

CCIV.—*The Nitrosation of Phenols. Part XI. The Constitution of 3-Chloro-4-nitrosophenol.*

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THE 4-nitroso-structure assigned to the greenish-yellow derivative obtained by the direct nitrosation of *m*-chlorophenol (Hodgson and Moore, J., 1923, **123**, 2499; Hodgson and Kershaw, J., 1929, 1553) has now been confirmed by reduction of the derivative to 3-chloro-4-aminophenol.

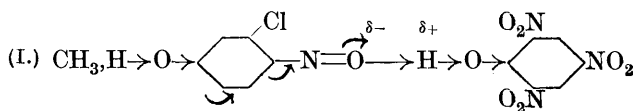
All attempts to attack the phenolic hydrogen in 3-chloro-4-nitrosophenol have resulted in the formation either of the tautomeride 3-chlorobenzoquinone-4-oxime or of the product which this affords under identical conditions. For instance, both substances

give the same *silver* salt: this on treatment with methyl iodide yields 3-chlorobenzoquinone-4-oxime methyl ether, which is also produced from 3-chloro-4-nitrosophenol by the action of methyl sulphate and alkali or of ethereal diazomethane. Both substances react with *p*-nitrophenylhydrazine hydrochloride to give the same *p*-nitrophenylhydrazone. Further, dry hydrogen chloride immediately converts the nitrosophenol into the quinoneoxime in ethereal solution. Also, aluminium chloride reacts vigorously with 3-chloro-4-nitrosoanisole in dry ether, 3-chlorobenzoquinone-4-oxime being formed.

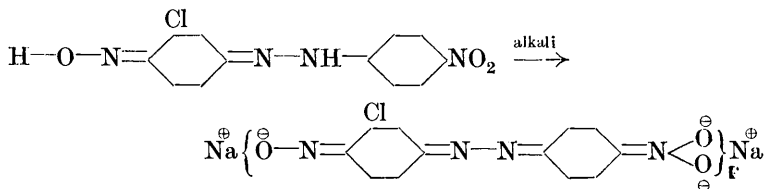
Further confirmation of the nitroso-structure of 3-chloro-4-nitrosophenol has been found in its great reactivity in comparison with the quinoneoxime.

Hydroxylamine reacts with true nitroso-compounds (*e.g.*, nitrosobenzene) to give diazo-compounds (Bamberger, *Ber.*, 1895, 28, 1218). In cold methyl- or ethyl-alcoholic solution or in aqueous suspension, 3-chloro-4-nitrosophenol and 3-chlorobenzoquinone-4-oxime react very slowly with hydroxylamine hydrochloride, but in boiling alcohol the former gives an appreciable amount of *m*-chlorophenol, formed by elimination of the diazo-group from the initial product, whereas the latter gives little if any: when a substance is also present with which the diazo-compound can readily couple, *e.g.*,  $\beta$ -naphthylamine, the nitroso-compound rapidly (in hot solution) yields 3-chloro-1-hydroxybenzene-4-azo- $\beta$ -naphthylamine, whereas the quinoneoxime gives a mixture of products in which the azo-compound has not been detected. Again, when cold solutions of the two isomerides in aqueous methyl alcohol containing hydroxylamine hydrochloride and  $\beta$ -naphthol are treated gradually with aqueous sodium acetate, an azo-compound is almost immediately formed from the nitrosophenol, but none from the quinoneoxime.

Yet another point in favour of the nitroso-structure for 3-chloro-4-nitrosophenol is the ready formation of a picrate. That such should be the case follows from electronic considerations (Hodgson and Kershaw, *loc. cit.*), since the activated nitroso-oxygen (I) will tend to attach the picric acid molecule, whereas the quinoneoxime, being a stabilised form, should be (and is) unreactive. This view is supported by the facts that 3-chloro-4-nitrosoanisole also readily forms a picrate (I), whereas 3-chlorobenzoquinone-4-oxime methyl ether crystallises unchanged from its solution in alcoholic picric acid.



The oximic structure for 3-chlorobenzoquinone-4-oxime follows from the formation of a *p*-nitrophenylhydrazone. This gives a brilliant pure blue colour when treated with aqueous or alcoholic caustic alkali or ammonia—a fact probably best explained by the structural change



inasmuch as the formation of a double indamine structure (double quinonoid) would account for the abrupt colour change from red to blue. In the anion above, the chromophoric group, =N=N=, the isomeride of the azo-group, would definitely appear to exist (compare Hewitt and Mitchell, J., 1907, **91**, 1251). With concentrated sulphuric acid, the colour produced (cherry-red, changing to crimson on dilution) is that to be expected from an azo-dye (hydrazone form).

The by-products formed during the preparation of 3-chloro-4-nitrosophenol (Hodgson and Kershaw, *loc. cit.*) include a small amount of 3-chloro-6-nitrosophenol, indicating nitration in the ortho-position by nitrous acid (compare Hodgson and Kershaw, J., 1930, 277), this being facilitated by the deactivating effect of the 3-chlorine atom on the 4-carbon in *m*-chlorophenol. When a large excess of nitrous acid is used, the yield of 3-chloro-4-nitrosophenol is only about 40%, the main product being a diazonium salt (Fischer and Hepp, *Annalen*, 1888, **243**, 282, found that certain nitroso-compounds are directly converted into diazonium salts by three equivalents of nitrous acid). Oxidation of the mother-liquor after removal of the nitrosophenol yielded a small amount of chlorobenzoquinone, the main product being non-volatile in steam.

#### EXPERIMENTAL.

*Note on the Reaction between Nitrous Acid and m-Chlorophenol.*—The mother-liquor from the preparation of 3-chloro-4-nitrosophenol (Hodgson and Kershaw, *loc. cit.*) was divided into aliquot portions, which afforded : (a) a small quantity of 3-chloro-6-nitrosophenol by steam distillation : that this was a product of the nitrosation, and not one formed subsequently by oxidation during the passage of steam, was proved by its presence in similar amount in a benzene extract of another portion of the original mother-liquor ; (b) an azo-compound, by coupling with alkaline  $\beta$ -naphthol, in amount

corresponding to at least 50% of the original *m*-chlorophenol nitrosated; (c) after removal of nitrous acid by prolonged contact with urea, a similar yield of an azo-compound with  $\beta$ -naphthylamine; (d) a small amount of chlorobenzoquinone, when steam-distilled after oxidation with cold chromic acid, and a large amount of a brown solid of indefinite m. p.

*Some Reactions of 3-Chloro-4-nitrosophenol.*—After recrystallisation from methyl alcohol (the best solvent), the nitrosophenol has m. p. 135° (Hodgson and Kershaw, *loc. cit.*, give 133°). The yellowish-green colour of the solution becomes a much deeper green on addition of a drop of concentrated sulphuric acid or oleum; on keeping or on further addition of oleum, a deep red colour (due to isomerisation) is produced.

When dry hydrogen chloride is passed into an ethereal solution of the nitrosophenol, 3-chlorobenzoquinone-4-oxime, m. p. 184° (decomp.), is immediately produced.

When diazomethane (from nitrosomethylurethane) is distilled into solutions of the nitrosophenol in dry ether, either alone or after treatment with hydrogen chloride or a drop of concentrated sulphuric acid, in all three cases 3-chlorobenzoquinone-4-oxime methyl ether is produced, m. p. and mixed m. p. 113°. When the nitrosophenol is reduced with a cold solution of sodium hyposulphite containing sodium carbonate, 3-chloro-4-aminophenol is formed, m. p. and mixed m. p. 159–160° (Hodgson and Kershaw, *J.*, 1928, 2703).

*Attempts to prepare the Silver Salt of 3-Chloro-4-nitrosophenol.*

(a) Molecular quantities of the nitrosophenol and silver nitrate in methyl-alcoholic solution remained unchanged for several days; on treatment with methyl iodide, all the silver nitrate was quantitatively precipitated as iodide and the nitrosophenol was recovered unaltered.

(b) Introduction of aqueous ammonia into a solution as (a) produced a brick-red *silver* salt (Found: Ag, 40.6.  $C_6H_3O_2NClAg$  requires Ag, 40.8%): this was also formed even when ammonia was blown over the surface of the solution. A similar result was obtained by using sodium acetate instead of aqueous ammonia, and silver acetate reacted with the nitrosophenol in methyl-alcoholic solution to give the same silver salt. Similarly, 3-chlorobenzoquinone-4-oxime gave the same salt. All the specimens reacted with methyl iodide in the cold to form 3-chlorobenzoquinone-4-oxime methyl ether, which was removed by steam distillation and crystallised from water, forming very pale yellow needles (elongated plates), m. p. and mixed m. p. 113° (Found for a mixture of specimens: Cl, 20.6. Calc.: Cl, 20.7%).

(c) Molecular quantities of the above silver salt and the nitrosophenol were shaken together in methyl alcohol, and also warmed together in the same medium, but in both cases reaction with methyl iodide resulted in the formation of 3-chlorobenzoquinone-4-oxime methyl ether, the nitrosophenol being recovered unchanged.

*3-Chlorobenzoquinone-4-oxime-1-p-nitrophenylhydrazone.*—When a methyl-alcoholic solution of 3-chloro-4-nitrosophenol or 3-chlorobenzoquinone-4-oxime and *p*-nitrophenylhydrazine hydrochloride in molecular proportion was boiled, the *p*-nitrophenylhydrazone rapidly separated as a microcrystalline powder, almost insoluble in methyl or ethyl alcohol and sparingly soluble in acetone or in glacial acetic acid, from which it crystallised in orange-red micro-plates of indefinite m. p. (slow decomp. about 200°) (Found for the two specimens: N, 19.4, 19.4.  $C_{12}H_9O_3N_4Cl$  requires N, 19.1%).

*Reactions of 3-Chloro-4-nitrosophenol and 3-Chlorobenzoquinone-4-oxime with Hydroxylamine Hydrochloride.*—(a) *In boiling methyl- or ethyl-alcoholic solution.* Qualitative experiments established that the nitrosophenol gave an appreciable quantity of *m*-chlorophenol, whereas the quinoneoxime gave only a trace, being transformed into a brown substance which was not volatile in steam and decomposed suddenly between 210° and 220°.

The nitrosophenol (0.5 g.) and the quinoneoxime (0.5 g.) were each dissolved in methyl alcohol (20 c.c.) and treated with solutions of hydroxylamine hydrochloride (2.0 g.) in water (5 c.c.). The mixtures were boiled for 30 minutes on the same water-bath, kept over-night, and steam distilled until 300 c.c. of liquor had passed over. Bromine water (in excess) was added to each distillate, and the precipitates of 3-chloro-2:4:6-tribromophenol (identified by m. p. and mixed m. p.) were dried and weighed; the nitrosophenol gave 0.154 g., and the quinoneoxime 0.013 g. A blank steam distillation of 0.5 g. of the nitrosophenol, followed by bromination as above, gave 0.055 g. of a substance, m. p. 135° [depressed by admixture with 3-chloro-2:4:6-tribromophenol (m. p. 105–106°)].

In one of the qualitative experiments referred to above, the *m*-chlorophenol solution on treatment with sulphuric acid and sodium nitrite deposited crystals of 3-chloro-4-nitrosophenol.

(b) *In presence of  $\beta$ -naphthylamine.* The nitrosophenol (1 g.), dissolved in methyl alcohol (20 c.c.), was treated with a solution of hydroxylamine hydrochloride (0.5 g.) in water (5 c.c.) and then with a solution of  $\beta$ -naphthylamine (1 g.) in methyl alcohol (20 c.c.). The mixture was boiled for 30 minutes, and the liquid filtered hot. A residue (0.4 g.) remained of dark red-brown needles with a strong green reflex, m. p. 210–212°, which analysis (Found: N, 14.4.  $C_{16}H_{12}ON_3Cl$  requires N, 14.6%) indicated to be 3-chloro-1-hydroxy-

*benzene-4-azo-β-naphthylamine*. The filtrate on cooling deposited a further crop, m. p. and mixed m. p. 210—212° (Found : N, 14·5%).

(c) *In presence of β-naphthol*. The nitrosophenol (0·2 g.) was dissolved in methyl alcohol in presence of hydroxylamine hydrochloride (0·2 g.) and β-naphthol (0·2 g.). No visible change occurred until an aqueous solution of sodium acetate was added; the mixture then immediately became light red and an azo-compound subsequently separated. The quinoneoxime, prepared from the silver salt and therefore free from the nitrosophenol, did not give this azo-compound but was converted into the brown product previously mentioned.

*Reaction of 3-Chloro-4-nitrosophenol with Picric Acid*.—A mixture of the nitrosophenol (0·5 g.) and picric acid (0·76 g.) was dissolved in hot methyl alcohol (15 c.c.), and the deep green solution was filtered and allowed to cool slowly; it almost immediately deposited a *picrate* in quantitative yield, which crystallised in large, bright greenish-yellow, hexagonal plates, m. p. 151° (decomp.) (Found : Cl, 9·1.  $C_6H_4O_2NCl, C_6H_3O_7N_3$  requires Cl, 9·2%). This observation was made in collaboration with Dr. A. Kershaw.

3-Chloro-4-nitrosoanisole similarly gave a *picrate*, which crystallised from 50% alcohol in sandy yellow micro-plates, m. p. 174·5° (decomp.) (Found : Cl, 8·7.  $C_7H_6O_2NCl, C_6H_3O_7N_3$  requires Cl, 8·9%).

*The Action of Aluminium Chloride on 3-Chloro-4-nitrosoanisole*.—Aluminium chloride was added gradually to a solution of 3-chloro-4-nitrosoanisole in dry ether (and also in dry benzene) until the vigorous reaction subsided, and, after decomposition of the mixture with ice and dilute hydrochloric acid, the ethereal (or benzene) layer was allowed to evaporate gradually; crystals of 3-chlorobenzoquinone-4-oxime were deposited, m. p. 184° after recrystallisation from alcohol. The silver salt obtained from it reacted with methyl iodide to give 3-chlorobenzoquinone-4-oxime methyl ether, m. p. and mixed m. p. 113°.

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