

XCV.—*The Nitration of m-Iodophenol.*

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THE investigation of the direct nitration of *m*-iodophenol proceeded on similar lines to the work on *m*-chloro- and *m*-bromo-phenols (*J.*, 1925, **127**, 1599; 1926, 155). 3-Iodo-2-, -4-, and -6-nitro-

phenols, 3-iodo-4 : 6- and -2 : 6-dinitrophenols, and 3-iodo-2 : 4 : 6-trinitrophenol were prepared, but 3-iodo-2-nitrophenol was obtained from the nitration mixture with difficulty owing to the instability of *m*-iodophenol towards sulphuric acid and oleum and to the tardy mono- but ready tri-nitration of the sulphonic acid produced.

The constitutions of 3-iodo-4- and -6-nitrophenols are determined by analogy with those of the corresponding chloro- and bromo-compounds (*loc. cit.*), by their conversion into 2 : 2'-dinitro- and 4 : 4'-dinitro-5 : 5'-dimethoxydiphenyl disulphides and into 2-nitro- and 4-nitro-5-methoxythioanisoles, respectively (Hodgson and Handley, J., 1926, 543), and also by the conversion of each by nitration into 3-iodo-4 : 6-dinitrophenol, which is converted into 4 : 6-dinitroresorcinol on prolonged boiling with aqueous potassium hydroxide. Since 3-iodo-5-nitrophenol has been described by Hodgson and Wignall (J., 1926, 2077), the constitution assigned to 3-iodo-2-nitrophenol is the only one left for this substance. The constitution of 3-iodo-2 : 6-dinitrophenol follows from its preparation from 3-iodo-2- and -6-nitrophenols, and that of 3-iodo-2 : 4 : 6-trinitrophenol from its formation from all the mono- and both the di-nitro-derivatives.

Owing to the extensive decomposition of *m*-iodophenol by concentrated sulphuric acid and the consequent paucity of 3-iodo-2-nitrophenol, we have been unable to obtain 3-iodo-2 : 4-dinitrophenol. Attempts to substitute an amino-group for the halogen in 3-chloro- or 3-bromo-2-nitrophenol and so provide an alternative method for the preparation of 3-iodo-2-nitrophenol were unsuccessful, although the most drastic conditions were employed. The great stability of the halogen thereby demonstrated is found also in 3-iodo-2-nitrophenol, and in 3-iodo-2 : 4 : 6-trinitrophenol, which readily sublimates from boiling concentrated sulphuric acid. On the other hand, 4 : 6-di-iodo-1 : 3-dinitrobenzene, when boiled with a dilute solution of an alkali hydroxide or carbonate, slowly but completely exchanges the whole of its iodine for hydroxyl.

Unlike the corresponding chloro- and bromo-compounds, 3-iodo-2-nitrophenol does not form a hydrate. This was to be expected, since the hydrate of the chloro-compound is very much more stable than that of the bromo-compound. 2-Chloro-6-nitrophenol also does not appear to form a hydrate. The property, therefore, seems to be peculiar to the 3-chloro- and 3-bromo-2-nitrophenols.

Busch's α - and β -iodonitrophenols (*Ber.*, 1874, 7, 462), which are stated to be 5- and 6-iodo-2-nitrophenols (Beilstein, "Organische Chemie," II, p. 700), are regarded as impure substances by Roberts (J., 1923, 123, 2710) and as 3- and 4-iodo-2-nitrophenols by Keimatsu (*J. Pharm. Soc. Japan*, 1924, No. 507, 319). Since all

the monoiodo-2-nitrophenols are now available, one of the authors (H. H. H.) is repeating Busch's work with the object of determining the mechanism of iodination in presence of mercury compounds.

EXPERIMENTAL.

m-Iodophenol was prepared by the general method (Hodgson, E.P. 200714) from diazotised *m*-iodoaniline. It loses iodine in the presence of boiling water.

Mononitration of m-Iodophenol.

3-Iodo-6- and -4-nitrophenols.—*m*-Iodophenol (21.3 g.), liquefied by alcohol (2 c.c.), was added slowly to a solution, vigorously stirred at 15°, of concentrated sulphuric acid (22 g.) and sodium nitrate (16 g.) in water (40 c.c.). After 2 hours, the tarry mass was removed, washed, and steam-distilled; some iodine accompanied the volatile product, *3*-iodo-6-nitrophenol (3.7 g.), which crystallised from light petroleum in long, yellow needles, m. p. 96° (Found : N, 5.5; I, 47.7. $C_6H_4O_3NI$ requires N, 5.3; I, 47.9%).

3-Iodo-6-nitrophenol forms a scarlet *sodium* salt and a stable, orange-brown *silver* salt. Its *methyl* ether was obtained by boiling a solution of 1 g. of the phenol in aqueous sodium carbonate (1 g. in 40 c.c. of water) with methyl sulphate (1.5 c.c.) for 5 minutes, and steam-distilling the product. The white solid thus obtained crystallised from dilute alcohol in shining plates, m. p. 92° (Found : I, 45.3. $C_7H_6O_3NI$ requires I, 45.5%). The *acetate* was prepared by warming an excess of acetyl chloride with a solution of *3*-iodo-6-nitrophenol in glacial acetic acid for a short time on the water-bath. On diluting the mixture with water and cooling it, *3*-iodo-6-nitrophenyl *acetate* separated in hexagonal plates which, after recrystallisation from acetic acid containing a little acetic anhydride, melted at 95° (Found : I, 41.1. $C_8H_6O_4NI$ requires I, 41.4%). The *benzoate*, which was prepared in the same way as the corresponding chloro-compound, separated from alcohol in colourless needles, m. p. 122°.

The liquid remaining after the steam distillation of *3*-iodo-6-nitrophenol was filtered hot from the tarry matter; on cooling, it deposited *3*-iodo-4-nitrophenol as a yellowish-white solid, which crystallised from light petroleum in very pale yellow needles, m. p. 124° (Found : N, 5.4; I, 47.6%). The tar solidified on cooling, and on crystallisation from benzene and light petroleum gave a further quantity of *3*-iodo-4-nitrophenol (total yield, 10 g.). The *sodium* salt formed amber-coloured needles; the yellow *silver* salt darkened on keeping. The *methyl* ether, prepared as described

above for the 6-nitro-isomeride, crystallised from dilute alcohol in cream-coloured needles, m. p. 69—70° (Found : I, 45·2%). The *benzoate* separated from alcohol in long, slender, colourless needles, m. p. 119°. The *acetate* separated from dilute acetic acid in fine, colourless needles, m. p. 73·7° (Found : I, 41·2%).

Oxidation of 3-Iodobenzoquinone-4-oxime.—A solution of the oxime (1 g.) in water (200 c.c.) containing sodium hydroxide (10 g.) and potassium ferricyanide (10 g.) was kept for 48 hours at room temperature; the dark red colour had then changed to amber. On acidification with dilute sulphuric acid, the solution became green and deposited a voluminous, white precipitate (0·3 g.); ether extracted from the filtrate a further 0·4 g. The product crystallised from benzene in pale yellow needles, m. p. 123° (Found : N, 5·5%), and was 3-iodo-4-nitrophenol. This result proves that the nitrosation of *m*-iodophenol takes place in the 4-position (see J., 1925, 127, 2260).

3-Iodo-2-nitrophenol.—*m*-Iodophenol (7·5 g.) was added very gradually to oleum (12 c.c.; 27%), the mixture being cooled after each addition. After 1 hour, the temperature was raised gradually to 70—80° and maintained for 1½ hours. The mixture, which had then become a paste of crystals, was cooled, diluted with concentrated sulphuric acid (10 c.c.), and nitrated with a solution of nitric acid (2·5 c.c.; *d* 1·5) in concentrated sulphuric acid (7·5 c.c.), added at such a rate that the temperature never exceeded 30°. After 2 hours, the whole was poured on ice, and the solution carefully concentrated in a current of steam; iodine was evolved continuously, and from the highly concentrated, extensively decomposed product a yellow oil distilled which was collected in numerous small fractions. The earlier fractions would not solidify and were mixtures of *m*-iodophenol and 3-iodo-2-nitrophenol, but the later ones, on cooling, crystallised in long, yellow needles, m. p. 70—71°. The yield was variable and never exceeded 12%. When the quantity of nitric acid was increased, 3-iodo-2 : 4 : 6-trinitrophenol was the main product with a little 3-iodo-2 : 6-dinitrophenol. Diminution of the quantity of nitric acid resulted in a product which did not solidify and was mainly *m*-iodophenol.

3-Iodo-2-nitrophenol crystallised from water or light petroleum in bright greenish-yellow, spear-shaped needles, m. p. 73·5° (Found : N, 5·3; I, 47·8. $C_6H_4O_3NI$ requires N, 5·3; I, 47·9%). No formation of hydrate could be detected. The *sodium* salt crystallises in orange needles and the *ammonium* salt in red, rectangular plates which readily hydrolyse; the *silver* salt has a deeper orange-brown colour than its 6-nitro-isomeride and rapidly darkens on keeping. The *methyl* ether prepared in the way described above, crystallises

from dilute alcohol in colourless micro-plates, m. p. 82—83° (Found : I, 45.2. $C_7H_6O_3NI$ requires I, 45.5%). The *acetate* separates from dilute acetic acid in colourless cubes, m. p. 102.5° (Found : I, 41.2. $C_8H_6O_4NI$ requires I, 41.4%). Mixed with the 6-nitro-isomeride, it melts at 80°.

Dinitration of m-Iodophenol.

3-Iodo-4 : 6-dinitrophenol was prepared from *m*-iodophenol and from 3-iodo-6- and -4-nitrophenols in the same way as the corresponding bromo-compound (*loc. cit.*, p. 158). It is readily volatile in steam and crystallises from light petroleum in yellowish-white needles and from water in yellowish-white plates, m. p. 98° (Found : N, 9.2; I, 40.7. $C_6H_3O_5N_2I$ requires N, 9.0; I, 40.9%). The *silver* salt formed as a bright yellow, gelatinous precipitate when a neutral solution of the ammonium salt was treated with aqueous silver nitrate; it is moderately easily soluble in ammonia, but readily soluble in boiling water, from which it crystallises in golden needles (Found : Ag, 25.6. $C_6H_2O_5N_2IAg$ requires Ag, 25.9%). The gelatinous form changes to a redder, crystalline variety on keeping.

3-Iodo-2 : 6-dinitrophenol.—*m*-Iodophenol (5.5 g.) was gradually dissolved in 20 c.c. of oleum (27% SO_3), the mixture being cooled after each addition. After 48 hours, nitration below 0° was effected during 30 minutes with a solution of nitric acid (5 c.c.; *d* 1.5) in oleum (15 c.c.), and 2 hours later the whole was poured on ice, and the deep orange solution steam-distilled. Iodine was evolved and almost at the outset of the distillation the main part of the reaction product, which was 3-iodo-2 : 4 : 6-trinitrophenol, separated and was filtered off. The concentration by steam distillation was then continued, with evolution of iodine, and finally *3-iodo-2 : 6-dinitrophenol* passed over slowly; it separated from the distillate in almost colourless, slender needles which, after recrystallisation from water, dilute acetic acid, or light petroleum, melted at 151—152° (Found : N, 9.2; I, 40.7. $C_6H_3O_5N_2I$ requires N, 9.0; I, 40.9%). *3-Iodo-2 : 6-dinitrophenol* is readily turned yellow by ammonia, forms yellow solutions in water and alcohol, and very deep yellow ones with dilute aqueous alkalis. The *silver* salt separates slowly in bright orange-red needles when prepared by the usual method, and is sparingly soluble in ammonia and hot water.

3-Iodo-2 : 6-dinitrophenol was also prepared from 3-iodo-2-nitrophenol and from 3-iodo-6-nitrophenol in the same ways as the corresponding chloro- (*loc. cit.*, p. 1602) and bromo- (*loc. cit.*, p. 159) compounds, respectively.

Trinitration of m-Iodophenol.

3-Iodo-2:4:6-trinitrophenol was prepared in excellent yield as described above, or by the method used for the preparation of the corresponding chloro-compound (*loc. cit.*, p. 1603). It is not volatile in ordinary or in superheated steam, but sublimes slowly from boiling concentrated sulphuric acid. It crystallises from water, in which it is much less soluble than the corresponding chloro- and bromo-compounds, in almost colourless needles, and from glacial acetic acid in characteristic parallelepipeds, m. p. 197° (Found: N, 11·6; I, 35·5. $C_6H_2O_7N_3I$ requires N, 11·8; I, 35·8%). The substance possesses pronounced sternutatory properties, forms deep yellow solutions in water and alcohol, and is not brominated when its solutions are treated with bromine. The yellow *silver* salt is insoluble in ammonia.

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