117. *The Coupling of* m-*Fluorophenol with some Diazotised Amines and the Preparation of 2-Fluorobenzoquinone.*

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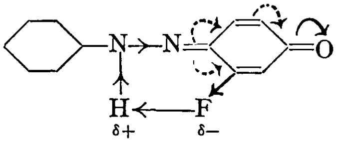
3-Fluorophenol in alkaline solution appears to couple only in the 4-position and to form monoazo-dyes with diazo-compounds. The preparation and properties of 2-*fluorobenzoquinone* are described.

In view of the powerful negative inductive (— *I*) effect of fluorine, it would be expected that in 3-fluorophenol the 4-position would be so deactivated that some coupling with diazonium salts might occur in the 6-position, particularly as 3-fluorophenol is more dissociated than phenol, a fact which should produce greater activation in the 6-position. Actually, aniline, sulphanilic acid, and *m*- and *p*-nitroaniline, when diazotised, all coupled in the 4-position only; even when a large excess of the diazo-compound was used, no evidence of the formation of a disazo-compound could be obtained. It is tentatively suggested that this may be due to the monoazo-dye having the quinonehydrazone form, with possible chelation between fluorine and hydrogen which would tend to retain the structure (annexed formula). There would thus be no active 2- and 6-positions.



Diazotised aniline and sulphanilic acid couple only slowly with 3-fluorophenol, but the velocity is considerably increased for diazotised *m*- and *p*-nitroanilines owing to the greater activity of the diazonium compounds. The resulting *p*-hydroxyazo-compounds are all readily reduced by sodium hyposulphite ("hydros") in an alkaline medium, to give 3-*fluoro*-4-*aminophenol* together with the original amine.

The constitution of 3-fluoro-4-aminophenol followed from its identity with a specimen obtained from authentic 3-fluoro-4-nitrophenol (Hodgson and Nixon, J., 1928, 1879), and on oxidation with ferric chloride or chromic acid there resulted 2-*fluorobenzoquinone*. This was so prone to reduction by hydroxylamine or phenylhydrazine that an oxime or hydrazone could not be prepared directly with these reagents.

It will be recalled that 3-fluoro-4-nitrosophenol (Hodgson and Nicholson, J., 1940,

1268) and 2-fluoro-4-nitrosophenol (*ibid.*, p. 810) could only be obtained in the nitrosophenolic form, and that 2- and 3-fluorobenzoquinone-4-oximes had no separate existence.

It is of interest that the melting points of *p*-benzoquinone and its 2-fluoro-, 2-chloro-, and 2-bromo-derivatives are in the descending order, 116°, 80°, 57°, and 55°, respectively.

EXPERIMENTAL.

3-*Fluoro*-4-*benzeneazophenol.*—A solution of aniline (2·0 g.) in hydrochloric acid (6 c.c., *d* 1·16) and water (20 c.c.) was diazotised at 0° with sodium nitrite (2·0 g.) in water (20 c.c.). The excess of nitrous acid was destroyed with urea, and the diazo-solution stirred into a solution at 0° of 3-fluorophenol (2·4 g.) in water (50 c.c.) containing sodium hydroxide (3·0 g.). The precipitate of 3-*fluoro*-4-*benzeneazophenol*, after being washed and dried, separated from glacial acetic acid in brown crystals, m. p. 139° (decomp.) (Found : N, 13·1. $C_{12}H_9ON_2F$ requires N, 12·9%), which gave a bright orange colour with concentrated sulphuric acid. The same compound was obtained when an excess of diazotised aniline over that required for coupling twice was used.

3-*Fluoro*-4-*aminophenol.*—3-Fluoro-4-benzeneazophenol (1·5 g.) was made into a thin paste with water and treated gradually on the water bath at 95—100° with sodium hyposulphite (4·5 g. in all) until reduction was complete. The aniline formed was removed by steam-distillation; on cooling, the residual liquor deposited 3-*fluoro*-4-*aminophenol*, which crystallised from ether or boiling water in long colourless needles, m. p. 139° (Found : N, 11·0. C_6H_6ONF requires N, 11·0%), identical with the compound prepared by reducing 3-fluoro-4-nitrophenol with iron and alcoholic hydrochloric acid.

Oxidation of 3-*Fluoro*-4-*aminophenol to* 2-*Fluorobenzoquinone.*—(a) A mixture of 3-fluoro-4-aminophenol (0·5 g.), ferric chloride (2 g.), and water (5 c.c.) was refluxed for 15 minutes. 2-*Fluorobenzoquinone*, removed by steam-distillation, crystallised from ether in golden-yellow plates, m. p. 80° (Found : C, 56·9; H, 2·4. $C_6H_3O_2F$ requires C, 57·1; H, 2·4%), having a strong odour of benzoquinone. Ether extracted a further quantity from the distillate (total yield, *ca.* 0·2 g.).

(b) A solution of 3-fluoro-4-aminophenol (0·5 g.) in 20% sulphuric acid (40 c.c.) was stirred below 10° with finely powdered potassium dichromate (1 g.). After 2 minutes an odour like that of benzoquinone was observed, and after 3 hours the precipitated 2-fluorobenzoquinone was collected. The filtrate, after treatment with a further quantity of potassium dichromate (2 g.), was kept overnight, and an additional amount of the quinone obtained by ether extraction (total yield, *ca.* 0·3 g.).

3-*Fluoro*-4-*hydroxyazobenzene*-4′-*sulphonic Acid.*—This was formed when diazotised sulphanilic acid, obtained by adding an aqueous solution of sodium sulphanilate and sodium nitrite to ice-cold dilute sulphuric acid, was stirred with the calculated quantity of 3-fluorophenol in alkaline solution. Coupling, as in the case of diazotised aniline, proceeded slowly; next day, the orange dye was reduced *in situ* with sodium hyposulphite as above, and the 3-fluoro-4-aminophenol formed was extracted with ether. When an excess of diazotised sulphanilic acid was used, the yield of 3-fluoro-4-aminophenol was undiminished, showing that only the monoazo-dye had been formed in the coupling process.

3-*Fluoro*-3′-*nitro*-4-*benzeneazophenol.*—A hydrochloric acid solution of diazotised *m*-nitroaniline was stirred into a solution of the calculated weight of *m*-fluorophenol in aqueous sodium hydroxide. The red precipitate formed separated from glacial acetic acid in light orange crystals, m. p. 116° (Found : N, 16·2. $C_{12}H_8O_3N_3F$ requires N, 16·1%). When it was reduced with sodium hyposulphite as above, a mixture of 3-fluoro-4-aminophenol and *m*-phenylenediamine was obtained. This mixture was neutralised with acetic acid and extracted with ether. The *m*-phenylenediamine in the solution was identified by conversion into Bismarck-brown by the addition of hydrochloric acid and sodium nitrite.

3-*Fluoro*-4′-*nitro*-4-*benzeneazophenol.*—*p*-Nitroaniline was diazotised and added to the calculated amount of 3-fluorophenol in alkaline solution as above. The precipitate obtained crystallised from glacial acetic acid or 50% aqueous alcohol in scarlet needles, m. p. 196° (Found : N, 16·2. $C_{12}H_8O_3N_3F$ requires N, 16·1%). Reduction with sodium hyposulphite gave 3-fluoro-4-aminophenol and *p*-phenylenediamine; the former was extracted with ether, and the latter identified by oxidation with ferric chloride to *p*-benzoquinone.

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