

CXIX.—*The Nitrosation of Phenols. Part IX. Further Study of the Nitrosation of m-Bromophenol.*

By HERBERT HENRY HODGSON and ARNOLD KERSHAW.

THE alleged geometrical isomerides of 3-bromobenzoquinone-4-oxime (Hodgson and Moore, J., 1925, **127**, 2260) prove to have been impure specimens of one individual (compare 3-chlorobenzoquinone-4-oxime, J., 1929, 1553).

The chelation between the halogen and the oximino-hydrogen atom previously assumed (*loc. cit.*) in order to account for the stability of 3-chlorobenzoquinone-4-oxime appears to be even stronger in 3-bromoquinone-4-oxime, since this is much more stable to boiling dilute mineral acids than its 3-chloro-analogue: Auwers cryoscopic data (*Z. physikal. Chem.*, 1903, **42**, 542) indicate that the co-ordination tendency of bromine is greater than that of chlorine.

3-Bromo-4-nitrosoanisole has an emerald-green colour, whereas 3-bromo-4-nitrosophenol is bright yellow, both in the solid state and in solution. 3-Bromobenzoquinone-4-oxime, however, gives pale green solutions, whereas its *methyl* ether is yellow and gives yellow solutions.

Similarly to the chloro-analogue, 3-bromo-4-nitrosophenol is converted immediately by concentrated sulphuric acid into the oxime; yet both substances give Liebermann nitrosoamine reactions, which differ in that the oxime produces a bluer colour.

The melting points of 3-bromo-4-nitrosoanisole (69°) and 3-bromobenzoquinone-4-oxime methyl ether (130°) are in accordance with the view expressed by Hodgson and Moore (*loc. cit.*), that nitroso-compounds melt at a lower temperature than the corresponding oximes.

E X P E R I M E N T A L.

3-Bromobenzoquinone-4-oxime, prepared both by the alkali and by the acid method (*loc. cit.*), crystallises from benzene, in which it is sparingly soluble, in pale greenish-yellow, elongated parallelepipeds, m. p. 196° (compare Hodgson and Moore, *loc. cit.*) (Found : Br, 39.5; N, 7.0. Calc. : Br, 39.6; N, 6.9%).

The molecular weight of 3-bromo-4-nitrosophenol, determined cryoscopically, is 207 in naphthalene and 187 in phenol (calc., 202); the oxime is very sparingly soluble in naphthalene, but has $M = 188$ in phenol. The benzoate, prepared and crystallised in the same way as the chloro-analogue, forms pale yellowish-brown, flat rhombs, m. p. 181° (Found : Br, 26.0. $C_{13}H_8O_3NBr$ requires Br, 26.1%).

3-Bromo-4-nitrosoanisole (2.4 g.), prepared in the same way as the chloro-analogue (*loc. cit.*) by the oxidation of 3-bromo-4-aminoanisole hydrochloride (4.3 g.) with Caro's acid but with only 2 hours' stirring, crystallises from alcohol in emerald-green needles or prisms, m. p. 69° (Found : Br, 37.0. $C_7H_6O_2NBr$ requires Br, 37.0%).

3-Bromobenzoquinone-4-oxime methyl ether is obtained by the addition of methyl sulphate to a solution of 3-bromobenzoquinone-4-oxime or 3-bromo-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 yellow needles, m. p. 130° (Found : Br, 37.1. $C_7H_6O_2NBr$ requires Br, 37.0%).

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TECHNICAL COLLEGE, HUDDERSFIELD. [Received, February 15th, 1930.]
