

CCLIV.—*The Nitrosation of Phenols. Part X. Further Study of the Nitrosation of m-Iodophenol.*

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WHEN *m*-iodophenol is nitrosated, the initial product is obtained in bright yellow needles which are rapidly tarnished by ultra-violet or sun-light, although unaffected in the dark. When this product is submitted to the transformation procedure employed for the chloro- and bromo-analogues (J., 1929, 1553; this vol., p. 967), 3-iodobenzoquinone-4-oxime is obtained in very pale yellow needles which are stable to light. Moreover, the bright yellow product is more soluble in chloroform (0.3%) than the oxime (0.1%), and the latter gives a bluer Liebermann nitrosoamine reaction. Neither product has a melting point, but the close analogy of all the other characteristics with those of the corresponding chloro- and bromo-analogues indicates the initial product of nitrosation to be the nitroso-compound. Hodgson and Moore's *syn*- and *anti*-forms (J., 1925, 127, 2260) would now appear to correspond to the nitroso- and quinone-oxime tautomerides respectively.

It is noteworthy that methylation of the 3-halogeno-benzoquinone-4-oximes by methyl sulphate in aqueous sodium hydroxide solution proceeds with increasing facility in the order  $\text{Cl} < \text{Br} < \text{I}$ , whereas benzylation has the reverse order,  $\text{Cl} > \text{Br} > \text{I}$ .

A specimen of 3-chloro-4-nitrosoanisole which had been kept in the dark for a year was almost completely converted into 3-chlorobenzoquinone-4-oxime, which, not being volatile in steam, could be completely separated from the original material by this method. The bromo- and iodo-analogues are more stable, although some crystals of the former, which were made at the same time as 3-chloro-4-nitrosoanisole, are now showing visible signs of partial transformation.

All the 3-halogeno-4-nitrosoanisoles are readily converted into the corresponding 3-halogenobenzoquinone-4-oximes when heated under reflux with dilute mineral acids.

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

*3-Iodo-4-nitrosophenol* (?)—This is prepared by the following modification of the nitrosation procedure hitherto employed: Solutions of *m*-iodophenol (4 g.) in aqueous 20% sodium hydroxide (8 c.c.) and water (40 c.c.), and of concentrated sulphuric acid (10 c.c.) in water (40 c.c.), are added simultaneously during 2 hours to an ice-cold solution of sodium nitrite (40 g.) and concentrated sulphuric acid (4 c.c.) in water (400 c.c.). The crude product (2.1 g.) is filtered off and washed first with water and subsequently with a little ether. The filtrate, after a further 2 hours' standing in the cold, deposited 0.5 g. of bright yellow micro-needles which darkened on heating and decomposed rapidly at about 190° (Found: N, 5.7; I, 51.2. Calc.: N, 5.6; I, 51.0%).

*3-Iodobenzoquinone-4-oxime* is produced from the above product both by the alkali and by the acid method (*loc. cit.*), and crystallises from the usual solvents, in which it is very sparingly soluble, in pale straw-coloured needles which, on being heated, behave very similarly to the nitroso-tautomeride (Found: N, 5.8; I, 51.2%). The *benzoate* crystallises from chloroform, on addition of light petroleum, in long stout prisms, m. p. 166° (Found: I, 36.2.  $C_{13}H_8O_3NI$  requires I, 35.9%). The *methyl* ether is obtained by the addition of methyl sulphate to a solution of the oxime in saturated aqueous sodium carbonate, followed by a few drops of aqueous sodium hydroxide, and is readily isolated by steam-distillation; it crystallises from aqueous alcohol (50%) in yellow needles, m. p. 143° (Found: I, 48.6.  $C_7H_6O_2NI$  requires I, 48.3%).

*3-Iodo-4-nitrosoanisole* is prepared in the same way as the chloro- and bromo-analogues (*loc. cit.*) by the oxidation of the 4-aminoanisole hydrochloride (1.5 g.) with Caro's acid (potassium persulphate, 6.6 g.; concentrated sulphuric acid, 7.3 c.c.), the mixture being stirred for 3 hours. The product (0.82 g.), isolated as usual, crystallises from alcohol in bright green prisms, m. p. 72.5 (Found: N, 5.4; I, 48.3.  $C_7H_6O_2NI$  requires N, 5.3; I, 48.3%).

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