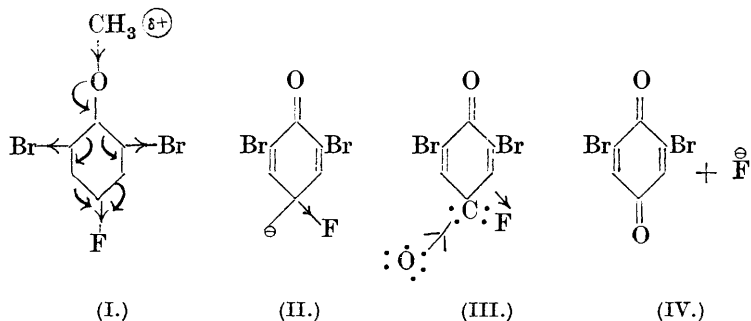


CXXXVI.—*The Action of Fuming Nitric Acid on the 4-Halogeno-2 : 6-dibromo-phenols and -anisoles. Anomalous Behaviour of Fluorine Derivatives.*

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KOHN and ROSENFELD (*Monatsh.*, 1925, **46**, 101) prepared 4-chloro-2 : 6-dibromo-3-nitro- and -3 : 5-dinitro-anisoles by the nitration of 4-chloro-2 : 6-dibromoanisole and of the mononitrated product. In an attempt to repeat their reaction with 4-fluoro-2 : 6-dibromoanisole, the product obtained was 2 : 6-dibromo-*p*-benzoquinone and consequently it appeared of interest to submit each of the 4-halogeno-2 : 6-dibromo-phenols and -anisoles to the action of fuming nitric acid in order to ascertain the rôle of the 4-halogen. All the phenols except the 4-iodo-compound (which was destroyed) gave 2 : 6-dibromo-*p*-benzoquinone, Kohn and Rosenfeld's results with 4-chloro-2 : 6-dibromoanisole (*loc. cit.*) were confirmed, and 2 : 4 : 6-tribromoanisole behaved similarly, *i.e.*, was mono- and di-nitrated. 4-Iodo-2 : 6-dibromoanisole, however, reacted anomalously to form 2 : 6-dibromo-4-nitroanisole.

The mechanism of reaction in the case of 4-fluoro-2 : 6-dibromoanisole can be regarded as a three-stage operation, *viz.*, the combined general effect (Allan, Oxford, Robinson, and Smith, J., 1926, 401) of the three halogens rendering the methyl group sufficiently mobile (positive) for detachment and oxidation (I); rearrangement of the residue to the quinonoid form (II), facilitated by the same general effect; and subsequent attack by oxygen (III) with separation of ionic fluorine (IV). The same mechanism will also apply to the phenols.



In the 4-chloro- and 4-bromo-2 : 6-dibromoanisoles, the combined general effect of the halogens is inadequate to produce the necessary reactivity (positivity) of the methyl group, and so normal nitration occurs. The above general effect is still further reduced in 4-iodo-

2 : 6-dibromoanisole, and consequently the methyl group remains intact, but the electron-donating power of the iodine is now sufficient to enable kationoid attack by the nitric acid to take place at the 4-carbon atom with nitration and elimination of iodine.

That fluorine exerts a far greater general effect than the other halogens is shown by the relatively much greater solubility of *p*-fluorophenol in water (indicating considerable ionisation) than is exhibited by the other *p*-halogenophenols, the order being $F > Cl > Br > I$, in accord with the order of general effects.

EXPERIMENTAL.

Preparation of p-Fluorophenol.—*p*-Fluoronitrobenzene, obtained in 25% yield by the authors' method for *m*-fluoronitrobenzene (J., 1928, 1879), was reduced by means of tin and hydrochloric acid to *p*-fluoroaniline, which was converted into *p*-fluorophenol by the standard procedure (Hodgson, E.P. 200,714).

4-Fluoro-2 : 6-dibromophenol was obtained when a solution of *p*-fluorophenol (11.2 g.) in water (250 c.c.) was treated gradually and shaken vigorously with a solution of bromine (10 c.c.; 2 mols.) in water (80 c.c.) containing potassium bromide (27 g.). The voluminous white precipitate produced was filtered off and washed with water; it crystallised from dilute alcohol in colourless needles, m. p. 48° (Found : Br, 59.2. $C_6H_5OFBr_2$ requires Br, 59.3%).

4-Fluoro-2 : 6-dibromoanisole.—Methylation of the above phenol was best carried out by Haworth and Lapworth's procedure in xylene solution with methyl sulphate and potassium carbonate (J., 1923, 123, 2986), the direct method with methyl sulphate and caustic alkali giving poor yields. The product crystallised from light petroleum in small colourless needles, m. p. 55° (Found : Br, 56.5. $C_7H_5OFBr_2$ requires Br, 56.3%).

Action of Fuming Nitric Acid on the 4-Halogeno-2 : 6-dibromophenols and -anisoles.—*General procedure.* The substance (5 g.) was dissolved in ice-cold nitric acid (50 c.c.; *d* 1.5), the mixture poured after 15 minutes on ice, and the resulting precipitate crystallised from alcohol.

Results. (1) 4-Fluoro-2 : 6-dibromo-phenol and -anisole each gave 2 : 6-dibromo-*p*-benzoquinone, m. p. and mixed m. p. 130—131° (Found : Br, 59.9, 60.2. Calc. : Br, 60.1%).

(2) 4-Chloro-2 : 6-dibromophenol gave 2 : 6-dibromo-*p*-benzoquinone, whereas 4-chloro-2 : 6-dibromoanisole gave 4-chloro-2 : 6-dibromo-3-nitroanisole, m. p. 58°, and this on further nitration with a mixture of fuming nitric and concentrated sulphuric acids gave 4-chloro-2 : 6-dibromo-3 : 5-dinitroanisole, m. p. 146° (compare Kohn and Rosenfeld, *loc. cit.*)

(3) 2 : 4 : 6-Tribromophenol gave 2 : 6-dibromo-*p*-benzoquinone, and 2 : 4 : 6-tribromoanisole gave 2 : 4 : 6-*tribromo-3-nitroanisole*, which crystallised in small colourless plates, m. p. 82° (Found : N, 3·9; Br, 61·8. $C_7H_4O_3NBr_3$ requires N, 3·6; Br, 61·5%), and gave 2 : 4 : 6-*tribromo-3 : 5-dinitroanisole*, which crystallised from alcohol in colourless needles, m. p. 148° (Found : N, 6·6; Br, 55·5. $C_7H_3O_5N_2Br_3$ requires N, 6·4; Br, 55·2%), on further nitration as above.

(4) 4-Iodo-2 : 6-dibromophenol (m. p. 105°; prepared by direct dibromination of *p*-iodophenol in glacial acetic acid; compare King and McCombie, J., 1913, **103**, 222) was completely destroyed by ice-cold fuming nitric acid.

2 : 6-*Dibromo-4-iodoanisole*, prepared from the above phenol by Haworth and Lapworth's method (*loc. cit.*), crystallised from light petroleum in colourless needles, m. p. 78° (0·1310 g. gave 0·2040 g. of mixed silver halides. Calc. : 0·2036 g.). On nitration with fuming nitric acid as above, 2 : 6-dibromo-4-nitroanisole was obtained, which crystallised in long colourless needles; the m. p. and mixed m. p. with an authentic specimen, prepared by dibromination of *p*-nitrophenol and subsequent methylation, was 122° (Found : N, 4·8; Br, 51·7. Calc. : N, 4·5; Br, 51·5%).

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