CCXLI.—*Studies in Aromatic Substitution. Part II. The Action of Fuming Nitric Acid on the* 4-*Fluoro*-2 : 6-*dihalogeno-phenols and -anisoles.*

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A PREVIOUS investigation (this vol., p. 1085) has established that 4-fluoro-2 : 6-dibromo-phenol and -anisole each react with cold fuming nitric acid to give 2 : 6-dibromo-*p*-benzoquinone, and a theoretical explanation based on modern electronic theory was then suggested. It is now found that whilst 4-*fluoro*-2 : 6-*dichloro-phenol* and *-anisole* and also 4-*fluoro*-2 : 6-*di-iodophenol* each exhibit the same type of reaction, giving 2 : 6-dichloro- or 2 : 6-di-iodo-*p*-benzoquinone, 4-*fluoro*-2 : 6-*di-iodoanisole*, on the other hand, undergoes iodine displacement with subsequent nitration to 4-*fluoro*-6-*iodo*-2-*nitroanisole*.

It is also noteworthy that whereas 4-fluoro-2 : 6-dichlorophenol is much more readily methylated by the methyl sulphate–xylene–potassium carbonate procedure (Haworth and Lapworth, J., 1923, **123**, 2986) than by methyl sulphate in aqueous alkaline solution, the reverse obtains with the methylation of 4-fluoro-2 : 6-di-iodo-phenol.

EXPERIMENTAL.

4-*Fluoro*-2 : 6-*dichlorophenol* was prepared by dissolving *p*-fluoro-phenol (11·2 g.) in water (200 c.c.) and adding gradually with vigorous shaking a solution of sodium hypochlorite (286 c.c.; 1·4*N* in available chlorine), prepared from 10% aqueous sodium hydroxide. After standing over-night, the reaction mixture was just acidified with dilute sulphuric acid; the required phenol was precipitated as an oil, removed by steam-distillation, frozen, and then crystallised from light petroleum; colourless plates, m. p. 42° (Found : Cl, 39·3. $C_6H_3OFCl_2$ requires Cl, 39·2%).

4-*Fluoro*-2 : 6-*dichloroanisole*, prepared from the phenol by Haworth and Lapworth's method (see above), crystallised from light petroleum in long white needles, m. p. 36° (Found : Cl, 36·6. $C_7H_5OFCl_2$ requires Cl, 36·4%).

Action of Fuming Nitric Acid on the above Products.—The product (1 g.) was added gradually to ice-cooled nitric acid (10 c.c.; *d* 1·5) and the mixture poured after 15 minutes on ice, the resulting precipitate being washed free from acid, steam-distilled, and then recrystallised from light petroleum. 2 : 6-Dichlorobenzoquinone was obtained in each case as long yellow needles, the m. p. of each specimen alone or mixed with one another or with an authentic

specimen being 120—121° (compare Faust, *Annalen*, 1869, **149**, 153) (Found : Cl, 40·05, 40·10. Calc. : Cl, 40·0%).

4-*Fluoro*-2 : 6-*di-iodophenol* was obtained by portionwise addition of a solution of iodine (50 g.) and potassium iodide (50 g.) in water (250 c.c.) to one of *p*-fluorophenol (10 g.) in water (80 c.c.) containing sodium hydroxide (9 g.). As the reaction proceeded, the 4-fluoro-2 : 6-di-iodophenol was precipitated owing to its sparing solubility in cold aqueous caustic soda solution; it was filtered off, washed with aqueous sodium bisulphite to remove free iodine, and crystallised from aqueous alcohol; small colourless plates, m. p. 67° (Found : I, 70·1. $C_6H_3OFI_2$ requires I, 69·8%).

4-*Fluoro*-2 : 6-*di-iodoanisole* was best obtained by dissolving the above phenol in a large volume of hot 20% aqueous sodium hydroxide (necessary because of its sparing solubility) and adding the requisite amount of methyl sulphate. Practically no yield was obtained by Haworth and Lapworth's method (*loc. cit.*). The product crystallised from light petroleum or aqueous alcohol in long colourless needles, m. p. 61° (Found : I, 67·5. $C_7H_5OFI_2$ requires I, 67·3%).

Action of Fuming Nitric Acid on the foregoing Products.—By the same method as above, 4-fluoro-2 : 6-di-iodophenol gave 2 : 6-di-iodobenzoquinone, which crystallised from light petroleum in small yellow plates, m. p. and mixed m. p. with an authentic specimen 179° (compare Kehrmann and Messinger, *Ber.*, 1893, **26**, 2377) (Found : I, 70·8. Calc. : I, 70·5%), but 4-fluoro-2 : 6-di-iodoanisole lost free iodine and gave 4-*fluoro*-6-*iodo*-2-*nitroanisole*; this was volatile in steam and crystallised from light petroleum in colourless needles, m. p. 53° (Found : N, 5·0; I, 43·0. $C_7H_5O_3NFI$ requires N, 4·7; I, 42·8%).

Analytical Note.—In halogen determinations by the Carius method of compounds which also contain fluorine, the small glass tube holding the substance to be analysed was severely etched in every case.

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