

111. *The Nitrosation of Phenols. Part XIII.* *o-Chlorophenol.*

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THE substance obtained (Kehrmann, *Ber.*, 1888, **21**, 3316; *Annalen*, 1894, **279**, 30; Bridge, *Annalen*, 1893, **277**, 100) by the oximation of 2-chloro-*p*-benzoquinone has now been prepared by the nitrosation of *o*-chlorophenol, and evidence is given that it is 2-chloro-4-nitrosophenol rather than 2-chloro-*p*-benzoquinone-4-oxime.

o-Chlorophenol undergoes nitrosation (40%) more rapidly than the *m*-isomeride, probably for steric reasons, and a diazonium salt is also formed.

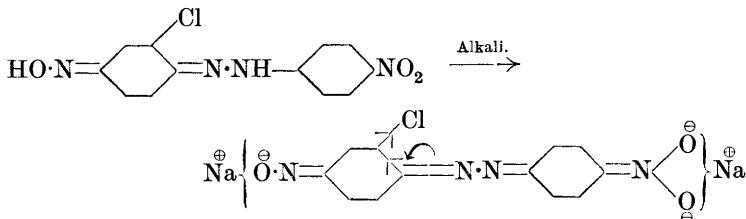
The quinonoid structure was previously assigned to 2-chloro-4-nitrosophenol on account of its mode of preparation and the quinonoid structure of its methyl ether. Its relatively low melting point (compare 3-chlorobenzoquinone-4-oxime), however, indicates the nitroso-structure (compare Hodgson and Moore, *J.*, 1925, **127**, 2260; Hodgson and Kershaw, *J.*, 1929, 1555), further support for which is afforded by the ready formation of a *picrate* and of molecular *compounds* with the 3-methyl- and 3-halogeno-2:4:6-trinitrophenols (compare Hodgson, *J.*, 1931, 1495, 2227). The m. p.'s of the above products are very close to those of their 3-chloro-isomerides.

2-Chloro-4-nitrosophenol is considerably less reactive than its 3-chloro-isomeride, probably owing to co-ordination of the chlorine with the hydroxyl group (compare Sidgwick and Callow, *J.*, 1924, **125**, 533); when treated in aqueous-alcoholic solution with hydroxylamine hydrochloride in the presence of β -naphthol (followed by sodium acetate) or β -naphthylamine, it yields only traces of azo-compounds. To this co-ordination may be ascribed its marked solubility in alcohol and in water, its crystallisation unchanged from ether saturated with hydrogen chloride (compare the ready

transformation of the 3-chloro-isomeride into the quinone-oxime modification), and its precipitation by acids from solutions in alkaline hydroxides and alkaline carbonates.

The quinone-oxime modification of 2-chloro-4-nitrosophenol has so far only been found in its salts, in a methyl ether, and in condensation products with *p*-nitrophenylhydrazine and semicarbazide. The highly coloured *silver* salt is readily formed and reacts with methyl iodide to give the light greenish-yellow 2-chloro-*p*-benzoquinone-4-oxime methyl ether (m. p. 118—120°), which is also obtained when 2-chloro-4-nitrosophenol, dissolved in alkali, is treated with methyl sulphate. 2-Chloro-4-nitrosoanisole is an entirely different substance, having a brilliant blue-green colour like all true nitroso-ethers, and melting at 89° in accordance with the rule referred to above.

2-Chloro-4-nitrosophenol appears to react with *p*-nitrophenylhydrazine hydrochloride only in the presence of sodium acetate, this indicating an inhibition of the preliminary isomerisation to the quinone-oxime structure which must precede condensation. The *p*-nitrophenylhydrazone is much more soluble in the usual solvents than its 3-chloro-isomeride, and gives a permanganate-violet colour with aqueous caustic alkalis as compared with the brilliant pure blue afforded by the latter. This hypsochromic result would appear to indicate a powerful electron-restraining ($-I$) effect on the part of the chlorine atom ortho to the double indamine chromophore :



The same effect is manifested in an inhibition of salt-formation with concentrated sulphuric acid, since the *p*-nitrophenylhydrazone merely dissolves to give a yellow solution instead of the anticipated cherry-red colour similar to that given by the 3-chloro-isomeride, in which the inductive effect of the chlorine emanates from the meta-position and is therefore very feeble.

EXPERIMENTAL.

Nitrosation of o-Chlorophenol.—Cold dilute sulphuric acid (8 c.c. of acid, 16 c.c. of water) is gradually added with stirring to a solution of *o*-chlorophenol (4 g.), sodium hydroxide (2 g.), and sodium

nitrite (10 g.) in water (300 c.c.) at 15°, and after 5 minutes the liquid is filtered as rapidly as possible from the initially formed tar. 2-Chloro-4-nitrosophenol quickly separates in fine, light orange yellow needles, which are immediately removed, and further crops are obtained on keeping (yield, *ca.* 2.5 g.). The filtrate couples readily with alkaline β -naphthol and with β -naphthylamine if free nitrous acid is previously removed, the weights of azo-product obtained corresponding approximately to the balance of the *o*-chlorophenol not obtained as the nitroso-compound.

Some Reactions of 2-Chloro-4-nitrosophenol.—The compound, which is much more soluble in methyl and ethyl alcohols and ether than the 3-chloro-isomeric, crystallises from benzene in very pale yellow, almost colourless, needles, m. p. 142° (decomp.) (Bridge, *loc. cit.*, gives m. p. 142°) (Found: Cl, 22.3. Calc.: Cl, 22.5%), has the normal molecular weight in phenol and *o*-cresol, and dissolves in the usual organic solvents, forming yellow-green solutions which become greener on dilution or on addition of mineral acids. A concentrated solution in 10% aqueous sodium hydroxide is deep red, but becomes green on dilution; the crude product precipitated by hydrochloric acid has m. p. 141° and crystallises from benzene in almost colourless needles, m. p. 145° (decomp.).

Silver Salt of 2-Chlorobenzoquinone-4-oxime.—Cautious addition of aqueous ammonia to equal molecular quantities of 2-chloro-4-nitrosophenol and silver nitrate in methyl-alcoholic solution precipitates a brown-red silver salt (Found: Ag, 40.6. $C_6H_3O_2NClAg$ requires Ag, 40.8%), which redissolves in excess of ammonia, forming a deep green solution.

2-Chlorobenzoquinone-4-oxime methyl ether, obtained from the above silver salt and methyl iodide in the cold and removed by steam distillation, is fairly readily soluble in hot water, from which it crystallises, on cooling, in pale greenish-yellow needles, m. p. 118—120° (Kehrmann, *loc. cit.*, gives m. p. 122—123°) (Found: Cl, 20.6. Calc.: Cl, 20.7%), which depress the m. p. 89° of authentic 2-chloro-4-nitrosoanisole.

2-Chlorobenzoquinone-4-oxime-1-p-nitrophenylhydrazone.—When a methyl-alcoholic solution containing equal molecular quantities of 2-chloro-4-nitrosophenol and *p*-nitrophenylhydrazine hydrochloride is boiled with sodium acetate, condensation occurs immediately. The *p*-nitrophenylhydrazone crystallises from glacial acetic acid, after addition of a little water, in yellow-brown micro-plates, m. p. 184—185° (decomp.) (Found: N, 19.3; Cl, 12.0. $C_{12}H_9O_3N_4Cl$ requires N, 19.1; Cl, 12.1%).

2-Chlorobenzoquinone-4-oxime-1-semicarbazone separates rapidly, when a solution containing 2-chloro-4-nitrosophenol and semicarbazone

azide hydrochloride in equal molecular proportion is heated, in light brown-yellow micro-needles, which are very sparingly soluble in the usual organic solvents and decompose from 150° upwards (Found: N, 26.4; Cl, 16.4. $C_7H_7O_2N_4Cl$ requires N, 26.1; Cl, 16.55%). The compound gives a deep yellow solution in concentrated sulphuric acid and a deep greenish-yellow solution in aqueous sodium hydroxide.

Reactions of 2-Chloro-4-nitrosophenol with Picric Acid and its Analogues.—A mixture of the nitrosophenol (0.5 g.) and picric acid (0.76 g.) or an analogue (corresponding stoichiometric quantity) is dissolved in hot methyl alcohol, and the deep green solution filtered; the *picrate* or an *analogue* is immediately deposited in good yield on cooling, and subsequently recrystallised from alcohol or acetic acid. The following *compounds* have been prepared: (from picric acid) greenish-yellow rectangular plates, m. p. $156-158^{\circ}$ (decomp.) (Found: Cl, 9.0. $C_{12}H_7O_9N_4Cl$ requires Cl, 9.2%); (from 2:4:6-trinitro-*m*-cresol) yellow hexagonal plates, m. p. 147.5 (decomp.) (Found: Cl, 8.6. $C_{13}H_9O_9N_4Cl$ requires Cl, 8.8%); (from 3-fluoro-2:4:6-trinitrophenol) yellow rectangular prisms, m. p. 151° (decomp.) (Found: Cl, 8.7. $C_{12}H_6O_9N_4ClF$ requires Cl, 8.8%); (from 3-chloro-2:4:6-trinitrophenol) yellow rectangular parallelepipeds, m. p. 164° (decomp.) (Found: Cl, 16.7. $C_{12}H_6O_9N_4Cl_2$ requires Cl, 16.86%); (from 3-bromo-2:4:6-trinitrophenol) yellow parallelepipeds, m. p. 163° (decomp.) (Found: Cl + Br, 24.6. $C_{12}H_6O_9N_4ClBr$ requires Cl + Br, 24.8%); (from 3-iodo-2:4:6-trinitrophenol) yellow parallelepipeds, m. p. 169° (decomp.) (Found: Cl + I, 31.4. $C_{12}H_6O_9N_4ClI$ requires Cl + I, 31.7%). 2-Chloro-4-nitrosophenol crystallises unchanged from solutions in various organic solvents containing urea or acridine.

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