

CCXLIV.—*The Nitration of m-Fluorophenol.*

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ALTHOUGH *m*-fluorophenol has been prepared (Swarts, *Bull. Acad. roy. Belg.*, 1913, 241), no mention of the nitro-derivatives appears in the literature. The present investigation proceeds on similar lines to those of the *m*-chloro- and *m*-bromo-analogues (J., 1925, 127, 1599; 1926, 155). A trustworthy method for the preparation of *m*-fluronitrobenzene from *m*-nitroaniline is described.

Monosulphonation of 3-fluoro-2-nitrophenol in the cold or at 100—120° appears to give exclusively 3-fluoro-2-nitrophenol-4-sulphonic acid, since only 3-fluoro-2 : 6-dinitrophenol could be obtained from it by further mononitration.

The orientations proposed for the dinitro-compounds follow from the modes of preparation and by analogy with the corresponding chloro- and bromo-compounds (*loc. cit.*). In addition is the following evidence: (1) All three dinitro-compounds are convertible into 3-fluoro-2 : 4 : 6-trinitrophenol, indicating that the two nitro-groups in each compound are in meta-positions to each other. (2) The 4 : 6-dinitro-compound gives 4 : 6-dinitro-*m*-phenylenediamine, and the 2 : 6- and 2 : 4-isomerides give the same 2 : 4-dinitro-*m*-phenylenediamine, when heated in a sealed tube with aqueous ammonia. (3) 3-Fluoro-2 : 4- and -2 : 6-dinitrophenols both give 2 : 4-dinitroresorcinol when boiled with aqueous sodium hydroxide.

Certain marked differences in behaviour of the fluoro- and the other halogeno-analogues have been observed: (a) 3-Fluoro-4 : 6-dinitrophenol forms a stable, yellow, crystalline silver derivative which does not exhibit transformations similar to those of the chloro-, bromo-, and iodo-compounds. The silver derivative of 3-fluoro-2 : 6-dinitrophenol, however, is produced initially as a yellow gel which rapidly passes through an orange-red gel stage into a permanent orange-red crystalline form. (b) The silver derivative of 3-fluoro-2 : 4-dinitrophenol has a deeper red colour than its 2 : 6-isomeride—the chloro- and bromo-analogues are yellow, crystalline substances. (c) All the silver derivatives are readily soluble in aqueous ammonia (compare the insolubility of the silver derivatives of the 3-halogeno-2 : 4 : 6-trinitrophenols and the varying solubility of the lower nitrated products). (d) The 3-fluoro-2-, -4-, and -6-nitrophenols resist acetylation. (e) Anomalies are exhibited in the m. p.'s: e.g., 3-fluoro-4-nitrophenol has m. p. 56.5°, its analogues have m. p.'s 122°, 131°, and 124°; 3-fluoro-2 : 4 : 6-trinitrophenol has m. p. 173°, whereas the chloro-, bromo-, and iodo-compounds melt at 114°, 149°, and 197°, respectively.

E X P E R I M E N T A L.

Initial Materials.—A solution of *m*-nitroaniline (140 g.) in 60% hydrofluoric acid (450 c.c.) in a copper beaker was diazotised at 0° with a rapid stream of nitrous fumes (30 minutes) and added gradually to 60% hydrofluoric acid (75 c.c.), in a lead pot with a copper reflux condenser, heated on a boiling water-bath. The mixture was kept hot for 1 hour and the *m*-fluoronitrobenzene then isolated, in 25% yield, by steam-distillation. It was reduced to *m*-fluoroaniline, which was converted in almost quantitative yield into *m*-fluorophenol (Hodgson, E.P. 200,714).

Nitration.—The methods of preparation of the 3-fluoronitrophenols are those described for the corresponding chloro- and bromo-analogues with appropriate modifications.

3-Fluoro-6-nitrophenol (yield, 6 g. from 29 g. of *m*-fluorophenol) is volatile in steam and crystallises from light petroleum in yellow needles, m. p. 32°, having a characteristic sweet nitrophenolic odour (Found : N, 9.1. $C_6H_4O_3NF$ requires N, 8.9%). The *sodium* salt crystallises from water in red needles. The orange-brown *silver* salt, which deepens in colour on keeping, is readily soluble in aqueous ammonia and gradually decomposes in boiling aqueous solution. The *methyl ether* crystallises from light petroleum in colourless micro-parallelepipeds, m. p. 52° (Found : N, 8.3. $C_7H_6O_3NF$ requires N, 8.2%), and the *benzoate* in colourless micro-scales, m. p. 110—111° (Found : N, 5.6. $C_{13}H_8O_4NF$ requires N, 5.4%). The acetates of this substance and of its isomerides could not be prepared by any of the usual methods.

3-Fluoro-4-nitrophenol (yield, 9 g.) is non-volatile in steam and crystallises from water or light petroleum in long, colourless needles, m. p. 42° (Found : N, 9.2%). The *sodium* salt crystallises from water in long, pale yellow needles. The bright yellow *silver* salt, although more soluble in water and aqueous ammonia than its isomerides, also decomposes on boiling (Found : Ag, 40.6. $C_6H_3O_3NFAg$ requires Ag, 40.9%). The *methyl ether* crystallises from light petroleum in colourless needles, m. p. 56.5° (Found : N, 8.3%), and the *benzoate* in colourless, rectangular micro-plates, m. p. 118° (Found : N, 5.6%).

3-Fluoro-2-nitrophenol, prepared by the nitration of disulphonated *m*-fluorophenol (J., 1925, 127, 1600), passes over on hydrolysis in a current of steam as a reddish oil which, after being frozen and pressed, crystallises from light petroleum in short red needles, m. p. 39° (Found : N, 9.0%). The formation of a hydrate could not be detected (compare J., 1926, 156, 631). The reddish-brown *sodium* salt is exceedingly soluble in water, and the very deep reddish-brown *silver* salt is readily soluble in hot water, but gradually decomposes,

and in aqueous ammonia. The *methyl ether* crystallises from light petroleum in long, colourless needles, m. p. 43.5° (Found : N, 8.4%), and the *benzoate* in clusters of white needles, m. p. 114° (Found : N, 5.5%).

3-Fluoro-4 : 6-dinitrophenol was prepared from *m*-fluorophenol and from 3-fluoro-6- and -4-nitrophenols in the same way as the corresponding bromo-compound (*loc. cit.*, p. 158). It is readily volatile in steam and crystallises from water or light petroleum in colourless needles, m. p. 80° (Found : N, 14.1. $C_6H_3O_5N_2F$ requires N, 13.9%).

In each preparation a non-volatile product was 3-fluoro-2 : 4 : 6 trinitrophenol. The silver salt, prepared like its analogues (*loc. cit.*, pp. 1603, 159, 634), separates very gradually in long, fine yellow needles and does not exhibit the phenomena recorded for the other three analogues. It is soluble in aqueous ammonia and stable in hot water (Found : Ag, 34.6. $C_6H_2O_5N_2F$ Ag requires Ag, 34.9%).

3-Fluoro-2 : 6-dinitrophenol was prepared by recorded methods (*loc. cit.*, pp. 1602, 159) from 3-fluoro-2- and -6-nitrophenols. It crystallises from light petroleum in colourless needles, m. p. 68.5° (Found : N, 14.05%). The *silver* salt is readily soluble in aqueous ammonia and hot water, giving deep yellow solutions; from the aqueous solution, on cooling, it separates in orange-red micro-needles (Found : Ag, 34.7%).

3-Fluoro-2 : 4-dinitrophenol was obtained together with 3-fluoro-2 : 6-dinitrophenol when *m*-fluorophenol was disulphonated and then dinitrated as in the procedure for the chloro-analogue (*loc. cit.*, p. 1602). The product was hydrolysed in a current of steam, the long, colourless needles of 3-fluoro-2 : 6-dinitrophenol which separated from the distillate on cooling were removed, and the filtrate was rendered alkaline and concentrated to a small bulk; on acidification, *3-fluoro-2 : 4-dinitrophenol* was precipitated. It crystallised from light petroleum in pale yellow micro-parallelepipeds, m. p. 138—139° (Found : N, 13.9%), and was much more soluble in water than the other two isomerides. The deep red *silver* salt (Found : Ag, 34.6%) is readily soluble in hot water and aqueous ammonia, giving deep yellow solutions.

Action of Ammonia on 3-Fluoro-4 : 6-, -2 : 6-, and -2 : 4-dinitrophenols.—These (0.5 g.) were separately heated in sealed tubes with concentrated ammonia (5 c.c.) at 150° during 2 hours. On cooling, the products were obtained as brownish-yellow needles. The 4 : 6-dinitro-*m*-phenylenediamine obtained from the first-named compound melted at about 300° (compare Nietzki and Schedler, *Ber.*, 1897, **30**, 1667) (Found : N, 28.5. Calc. : N, 28.3%). 3-Fluoro-2 : 6- and -2 : 4-dinitrophenols each gave 2 : 4-dinitro-*m*-phenylenediamine, m. p. and mixed m. p. 264° (Barr, *Ber.*, 1888,

21, 5545, gives m. p. 250°; Hodgson and Moore, *loc. cit.*, give m. p. 258° (Found : N, 28·4% and 28·2%, respectively).

The two specimens of 2 : 4-dinitroresorcinol obtained from 3-fluoro-2 : 6- and -2 : 4-dinitrophenols by the action of boiling aqueous sodium hydroxide melted, alone or mixed with each other, at 146° (compare *loc. cit.*, p. 160).

3-Fluoro-2 : 4 : 6-trinitrophenol crystallises from water in characteristic, almost colourless, hexagonal plates, m. p. 173° (Found : N, 17·1. $C_6H_2O_7N_3F$ requires N, 17·0%), which are not volatile in steam but sublime slowly from boiling concentrated sulphuric acid. This property is exhibited also by the other halogeno-analogues. The substance does not possess the violent sternutatory properties of the iodo-analogue, forms deep yellow solutions in water and alcohol, and is not brominated when its aqueous solution is treated with bromine. The bright yellow crystalline *silver* salt is readily soluble in aqueous ammonia and hot water.

The authors' thanks are due to the British Dyestuffs Corporation for gifts of chemicals.

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[Received, April 27th, 1928.]
