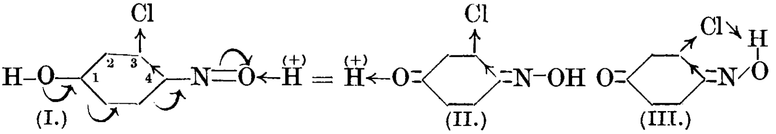
CCI.—*The Nitrosation of Phenols. Part VI. Further Study of the Nitrosation of* m-*Chlorophenol.*

By Herbert Henry Hodgson and Arnold Kershaw.

The two alleged forms of 3-chlorobenzoquinone-4-oxime, stable respectively towards acid and alkali (Hodgson and Moore, J., 1923, **123**, 2499), are now shown to be impure specimens of one 3-chlorobenzoquinone-4-oxime, the reddish colour of the acid-stable specimen being due to traces of decomposition products formed during the drastic acid treatment. As Hodgson and Moore have shown (J., 1926, 2036) that Kehrmann's stereoisomeric 4-chloro- and 4-bromo-2 : 5-toluquinoneoximes are also impure specimens of individual compounds, geometrical isomerides of this type of product have not yet been prepared.

The conversion of 3-chloro-4-nitrosophenol into the oxime by acid and by alkali is readily explained by current electronic theories (see Allan, Oxford, Robinson, and Smith, J., 1926, 401; numerous papers by Ingold and collaborators; and especially Baker, J., 1928, 1583), as are also the relative stabilities of the nitroso-compound and the quinoneoxime, the probable non-reversibility of the conversion, the pronounced yellow colour of the nitroso-compound in contrast to the almost complete absence of colour from the quinoneoxime, and the individual character of the latter, which is emphasised by its crystallisation from media containing pyridine on the one hand and acetic acid on the other.

The nitroso-group is peculiar in possessing mobile electrons which enable it to function as an electron-source or -sink as the occasion demands. In hot acid solution the proximity of a hydrogen ion will induce a polarisation (I) such that the nitroso-oxygen atom tends to become negatively charged. Simultaneously with the



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

attachment of this hydrogen the hydroxyl hydrogen will ionise (II), and all the more readily owing to the general effect of the *m*-substituted chlorine atom.

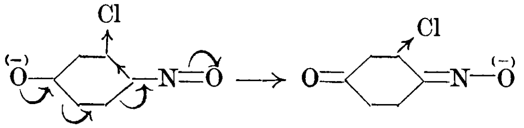
That the *m*-chlorine atom is exerting a deactivating influence on the 4-carbon atom is shown by the fact that *m*-chlorophenol undergoes nitrosation much more slowly than phenol itself. The tardiness of the conversion into the quinoneoxime may perhaps be ascribed to the constraint placed upon the lone pair of electrons of the nitrogen atom by the inductive effect of the chlorine. This conversion is in striking contrast to the rapid destructive action of hot acids upon *p*-nitrosophenol itself. *m*-Bromo- and *m*-iodo-phenol behave in like manner on nitrosation.

Once it is produced, 3-chlorobenzoquinone-4-oxime may form a chelate ring (III) through the chlorine and the hydrogen (compare Sidgwick and Callow, J., 1924, **125**, 533, for co-ordination in the case of *o*-chlorophenol) : this would considerably tighten the electronic framework of the molecule and so account for its very feeble colour, which is in striking contrast to the brilliant yellow colour of the electronically looser 3-chloro-4-nitrosophenol (compare the views expressed by Hodgson and Cooper, this vol., p. 231, on the colours of the nitrophenylhydrazones).

Co-ordination or direct effect or steric hindrance or associations of these influences may secure the individual character of the oxime when once formed and also the impossibility of reversion to the nitroso-compound and of its existence in geometrical isomerides.

The action of alkalis on 3-chloro-4-nitrosophenol is readily explained by the approach of the hydroxyl ion to the phenolic hydroxyl group with consequent ionisation of the molecule (IV) and rearrangement, by electronic transfer, to the ion (V) of the oxime tautomeride :

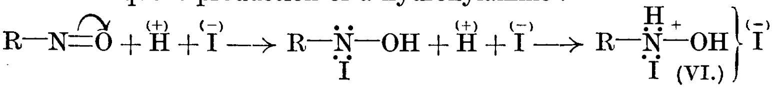
(IV.)



(V.)

On acidification the proton will attach itself to the negative nitroso-oxygen atom and not to the depolarised phenolic oxygen atom.

The explanation of the reducing action of hydriodic acid on nitroso-compounds given by Earl, Ellsworth, Jones, and Kenner (J., 1928, 2697) as an additive reaction in the first instance may be substantiated by a similar application of electronic theory : The nitrogen atom is subject to electron demand owing to the tendency of the double-bonded oxygen atom to become negatively charged in the presence of hydrogen ions ; therefore, on attachment of the proton to the oxygen, the nitrogen atom will become positively charged and capture the iodine ion. Having again acquired a lone pair of electrons, the nitrogen atom can now attach a hydrogen ion and so facilitate the separation of a neutral iodine molecule from the intermediate unstable ammonium salt (VI) thereby formed, with consequent production of a hydroxylamine :



$$R-N\overset{\curvearrowright}{=O} + \overset{(+)}{H} + \overset{(-)}{I} \longrightarrow R-\underset{\dot{I}}{\overset{\cdot\cdot}{N}}-OH + \overset{(+)}{H} + \overset{(-)}{I} \longrightarrow \left.\begin{matrix} \overset{H}{\underset{\dot{I}}{R-N^{+}-OH}} \\ \text{(VI.)} \end{matrix}\right\}\overset{(-)}{I}$$

3-*Chloro*-4-*nitrosoanisole* is bright green, and the so-called 3-chloro-4-nitrosophenol is bright yellow, both in the solid state and in solution. 3-Chlorobenzoquinone-4-oxime, however, gives feebly coloured, light green solutions, and its methyl ether is light yellow and gives feebly coloured, light yellow solutions. Further it is remarkable that, although concentrated sulphuric acid immediately converts the nitroso-compound into the oxime, the two substances give Liebermann nitrosoamine reactions which differ appreciably, the oxime yielding a definitely bluer colour. Solutions of p-*benzoquinonedioxime* 4-*methyl ether* in water and in alcohol are greenish-yellow.

The melting points of 3-chloro-4-nitrosoanisole (60°) and 3-chlorobenzoquinone-4-oxime methyl ether (113°) are in accordance with the view expressed by Hodgson and Moore (J., 1925, **127**, 2260) that nitroso-compounds appear always to melt at a lower temperature than the corresponding oximes.

EXPERIMENTAL.

Preparation of 3-*Chloro*-4-*nitrosophenol*.—*m*-Chlorophenol (4 g.), dissolved in a solution of sodium hydroxide (2 g.) and sodium nitrite (10 g.) in water (300 c.c.), is ice-cooled externally while a mixture of sulphuric acid (8 c.c.) and water (12 c.c.) is added with vigorous stirring during 2 hours. The filtered solution is placed in a flask which it just fills and which is closed and kept in the dark overnight. The deposited 3-chloro-4-nitrosophenol (yield, 40%) is washed with water and dried in the dark. The product melts at 133° (Hodgson and Moore, *loc. cit.*, give m. p. 129·6°), but rapidly tarnishes in daylight. On exposure in alcoholic solution to ultraviolet light it is transformed into resinous products. It is readily soluble in ether, the yellow colour of the solution being much more intense than the green colour of a similar solution of the oxime.

3-*Chloro*-4-*nitrosoanisole*.—Potassium persulphate (20 g.) is stirred into sulphuric acid (40 g.), the mixture kept for 1 hour at room temperature, poured on ice (300 g.), neutralised with potassium carbonate, and just made acid with acetic acid. This mixture is added to a solution of 3-chloro-4-aminoanisole hydrochloride (3·5 g.) in ice-cold water (300 c.c.) which has previously been rendered first faintly alkaline with sodium hydroxide and finally just acid with acetic acid. The resulting mixture is stirred for 3 hours at 0° and filtered, and the residue is extracted with water (300 c.c.) to remove the entangled potassium sulphate and distilled with steam. 3-*Chloro-4-nitrosoanisole* passes over rapidly; it crystallises from alcohol or light petroleum in stout, bright green prisms or plates, m. p. 60° (Found : Cl, 20·6. $C_7H_6O_2NCl$ requires Cl, 20·7%).

3-*Chlorobenzoquinone*-4-*oxime*.—(a) *Alkali method.* A solution of 3-chloro-4-nitrosophenol (4 g.) in the minimum quantity of saturated aqueous sodium carbonate is filtered and immediately acidified with dilute hydrochloric acid. The precipitated oxime is washed with water, dried, ground with five times its weight of animal charcoal, and repeatedly extracted with boiling benzene (30 c.c.). The earlier extracts remove the coloured impurity and from the later ones 3-chlorobenzoquinone-4-oxime crystallises in very pale greenish-yellow needles or larger parallelograms according to the rate of crystallisation; m. p. 184° (decomp.) (Hodgson and Moore, *loc. cit.*, give m. p. 178°) (Found : Cl, 22·5%).

(b) *Acid method.* 3-Chloro-4-nitrosophenol is boiled for 1 minute with insufficient 10% sulphuric acid to dissolve it entirely. The residue is dissolved separately in excess of the hot acid and the product which separates on cooling is twice crystallised from benzene containing 2% of acetic acid; it then has m. p. 184° (decomp.), which is not depressed by admixture with a specimen prepared by the alkali method. This product has a somewhat deeper tint than that prepared by method (a), owing to the presence of a red impurity, produced by the boiling acid, the last traces of which are very difficult to remove.

The molecular weights of the nitroso-compound and of the alkali and acid conversion products, determined cryoscopically in phenol and in naphthalene, are normal.

3-Chlorobenzoquinone-4-oxime gives in dilute aqueous sodium hydroxide and sodium carbonate red solutions which become green on dilution, behaving in this respect like *p*-nitrosophenol. It is much more soluble in water than the nitroso-compound; a cold solution has a feeble yellow-green colour, and a hot one a more pronounced green.

The *benzoate* is prepared by the addition of benzoyl chloride to a solution of either the oxime or the nitroso-compound in aqueous sodium carbonate, and separates from chloroform, on careful addition of light petroleum, in golden-brown prisms, m. p. 189·5° (Found : Cl, 13·7. $C_{13}H_8O_3NCl$ requires Cl, 13·6%).

3-*Chlorobenzoquinone-4-oxime methyl ether* is obtained by the addition of methyl sulphate to a solution of either 3-chlorobenzoquinone-4-oxime or 3-chloro-4-nitrosophenol in saturated aqueous sodium carbonate, followed by a few drops of aqueous sodium hydroxide. It is readily isolated by steam distillation and crystallises from 50% aqueous alcohol in pale yellow needles, m. p. 113° (Found : Cl, 20·6. $C_7H_6O_2NCl$ requires Cl, 20·7%).

p-*Benzoquinonedioxime* 4-*methyl ether* is prepared by heating a mixture of *p*-benzoquinoneoxime 4-methyl ether (1 g.), hydroxylamine hydrochloride (2 g.), concentrated hydrochloric acid (4 c.c.), alcohol (20 c.c.), and water (3 c.c.) until dissolution occurs. The cooled mixture is kept for 3 days and then steam-distilled. From the greenish-yellow distillate, *p*-benzoquinonedioxime 4-methyl ether crystallises in almost colourless needles, m. p. 115° (Found : N, 18·5. $C_7H_8O_2N_2$ requires N, 18·4%).

Correction.—In J., 1926, 2040, "4-Halogenotoluquinone-5-monoximes" should read "4-Halogenotoluquinone-2-monoximes," and the 4-chloro-, 4-bromo-, and 4-iodo-toluquinone-5-oximes should each read "-2-oxime."

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TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, May 8th,* 1929.]