39. *The Action of Nitrosylsulphuric Acid on* m-*Fluorophenol. A New Red* o-*Quinoneimine.*

By Herbert H. Hodgson and Donald E. Nicholson.

Nitrosylsulphuric acid reacts with *m*-fluorophenol in glacial acetic acid to give a red compound, probably 4 : *2'-difluoro-4'-hydroxy-*o*-benzoquinone-1-phenylimine*, together with a very small amount of *3-fluoro-4-nitrosophenol* (or *3-fluorobenzoquinone-4-oxime*).

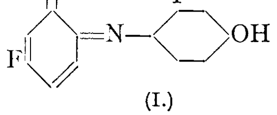
When a glacial acetic acid solution of *m*-fluorophenol is added to one of sodium nitrite in concentrated sulphuric acid, the principal product obtained is not the expected 3-fluorobenzoquinone-4-oxime as in the case of the other three *m*-halogenophenols (Hodgson and Nicholson, J., 1939, 1808), but a red *o*-quinoneimine of probable structure (I); it is contaminated with a minute amount of a green compound which is either *3-fluoro-4-nitrosophenol* or the isomeric *3-fluorobenzoquinone-4-oxime.* This reaction differs from that of aqueous nitrous acid on *m*-fluorophenol (Hodgson and Nicholson, J., 1939, 1405), whereby *mm'*-difluoro-*o*-indophenol (II) arises, although in both cases 5-fluoro-2-nitrophenol is formed in small amounts by a simultaneous reaction.

The following evidence indicates that the new red *o*-quinoneimine has the structure (I) of a 4 : *2'-difluoro-4'-hydroxy-*o*-benzoquinone-1-phenylimine* : (1) It has the correct composition and molecular weight, and the red colour excludes structures (III) and (IV), since such compounds would be blue (cf. Hodgson and Nicholson, *loc. cit.*) : all three formulæ exclude the possibility of oxazone formation.

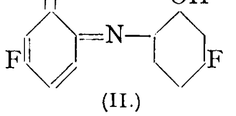
(2) It is more readily soluble in aqueous alkali hydroxides and carbonates, which is to be expected from the position of the hydroxyl group, and consequently less soluble in acetic acid of various strengths, than *mm'*-difluoro-*o*-indophenol (II).

(3) Both (I) and (II) give condensation products with aniline, that from (I) having the higher m. p., and the leuco-compounds of (I) and (II) can be triacetylated, the latter product having a m. p. whereas the former does not melt. The products from (I) are less soluble in alcohol and glacial acetic acid than those from (II).

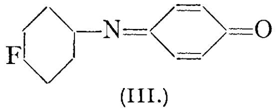
(4) When boiled with an aqueous solution of potassium permanganate and sulphuric acid, (I) gives, as would be expected, a pronounced odour, that of a steam-volatile *p*-benzoquinone, whereas (II) does not, its product of oxidation being a non-steam-volatile *o*-benzoquinone.



(I.)

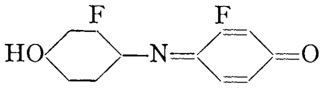


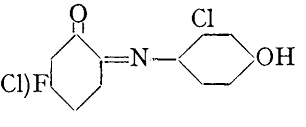
(II.)



(III.)

(IV.)





(V.)

(5) When reduced in glacial acetic acid solution with zinc dust, (I) gives a colourless leuco-compound, which is reoxidised in the air in the presence of hydrochloric acid to

re-form (I) (a process accelerated by ferric chloride), whereas (II), undergoing the same sequence of reactions, gives the expected blue oxazine (cf. Hodgson and Nicholson, *loc. cit.*). This reaction is supported by the analogous reactions observed when *m*-chloro-*p*-nitrosophenol is condensed with either *m*-fluoro- or *m*-chloro-phenol in glacial acetic acid solution, the respective red products (V) undergoing the above sequence of reactions with no intermediate blue oxazine formation.

The green compound that contaminates the *o*-quinoneimine (I) and is removable by solution in ligroin is either 3-fluoro-4-nitrosophenol or 3-fluorobenzoquinone-4-oxime; the amount obtained is too small for macroscopic examination. That the nitroso- (or oximino-) group is in the *p*-position to the hydroxyl (or quinone) group is indicated by the oxidation of the compound to 3-fluoro-4-nitrophenol and by the blue colour given when the compound is heated with dimethylaniline, *o*-chlorophenol, and *o*-cresol (cf. Hodgson and Nicholson, *loc. cit.*).

Mechanism of the Reaction.—From the foregoing data it is tentatively suggested that the reaction of nitrosylsulphuric acid with *m*-fluorophenol takes place in two stages: (1) nitrosation in position 4 and, in small degree, nitration in position 6, and (2) rapid condensation of the nitroso-compound (or quinoneoxime) with unchanged *m*-fluorophenol to form the red *o*-quinoneimine (I) (cf. also Schoutissen, *Rec. Trav. chim.*, 1921, **40**, 753).

The other *m*-halogenophenols only react as far as stage (1), although the traces of coloured products obtained are probably due to condensation (2) on a micro-scale. Nitrous acid in aqueous solution appears to react with *m*-fluorophenol exclusively in position 6 (Hodgson and Nicholson, *loc. cit.*), whereas the more energetic nitrosylsulphuric acid is able to attack the phenol normally at position 4 even though this position is deactivated by the powerful negative (— *I*) effect of the neighbouring fluorine atom. That the 6-position also is attacked to a slight extent, however, is shown by the concurrent formation of 3-fluoro-6-nitrophenol.

EXPERIMENTAL.

Action of Nitrosylsulphuric Acid on m-*Fluorophenol.*—*m*-Fluorophenol (2 g.), dissolved in glacial acetic acid (20 c.c.), was added below 20° to a solution of sodium nitrite (2 g.) in concentrated sulphuric acid (10 c.c.) which had been previously heated to 70°. The mixture was kept at 0° for 10 minutes and then poured on ice; the yellow-brown precipitate produced became superficially green when dried. The finely powdered product was a mixture of a red and a green compound (the red greatly predominating). Extraction with boiling ligroin (b. p. 80—100°) dissolved the green compound, which separated from the cooling extracts in green micro-crystals of 3-*fluoro*-4-*nitrosophenol* (or 3-*fluorobenzoquinone*-4-*oxime*), m. p. 158° after crystallisation from dilute alcohol (Found: N, 9·8. $C_6H_4O_2NF$ requires N, 10·0%). This compound gave a vivid Liebermann nitroso-reaction with cold phenol and concentrated sulphuric acid, the sequence of colours being green, blue (intensified on heating), scarlet (on dilution with water), and finally blue, becoming permanganate-violet, on addition of aqueous sodium hydroxide. The wet m. p. was unchanged at 158°, indicating that the compound was not associated (cf. Baker, J., 1934, 1687). Oxidation with hot aqueous potassium ferricyanide gave 3-fluoro-4-nitrophenol, m. p. and mixed m. p. with an authentic specimen (Hodgson and Nixon, J., 1928, 1879) 42° (Found: N, 9·1. Calc.: N, 8·9%).

The residue remaining after the ligroin extractions (*ca.* 1·8 g.) separated from boiling alcohol or boiling glacial acetic acid in dark red, microcrystalline plates, which did not melt below 300° (Found: C, 61·2; H, 2·9; N, 6·0; *M*, cryoscopic in phenol, 239. The presence of fluorine was established qualitatively. $C_{12}H_7O_2NF_2$ requires C, 61·3; H, 3·0; N, 6·0%; *M*, 235). They were odourless, non-volatile in steam, and very resistant to oxidation by nitric acid, but evolved ammonia when boiled with caustic alkali.

Reductive Acetylation of 4 : 2′-*Difluoro*-4′-*hydroxy*-o-*benzoquinone*-1-*phenylimine* (I) *and of* mm′-*Difluoro*-o-*indophenol* (II).—The substance (0·2 g.) was mixed with fused sodium acetate (0·2 g.) and boiled with acetic anhydride (4 c.c.), and a small quantity of zinc dust added; the red colour then faded. The solution was filtered from unchanged zinc, mixed with ice, and left until it became solid; it was then crystallised several times from aqueous alcohol. N-*Acetyl*-4 : 2′-*difluoro*-2 : 4′-*diacetoxydiphenylamine*, obtained from (I), formed very pale yellow microplates, which had no m. p. (Found: N, 4·0; *M*, by Rast's method, 365. $C_{18}H_{15}O_5NF_2$ requires N, 3·9%; *M*, 363) and gave a blue-green colour with concentrated sulphuric acid. N-*Acetyl*-

[4 : 4′-*difluoro*-2 : 2′-*diacetoxydiphenylamine*, obtained from (II), also crystallised in very pale yellow micro-plates, m. p. 175° (Found : N, 4·0% ; *M*, 363) ; it gave a violet colour with concentrated sulphuric acid. The presence of fluorine was established qualitatively in both compounds.

Condensation of (I) *and* (II) *with Aniline.*—The compound (0·2 g.) was heated to boiling with aniline (0·5 c.c.) and glacial acetic acid (5 c.c.), and the mixture diluted with water. 4 : 2′-*Difluoro*-4′-*hydroxy*-o-*benzoquinonebisphenylimine*, obtained from (I), crystallised from glacial acetic acid in maroon needles, m. p. 200° (Found : N, 8·3. $C_{18}H_{12}ON_2F_2$ requires N, 8·1%), and 4 : 4′-*difluoro*-2′-*hydroxy*-o-*benzoquinonebisphenylimine*, from (II), crystallised from 80% acetic acid in deep red micro-plates, m. p. 175° (depressed by the above isomer) (Found : N, 8·2%). The presence of fluorine was established qualitatively in both compounds.

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