

151. *The Nitrosation of Phenols. Part XVII. o-Fluorophenol, and a Comparative Study of the Four o-Halogenophenols.*

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Nitrous acid reacts with *o*-fluorophenol to form a little *2-fluoro-6-nitrophenol*, but mainly *2-fluoro-4-nitrosophenol*, of which the quinoneoxime modification, like those of the other 2-halogeno-analogues, only exists in derivatives and not in the free state. In its properties and derivatives it resembles the other 2-halogeno-4-nitrosophenols now described. Further examples of the rule that nitroso-compounds melt at a lower temperature than the isomeric quinoneoximes are given.

THE action of nitrous acid on *o*-fluorophenol in aqueous solution is analogous to that on *o*-chloro-, *o*-bromo-, and *o*-iodo-phenol (Hodgson and Moore, J., 1925, **127**, 2260), *2-fluoro-4-nitrosophenol* being produced. In like manner, the quinoneoxime modification is found to exist only in salts, in a methyl ether, and in such condensation products as the *p*-nitrophenylhydrazone; *e.g.*, the highly coloured silver salt of 2-fluorobenzoquinone-4-oxime is readily formed and reacts with methyl iodide to give the steam-volatile, pale yellow *2-fluorobenzoquinone-4-oxime methyl ether*, which is also obtained when 2-fluoro-4-nitrosophenol, dissolved in alkali, is treated with methyl sulphate. *2-Fluoro-4-nitrosoanisole* is of entirely different character, having, like all true nitroso-ethers, a brilliant dark green colour. The four 2-halogeno-4-nitrosoanisoles and the corresponding 2-halogenobenzoquinone-4-oxime methyl ethers have been prepared; the former all have lower melting points than the latter, thereby furnishing further examples of the rule (Hodgson and Moore,

loc. cit.; see also Hodgson and Kershaw, J., 1929, 1555) that nitroso-compounds have lower m. p.'s than the isomeric quinone-oximes.

Support for the nitroso-structure of the nitrosation product of *o*-fluorophenol is given by the formation of *glyoxime NN'-bis-3-fluoro-4-methoxyphenyl ether* (cf. Hodgson, J., 1932, 1395) when diazomethane reacts with either 2-fluoro-4-nitrosophenol or 2-fluoro-4-nitrosoanisole.

The four glyoxime *NN'*-bis-3-halogeno-4-methoxyphenyl ethers have colours which become redder in the sequence *o*-fluoro- (bright orange) to *o*-iodo- (brick-red), and give brilliant colours with concentrated sulphuric acid which become bluer in the sequence: *o*-fluoro- (blue-violet), *o*-chloro- (blue), *o*-bromo- (dark blue), *o*-iodo- (very deep blue).

As in the attempted nitrosation of *m*-fluorophenol (Hodgson and Nicholson, J., 1939, 1405), so in the nitrosation of *o*-fluorophenol a certain amount of nitration also occurs in the 6-position to form the steam-volatile 2-fluoro-6-nitrophenol.

The results of Schiemann and Miao (*Ber.*, 1933, 66, 1179) on the nitration of *o*-fluoroanisole, as opposed to those of Holmes and Ingold (J., 1926, 1336), have been confirmed, and similar results have been obtained for the other three *o*-halogenoanisoles.

EXPERIMENTAL.

Nitrosation of o-Fluorophenol.—*o*-Fluorophenol (0.5 g.), prepared from *o*-fluoroanisole by the method of Bennett, Brookes, and Glasstone (J., 1935, 1822), was dissolved in water (60 c.c.) containing sodium nitrite (1 g.), and the solution acidified at 0° with hydrochloric acid (1 c.c., *d* 1.16); its colour changed through yellow to red and *o*-fluorophenol was precipitated in fine drops. After 1 hour, 2-fluoro-4-nitrosophenol separated in light orange-yellow needles, which were removed; the filtrate, treated with a further quantity of sodium nitrite (1 g.) in water (10 c.c.), gave a further crop after 12 hours. The combined yield (*ca.* 0.25 g.) crystallised from benzene in very pale yellow needles, m. p. 144° (decomp.) (Found: N, 10.3. C₆H₄O₂NF requires N, 10.0%), which gave the Liebermann nitroso-reaction. A concentrated solution of 2-fluoro-4-nitrosophenol in 20% aqueous sodium hydroxide was dark red-brown, but became green on dilution; on acidification it gave the original substance and not one of higher m. p. (cf. the 3-halogeno-4-nitrosophenols; Hodgson and Moore, *loc. cit.*). After removal of the 2-fluoro-4-nitrosophenol, the filtrate was extracted with benzene, the benzene layer washed with water to remove acid and extracted with dilute caustic soda solution, and this extract just acidified and steam-distilled; 2-fluoro-6-nitrophenol, which passed over, crystallised from water in golden-yellow rectangular plates, m. p. 87° (Found: N, 9.0. C₆H₄O₃NF requires N, 8.9%), which gave a red sodium salt.

Nitrosation of o-Chloro-, o-Bromo-, and o-Iodo-phenol.—Since difficulties were experienced (Hodgson and Moore, *loc. cit.*) in the nitrosation of *o*-iodophenol by standard methods (J., 1923, 123, 2502), the acetic acid and the nitrosylsulphuric acid procedure of Hodgson and Nicholson (J., 1939, 1808) were tried with the *o*-halogenophenols, and the quality and yield of the nitrosation products improved as follows:

Phenol.	Percentage yield of nitroso-compound.	
	Acetic acid method.	Nitrosylsulphuric acid method.
<i>o</i> -Chloro-	50	96
<i>o</i> -Bromo-	60	96
<i>o</i> -Iodo-	30 (with tar)	50 (no tar)

2-Chloro-4-nitrosophenol crystallised from benzene in pale yellow needles, m. p. 145° (Hodgson, J., 1932, 868, gives m. p. 142°). 2-Bromo-4-nitrosophenol crystallised from benzene or water in pale yellow needles, m. p. 156° (decomp.) (Hodgson and Moore, J., 1925, 127, 2262, give m. p. 150°). 2-Iodo-4-nitrosophenol crystallised from water in pale yellow needles, m. p. 162° (Hodgson and Moore, *loc. cit.*, give m. p. 152°). Concentrated solutions of all four 2-halogeno-4-nitrosophenols in 20% aqueous sodium hydroxide were dark red-brown and became green on dilution with water. All gave Liebermann nitroso-reactions similar to that of 2-fluoro-4-nitrosophenol.

2-Halogenobenzoquinone-4-oxime Methyl Ethers.—(a) Aqueous ammonia was added to a solution of the 2-halogeno-4-nitrosophenol in aqueous methyl alcohol containing the equivalent amount of silver nitrate, and the dark brown silver salt of the 2-halogenobenzoquinone-4-oxime which separated was treated with methyl iodide. The 2-halogenobenzoquinone-4-oxime methyl ether produced was isolated by steam-distillation. Excess of ammonia redissolved the silver salts, forming deep green solutions.

(b) An intimate mixture of the 2-halogeno-4-nitrosophenol, an excess of slightly moist potassium carbonate, and the requisite amount of methyl sulphate was heated for some time under reflux, and the 2-halogenobenzoquinone-4-oxime methyl ether isolated by steam-distillation.

The ethers all recrystallised from hot water in pale yellow needles. *2-Fluorobenzoquinone-4-oxime methyl ether* had m. p. 89° (Found: N, 9.2. $C_7H_6O_2NF$ requires N, 9.0%), *2-chlorobenzoquinone-4-oxime methyl ether*, m. p. 118—120° (Hodgson, *loc. cit.*, gives m. p. 118—120°) (Found: N, 8.3. Calc.: N, 8.1%), *2-bromobenzoquinone-4-oxime methyl ether*, m. p. 105° (Found: N, 6.8. $C_7H_6O_2NBr$ requires N, 6.5%), and *2-iodobenzoquinone-4-oxime methyl ether*, m. p. 120° (Found: N, 5.5. $C_7H_6O_2NI$ requires N, 5.3%).

2-Halogenobenzoquinone-4-oxime-1-p-nitrophenylhydrazones.—A methyl-alcoholic solution containing equimolecular quantities of the 2-halogeno-4-nitrosophenol (e.g., 0.14 g. of 2-fluoro-4-nitrosophenol) and *p*-nitrophenylhydrazine hydrochloride (0.19 g.) was boiled with sodium acetate (0.2 g.), and the precipitated 2-halogenobenzoquinone-4-oxime-1-*p*-nitrophenylhydrazone crystallised from glacial acetic acid. All four compounds gave permanganate-violet colours with aqueous alkali hydroxide, but with concentrated sulphuric acid only yellow solutions were produced. *2-Fluorobenzoquinone-4-oxime-1-p-nitrophenylhydrazone* crystallised in yellow micro-plates, m. p. 195° (decomp.) (Found: N, 20.4. $C_{12}H_9O_3N_4F$ requires N, 20.3%), *2-chlorobenzoquinone-4-oxime-1-p-nitrophenylhydrazone* in yellow-brown micro-plates, m. p. 184—185° (decomp.) [Hodgson, *loc. cit.*, gives m. p. 184—185° (decomp.)] (Found: N, 19.3. Calc.: N, 19.1%), *2-bromobenzoquinone-4-oxime-1-p-nitrophenylhydrazone* in brown micro-plates, m. p. 191° (decomp.) (Found: N, 16.8. $C_{12}H_9O_3N_4Br$ requires N, 16.6%), and *2-iodobenzoquinone-4-oxime-1-p-nitrophenylhydrazone* in brown micro-plates, m. p. 187° (decomp.) (Found: N, 14.8. $C_{12}H_9O_3N_4I$ requires N, 14.6%).

2-Halogeno-4-nitrosoanisoles.—The 2-halogenoanisoles underwent mononitration in the 4-position (cf. Schiemann and Miao, *loc. cit.*, for the case of *o*-fluoroanisole) to give 2-halogeno-4-nitrosoanisoles, which were readily reduced to the steam-volatile 2-halogeno-4-aminoanisoles by the usual iron-alcoholic hydrochloric acid method. The 2-halogeno-4-nitrosoanisoles were then prepared as follows: Potassium persulphate (3 g.) was added to sulphuric acid (6 g., *d* 1.84) and the mixture was kept for 45 minutes with occasional stirring, then poured on ice (40 g.), neutralised with potassium carbonate, and made slightly acid with acetic acid. This solution of Caro's acid was mixed with a suspension of the 2-halogeno-4-aminoanisole (0.5 g.) in water (40 c.c.) at 0°, the mixture stirred for 3 hours, the liquid filtered, and the green residue washed with water and steam-distilled. The 2-halogeno-4-nitrosoanisole which passed over was crystallised from light petroleum.

2-Fluoro-4-nitrosoanisole formed dark green needles, m. p. 69° (Found: N, 9.2. $C_7H_6O_2NF$ requires N, 9.0%), *2-chloro-4-nitrosoanisole*, brilliant blue-green needles, m. p. 89° (Found: N, 8.2. Calc.: N, 8.1%), *2-bromo-4-nitrosoanisole*, green needles, m. p. 85° (Found: N, 6.6. $C_7H_6O_2NBr$ requires N, 6.5%), and *2-iodo-4-nitrosoanisole*, yellowish-green needles, m. p. 77° (Found: N, 5.5. $C_7H_6O_2NI$ requires N, 5.3%).

Glyoxime NN'-Bis-3-halogeno-4-methoxyphenyl Ethers.—When ethereal solutions of 2-halogeno-4-nitrosophenols (0.1 g.) and diazomethane (from 1 c.c. of nitrosomethylurethane) were mixed together, evolution of nitrogen occurred and the glyoxime *NN'*-bis-3-halogeno-4-methoxyphenyl ether was precipitated; it was crystallised from ether or methyl alcohol. Identical products were obtained when diazomethane reacted with the 2-halogeno-4-nitrosoanisoles. Steam-distillation of the filtered ethereal solutions above afforded in each case small amounts of the corresponding 2-halogenobenzoquinone-4-oxime methyl ether. The characteristic colours given with concentrated sulphuric acid are placed after the m. p.

Glyoxime NN'-bis-3-fluoro-4-methoxyphenyl ether formed bright orange needles, m. p. 211° (blue-violet) (Found: N, 8.6. $C_{16}H_{14}O_4N_2F_2$ requires N, 7.6%), *glyoxime NN'-bis-3-chloro-4-methoxyphenyl ether*, orange-red needles, m. p. 223° (blue) (Found: N, 7.6. Calc.: N, 7.6%), *glyoxime NN'-bis-3-bromo-4-methoxyphenyl ether*, dark orange-red needles, m. p. 211° (deep blue) (Found: N, 6.2. $C_{16}H_{14}O_4N_2Br_2$ requires N, 6.1%), and *glyoxime NN'-bis-3-iodo-4-methoxyphenyl ether*, brick-red needles, m. p. 219° (very deep blue) (Found: N, 5.3. $C_{16}H_{14}O_4N_2I_2$ requires N, 5.1%).

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