, for whereas 3-*fluoro*-2 : 4 : 6-*tribromoanisole* is nitrated normally in the 5-position (compare Kohn and Rosenfeld, *Monatsh.*, 1925, **46**, 101), yet with 3-*fluoro*-2 : 4 : 6-*tri-iodoanisole* the 6-iodine atom is displaced by the nitro-group with formation of 3-*fluoro*-2 : 4-*di-iodo*-6-*nitroanisole* (compare the similar formation of 4-fluoro-6-iodo-2-nitroanisole from 4-fluoro-2 : 6-di-iodoanisole, *loc. cit.*), and, still more remarkable, every chlorine atom in 3-*fluoro*-2 : 4 : 6-*trichloroanisole* is replaced by the nitro-group to give 3-*fluoro*-2 : 4 : 6-*trinitroanisole.*

It is noteworthy that 3-*fluoro*-2 : 4 : 6-*tribromo*- and -*tri-iodo-phenols* are readily methylated by methyl sulphate in alkaline solution, whereas the *trichloro*-analogue requires the application of Haworth and Lapworth's procedure (J., 1923, **123**, 2986).

EXPERIMENTAL.

Preparation of the 3-*Fluoro*-2 : 4 : 6-*trihalogeno-phenols and -anisoles.*—3-*Fluoro*-2 : 4 : 6-*trichlorophenol.* *m*-Fluorophenol (11·2 g.), dissolved in water (200 c.c.) containing sodium hydroxide (4 g.), was chlorinated by the gradual addition of sodium hypochlorite solution (430 c.c.; 1·4*N* in available chlorine), prepared from aqueous 10% sodium hydroxide. After standing for 2 hours at room temperature, the mixture was warmed on the water-bath for 5 minutes, cooled, and acidified with dilute sulphuric acid; 3-*fluoro*-2 : 4 : 6-*trichlorophenol* was precipitated as an oil, which was separated, washed with water, steam-distilled, and crystallised from light petroleum, separating in long colourless needles, m. p. 55° (Found : Cl, 49·8. $C_6H_2OFCl_3$ requires Cl, 49·4%).

3-*Fluoro*-2 : 4 : 6-*trichloroanisole* was obtained from this phenol by Haworth and Lapworth's method (*loc. cit.*), and, after removal from the reaction mixture by steam-distillation, it crystallised from light petroleum in long colourless needles, m. p. 35° (Found : Cl, 46·8. $C_7H_4OFCl_3$ requires Cl, 46·4%).

3-*Fluoro*-2 : 4 : 6-*tribromophenol*. *m*-Fluorophenol (11·2 g.), dissolved in water (1000 c.c.), was brominated by the portionwise addition of a mixture of bromine (15 c.c.) in water (100 c.c.) containing potassium bromide (50 g.). The heavy white precipitate was kept for 30 minutes, filtered off, and recrystallised from dilute alcohol or light petroleum; long colourless needles, m. p. 90° (Found : Br, 69·1. $C_6H_2OFBr_3$ requires Br, 68·8%).

3-*Fluoro*-2 : 4 : 6-*tribromoanisole*, obtained from the above phenol by addition of methyl sulphate to its solution in 20% aqueous sodium hydroxide, crystallised from light petroleum in slender, colourless needles, m. p. 55° (Found : Br, 66·5. $C_7H_4OFBr_3$ requires Br, 66·2%).

3-*Fluoro*-2 : 4 : 6-*tri-iodophenol*. *m*-Fluorophenol (11·2 g.), dissolved in water (200 c.c.) containing potassium hydroxide (6 g.), was iodinated by the portionwise addition at 0° of a solution of iodine (77 g.) and potassium iodide (80 g.) in water (200 c.c.). The precipitated 3-*fluoro*-2 : 4 : 6-*tri-iodophenol* was filtered off after 2 hours and washed with aqueous sodium bisulphite solution to remove any free iodine; it crystallised from dilute alcohol in short colourless needles, m. p. 138—139° (Found : I, 77·8. $C_6H_2OFI_3$ requires I, 77·8%).

3-*Fluoro*-2 : 4 : 6-*tri-iodoanisole* was obtained in the same way as the bromo-analogue except that a large excess of 20% aqueous sodium hydroxide was required to dissolve the phenol. It crystallised from dilute alcohol in small colourless needles, m. p. 107° (Found : I, 76·0. $C_7H_4OFI_3$ requires I, 75·6%).

Action of Fuming Nitric Acid on the 3-*Fluoro*-2 : 4 : 6-*trihalogenophenols and -anisoles.—General procedure.* The substance (5 g.) was dissolved in ice-cold nitric acid (50 c.c.; *d* 1·5), the mixture poured on ice after 15 minutes, and the resulting precipitate crystallised from alcohol.

Phenols. Each of the three phenols yielded the corresponding 3-fluoro-2 : 6-dihalogeno-*p*-benzoquinone : 3-*Fluoro*-2 : 6-*dichloro*-p-*benzoquinone* sublimes when heated in a vacuum, giving bright yellow plates, m. p. 145° (Found : Cl, 36·8. $C_6HO_2FCl_2$ requires Cl, 36·4%); 3-*fluoro*-2 : 6-*dibromo*-p-*benzoquinone*, small yellow plates, m. p. 150° (Found : Br, 56·9. $C_6HO_2FBr_2$ requires Br, 56·4%); 3-*fluoro*-2 : 6-*di-iodo*-p-*benzoquinone*, small orange-red plates, m. p. 195° (Found : I, 67·3. $C_6HO_2FI_2$ requires I, 67·3%).

Anisoles. (*a*) 3-Fluoro-2 : 4 : 6-trichloroanisole gave 3-*fluoro*-2 : 4 : 6-*trinitroanisole*, which crystallised from alcohol in long colourless needles, m. p. 180° (Found : N, 16·5. $C_7H_4O_7N_3F$ requires N, 16·1%). The absence of chlorine was proved both qualitatively and quantitatively.

(*b*) 3-Fluoro-2 : 4 : 6-tribromoanisole was nitrated to 3-*fluoro*-2 : 4 : 6-*tribromo*-5-*nitroanisole*, which crystallised from dilute alcohol in small colourless needles, m. p. 87° (Found : Br, 59·2. $C_7H_3O_3NFBr_3$ requires Br, 58·8%).

(*c*) 3-Fluoro-2 : 4 : 6-tri-iodoanisole gave iodine and 3-*fluoro*-2 : 4-*di-iodo*-6-*nitroanisole*, which crystallised from alcohol or light petroleum in small colourless needles, m. p. 102° (Found : I, 60·6. $C_7H_4O_3NFI_2$ requires I, 60·2%). Its constitution was proved by the following independent synthesis.

Synthesis of 3-*Fluoro*-2 : 4-*di-iodo*-6-*nitroanisole*.—Iodine (50 g.), dissolved in hot alcohol (150 c.c.), was obtained in a fine suspension by chilling, and to the mixture a solution of 3-fluoro-6-nitrophenol (15·7 g.) in alcohol (50 c.c.) was added with vigorous stirring, after which yellow mercuric oxide (5 g.) was introduced portionwise during 2 hours' stirring. The reaction mixture was then heated to boiling, filtered to remove mercuric iodide, the filtrate treated hot with just sufficient aqueous sodium bisulphite to remove free iodine, and then cooled; 3-*fluoro*-2 : 4-*di-iodo*-6-*nitrophenol* was deposited in bright yellow needles which, after recrystallisation from alcohol, melted at 106° (Found : I, 62·4. $C_6H_2O_3NFI_2$ requires I, 62·0%). Methylation was effected by Haworth and Lapworth's method (*loc. cit.*), since methyl sulphate did not react with the aqueous caustic alkaline solution of the phenol, and the 3-fluoro-2 : 4-di-iodo-6-nitroanisole so obtained crystallised from light petroleum in colourless needles, m. p. 102° (Found : I, 60·55%). Its identity with the foregoing product was established by a mixed m. p. determination.

Analytical Note.—As in previous work all the Carius halogen analyses are high, whilst considerable etching occurs in the inner tube.

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