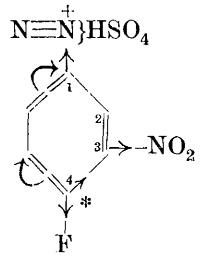
CCCX.—*The Lability of Fluorine in 4-Fluoro-3-nitroaniline. A Singular Replacement of Fluorine by the Ethoxyl Group in Acid Solution.*

By Herbert Henry Hodgson and Joseph Nixon.

Unlike its analogue 4-chloro-3-nitroaniline, which when diazotised in hydrochloric or sulphuric acid solution gives either the corresponding 4-chloro-3-nitrobenzenediazonium salt or 2-nitrobenzene-4-diazo-1-oxide according to the acidity of the medium (Morgan and Porter, J., 1915, **107**, 645), 4-fluoro-3-nitroaniline under the same conditions always yields the diazo-oxide. This compound, which is stable towards boiling 25% sulphuric acid, is decomposed normally by cuprous chloride or bromide in the appropriate acid, giving 4-chloro- or 4-bromo-2-nitrophenol, and by aqueous potassium iodide, giving 4-iodo-2-nitrophenol, but is converted by copper sulphate and sodium bromide in dilute sulphuric acid into 4 : 6-dibromo-2-nitrophenol.

Bromination of 2-nitrobenzene-4-diazo-1-oxide affords a very stable 6-bromo-derivative, which, although decomposed normally by copper salts, is unaffected by aqueous potassium iodide but reacts on addition of copper sulphate.

When 4-fluoro-3-nitroaniline is treated with sodium nitrite in ethyl-alcoholic sulphuric acid solution, *o*-nitrophenetole is produced, the normal replacement of the diazo-nitrogen by hydrogen (compare the usual decomposition of nitro-diazonium salts; Orndorff and Cauffman, *J. Amer. Chem. Soc.*, 1892, **14**, 45; Orndorff and Kortright, *ibid.*, 1891, **13**, 153) being effected together with an unusual replacement of fluorine by ethoxyl. It would appear, therefore, that in alcoholic solution the 4-fluoro-3-nitrodiazonium salt has been first produced and not the diazo-oxide as above, whereby the 4-carbon atom * is rendered so intensely kationoid, by the combination of the alternating effect due to the positive diazo-group with the general electron-attraction effects of the fluorine atom and the nitro-group, that anionoid attack by ethyl alcohol is made possible.



Usually, halogen replacements in *o*- and *p*-halogeno-nitro-compounds by anionoid alkoxy-groups take place in alkaline medium (sodium alkoxide), but alkalinity is now found to be by no means a *sine qua non*, since replacement can occur in acid environment when the carbon atom is sufficiently kationoid.

EXPERIMENTAL.

Diazotisation of 4-*Fluoro*-3-*nitroaniline*.—The substance (2 g.), dissolved in ice-cold dilute sulphuric acid (concentrated acid, 10 c.c.; water, 30 c.c.), was treated with the requisite amount of aqueous sodium nitrite, and after 5 minutes the heavy yellow precipitate of 2-nitrobenzene-4-diazo-1-oxide (2-nitro-*p*-quinodiazine) was filtered off; this crystallised from boiling alcohol and from hot water in small yellow plates which decomposed with great violence when heated to 178° (Morgan and Porter, *loc. cit.*, give 168°) (Found: N, 26·0. Calc.: N, 25·45%). The same product was obtained when dilute hydrochloric or hydrobromic acid was substituted for sulphuric acid.

Conversion of 2-*Nitrobenzene*-4-*diazo*-1-*oxide into* 4 : 6-*Dibromo*-2-*nitrophenol*.—The diazo-oxide (2 g.) was added to a hot solution of copper sulphate (4 g.) and sodium bromide (6 g.) in water (50 c.c.), and the resulting 4 : 6-dibromo-2-nitrophenol removed by steam-distillation; it crystallised from alcohol in bright yellow plates, m. p. and mixed m. p. with an authentic specimen, 119° (Found: Br, 53·6. Calc.: Br, 53·8%).

Bromination of 2-*Nitrobenzene*-4-*diazo*-1-*oxide*.—The diazo-oxide (1·6 g.) was suspended in water (30 c.c.) and vigorously shaken with a solution of bromine (0·6 c.c.) and potassium bromide (3 g.) in water (10 c.c.). After 1 hour's stirring, the 6-*bromo*-2-*nitrobenzene*-4-*diazo*-1-*oxide* was filtered off; it crystallised from boiling alcohol in small, pale yellow plates, which decomposed violently at 185° (Found: Br, 32·4. $C_6H_2O_3N_3Br$ requires Br, 32·8%).

Treatment of this diazo-oxide with a solution of cuprous chloride in concentrated hydrochloric acid converted it into 4-chloro-6-bromo-2-nitrophenol, which was volatile in steam and crystallised from alcohol in yellow plates, m. p. 125° (Ling, J., 1887, **51**, 787, gives m. p. 125°); similarly, cuprous bromide in hydrobromic acid solution gave 4 : 6-dibromo-2-nitrophenol, m. p. 119° (*loc. cit.*), but hot aqueous potassium iodide was without action on the diazo-oxide. Addition of a few drops of aqueous copper sulphate to the last suspension, however, caused a sluggish reaction whereby 6-*bromo*-4-*iodo*-2-*nitrophenol* was produced; this was removed by steam-distillation, and crystallised from aqueous alcohol, forming bright yellow needles, m. p. 85° (Found : Br + I, 59·8. $C_6H_3O_3NBrI$ requires Br + I, 60·2%). Heated with 10% alcoholic potassium hydroxide, 6-bromo-2-nitrobenzene-4-diazo-1-oxide gave 6-bromo-2-nitrophenol, m. p. 68° (Meldola and Streatfeild, J., 1898, **73**, 685, give m. p. 67—68°), and 2-nitrobenzene-4-diazo-1-oxide gave *o*-nitrophenol.

Diazotisation of 4-*Fluoro*-3-*nitroaniline in Ethyl Alcohol.*—A solution of the amine (20 g.) in concentrated sulphuric acid (100 c.c.) and alcohol (400 c.c.) was heated on the water-bath under reflux, and treated gradually with solid sodium nitrite (80 g.) during 1 hour. Fractional steam-distillation removed first the alcohol and then *o*-nitrophenetole, which was purified by distillation, b. p. 267° (Found : N, 8·6. Calc. : N, 8·4%). This product was converted into *o*-phenetidine hydrochloride, which crystallised from alcohol or water in white needles, m. p. 202° (Found : Cl, 20·8. Calc. : Cl, 20·5%).

Preparation of o-*Nitrosophenetole.*—The *o*-phenetidine hydrochloride (4 g.) was stirred into cold water (400 c.c.) and just basified by careful addition of aqueous sodium hydroxide, the solution being subsequently faintly acidified with acetic acid. Caro's acid [potassium persulphate (30 g.) ground with concentrated sulphuric acid (30 c.c.), poured on ice (450 g.) after 1 hour, neutralised with potassium carbonate, and just acidified with acetic acid] was stirred into the ice-cold amine solution during 3 hours, the mixture becoming green; the solid reaction product was filtered off, washed with water, and steam-distilled. o-*Nitrosophenetole* passed over as a green oil, which solidified to a white solid; this crystallised from alcohol in short needles, m. p. 93° (Found : N, 9·5. $C_8H_9O_2N$ requires N, 9·3%).

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