XLV.—*Nitrosation of Phenols. Part V. Preparation of an* o-*Nitrosophenol.*

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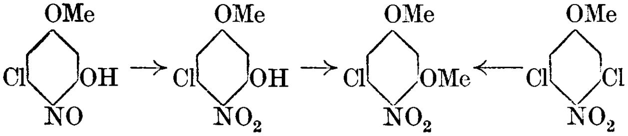
NITROSATION of 5-chloro-3-hydroxyanisole proceeds readily (compare 3 : 5-dichlorophenol; J., 1927, 2216). The constitution of the product (I) was proved by oxidation to the *nitro*-compound (II), the methyl ether of which was identical with 5-*chloro*-4-*nitroresorcinol dimethyl ether* (III), prepared by the action of sodium methoxide on 3 : 5-dichloro-4-nitroanisole (IV). The directive power of the methoxyl group in 5-chloro-3-hydroxyanisole has therefore completely overcome the para-directing influence of the chlorine atom.

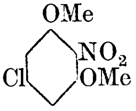
The nitroso-formula is preferred to the quinone-oxime formula for 5-*chloro*-4-*nitroso*-3-*hydroxyanisole* (I) on account of its deep green colour and low m. p. (compare Hodgson and Moore, J., 1925, **127**, 2260).

3 : 5-Dichloro-2-nitroanisole reacts readily with sodium methoxide to give 5-*chloro*-2-*nitroresorcinol·dimethyl ether* (V); the reactivity of the 3-chlorine atom contrasts strongly with the

stability of the halogen in 3-chloro-2-nitroanisole (Hodgson and Handley, J., 1926, 542).



(I.) (II.) (III.) (IV.)



(V.)

Unlike 3 : 5-dichlorodimethylaniline, 5-*chloro*-3-*methoxydimethylaniline* is readily nitrosated. The product is probably 5-chloro-4-nitroso-3-methoxydimethylaniline, but on boiling with dilute alkali solution it gives, not the expected 5-chloro-6-nitroso-3-hydroxyanisole, but products of profound decomposition.

EXPERIMENTAL.

5-*Chloro*-4-*nitroso*-3-*hydroxyanisole* (I).—A solution of 5-chloro-3-hydroxyanisole (8 g.) in water (900 c.c.) containing sodium hydroxide (2·5 g.) and sodium nitrite (20 g.) was cooled to 0°, and sulphuric acid (6 g. of 98% acid in 30 c.c. of water) added during 2 hours. The 5-*chloro*-4-*nitroso*-3-*hydroxyanisole*, obtained in almost theoretical yield after 6 hours, crystallised from methyl alcohol in deep green needles, m. p. 132° (decomp.) (Found: Cl, 18·9. $C_7H_6O_3NCl$ requires Cl, 18·9%), which are insoluble in light petroleum, slightly soluble in benzene, alcohol, carbon tetrachloride, and water, and moderately easily soluble in acetone, ether, and glacial acetic acid. The nitroso-compound does not respond to the Liebermann nitrosoamine test, gives a Bordeaux-red colour in concentrated sulphuric acid, is not affected by hot *N*-hydrochloric acid but is decomposed by the hot concentrated acid. From its deep green solution in 10% aqueous sodium hydroxide it is precipitated unchanged on acidification; hot concentrated alkalis decompose it.

5-*Chloro*-4-*nitro*-3-*hydroxyanisole* (II) was obtained by dissolving 5-chloro-4-nitroso-3-hydroxyanisole (3·3 g.) in a hot solution of potassium hydroxide (1 g.) in water (50 c.c.) and then adding potassium hydroxide (9 g. in 20 c.c. of water), followed by finely powdered potassium ferricyanide (17·5 g.); the whole was kept at 60° for about 3 hours until the colour changed from deep green to orange. (This procedure is necessary to avoid the decomposition referred to above.) The mixture was then faintly acidified and the 5-*chloro*-4-*nitro*-3-*hydroxyanisole* (2·2 g.) removed by steam distillation. The product crystallised from dilute methyl alcohol in light golden needles, m. p. 105°,(Found : Cl, 17·2. $C_7H_6O_4NCl$ requires Cl, 17·4%), which are only slightly soluble in water and light petroleum but very soluble in carbon tetrachloride, chloroform, ether, benzene, and glacial acetic acid. It gives a red colour with sulphuric acid and an orange solution in aqueous sodium hydroxide.

Nitration of 5-*Chloro*-3-*hydroxyanisole.*—A solution of the chlorohydroxyanisole (4 g.) in water (80 c.c.) containing sodium nitrate (3 g.) was treated at 100° with a mixture of sulphuric acid (98%; 3 c.c.) and water (20 c.c.), added gradually during 1 hour. After remaining for 2 hours at 100°, the bulk of the initial material was recovered unchanged, but distillation with steam gave a small quantity of 5-chloro-4-nitro-3-hydroxyanisole, identical with the compound described above.

5-*Chloro*-4-*nitroresorcinol dimethyl ether* (III) was prepared by treating either of the above products in boiling xylene with excess of methyl sulphate in presence of potassium carbonate. It crystallised from methyl alcohol in light yellow needles, m. p. 123° (Found : Cl, 16·1. $C_8H_8O_4NCl$ requires Cl, 16·3%).

Action of Sodium Methoxide on (a) 3 : 5-*Dichloro*-2-*nitroanisole and* (b) 3 : 5-*Dichloro*-4-*nitroanisole.*—2- and 4-Nitro-3 : 5-dichlorophenols were prepared by a modification of Hodgson and Wignall's method (J., 1927, 2218), the resinous nitration product from 3 : 5-dichlorophenol being separated from the acid liquor, washed free from acid, and very slowly steam-distilled. 3 : 5-Dichloro-2-nitrophenol then passed over as a colourless solid, which, on heating or on exposure to air, was transformed into the lemon-yellow anhydrous substance previously described (*loc. cit.*), the change indicating the existence of a hydrate similar to, although more labile than, that formed by 3-chloro-2-nitrophenol (Hodgson and Moore, J., 1926, 155).

(*a*) A mixture of 3 : 5-dichloro-2-nitroanisole (2·2 g.) and sodium methoxide (methyl alcohol, 18 c.c.; sodium, 0·8 g.) was gently boiled under reflux for 4 hours. 5-*Chloro*-2-*nitroresorcinol dimethyl ether* (V) was deposited on cooling. It crystallised from methyl alcohol in colourless needles, m. p. 171° (Found : Cl, 16·0. $C_8H_8O_4NCl$ requires Cl, 16·3%), and was less soluble in most solvents than the 4-nitro-isomeride (below).

(*b*) Similar treatment of 3 : 5-dichloro-4-nitroanisole gave a substance identical with 5-chloro-4-nitroresorcinol dimethyl ether, described above; " mixed " m. p. 123° (Found : Cl, 16·2%).

5-*Chloro*-3-*methoxydimethylaniline.*—5-Chloro-3-methoxyaniline (6 g.), methyl alcohol (12 c.c.), and methyl sulphate (11 c.c.) were heated together in a sealed tube at 165° for 6 hours. (At a higher temperature charring takes place.) The mixture was diluted with water (200 c.c.), made faintly alkaline, and steam-distilled. The oil that passed over was treated with acetic anhydride and again steam-distilled, 5-*chloro*-3-*methoxydimethylaniline* being thus obtained as a colourless oil (Found : Cl, 19·2. $C_9H_{12}ONCl$ requires Cl, 19·1%) readily soluble in dilute acids.

Nitrosation. A solution of 5-chloro-3-methoxydimethylaniline (2 g.) in concentrated hydrochloric acid (3 c.c.) was diluted with water (30 c.c.), cooled to 0°, and treated gradually with sodium nitrite (1·5 g. in water, 10 c.c.); a yellow hydrochloride separated. 5-*Chloro*-4-*nitroso*-3-*methoxydimethylaniline* was liberated from this. After being washed with ether, it crystallised from methyl alcohol in green needles, decomp. 155° (Found : Cl, 16·4. $C_9H_{11}O_2N_2Cl$ requires Cl, 16·6%). It is insoluble in light petroleum, sparingly soluble in ether and carbon tetrachloride, but more readily soluble in chloroform, benzene, and acetone; the solutions are green. It does not give the Liebermann nitrosoamine reaction, develops a deep cherry-red colour in concentrated sulphuric acid, and is completely decomposed on prolonged boiling with 10% aqueous potassium hydroxide, methylamine being evolved.

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