CCCLVII.—*The 3-Halogeno-2-, -4-, and -6-aminophenols.*

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THE compounds herein described include all the 3-halogeno-2-, -4-, and -6-aminophenols except the fluoro-compounds. They are much stabler than the unsubstituted aminophenols, remaining colourless after prolonged exposure to air and having no action on Fehling's solution. Ammoniacal silver nitrate, however, is reduced, rapidly by the 3-halogeno-6-aminophenols (order: Cl > Br > I), much more slowly by the 3-halogeno-2-aminophenols (I > Br > Cl), and relatively most slowly by the 3-halogeno-4-aminophenols (Cl > Br > I). The solubilities of the 3-halogenoaminophenols in water decrease in the order Cl > Br > I. The hydrochlorides of the 3-halogeno-2- and -6-aminophenols are very soluble in water; those of the 4-amino-isomerides are only moderately easily soluble.

EXPERIMENTAL.

General Method of Preparation.—The 3-halogeno-2-, -4-, and -6-nitrophenols are dissolved in hot aqueous sodium hydroxide, and solid sodium hyposulphite is gradually added. The resulting 3-halogenoaminophenols all crystallise from water containing a little sodium bisulphite, and their hydrochlorides from dilute

* The result of the nitrogen determination was only satisfactory when the salt was mixed with potassium dichromate (compare Schmidt and Wilkendorf, *loc. cit.*). For the sodium determination, the salt was moistened with water before treatment with sulphuric acid.

hydrochloric acid, in colourless needles or plates. The hydrochlorides melt with extensive decomposition.

The 3-Halogeno-2-aminophenols.—Colour reactions. (1) Ferric chloride produces a transient reddish-violet colour and then a brown precipitate, the solution of which in concentrated hydrochloric acid retains its deep brownish-red colour on dilution. (2) Bleaching powder solution produces a light brown precipitate which deepens in colour on the gradual addition of hydrochloric acid but finally dissolves, forming deep brown solutions from the chloro- and bromo-compounds and a yellow solution from the iodo-compound. (3) Bromine water gives initially a brown coloration and then a pale yellow precipitate, the solution of which in hydrochloric acid is yellow.

3-Chloro-2-aminophenol, flat needles, m. p. 122° (Found : Cl, 24·8. C_6H_6ONCl requires Cl, 24·7%); *hydrochloride*, plates (Found : Cl, 39·2. C_6H_6ONCl,HCl requires Cl, 39·4%). *3-Bromo-2-aminophenol*, needles, m. p. 138° (Found : Br, 42·3. C_6H_6ONBr requires Br, 42·6%); *hydrochloride*, needles (0·0930 g. gave 0·1369 g. of mixed silver halides. Calc., 0·1372 g.). *3-Iodo-2-aminophenol*, needles, m. p. 137° (decomp.) (Found : I, 54·2. C_6H_6ONI requires I, 54·0%); *hydrochloride*, plates (0·1597 g. gave 0·2228 g. of mixed silver halides. Calc., 0·2226 g.).

The 3-Halogeno-4-aminophenols.—Colour reactions. (1) Ferric chloride gives with the chloro- and bromo-compounds intense violet colours which are changed to greenish-brown by concentrated hydrochloric acid and restored on dilution, whereas the iodo-compound gives only a faint brown colour changing to orange-brown. (2) Bleaching powder solution produces with the chloro- and bromo-compounds purple colorations and then brown precipitates giving orange-brown solutions in hydrochloric acid, whereas the iodo-compound exhibits only a faint violet coloration changing to light yellow on acidification. (3) Bromine water produces initially a violet colour, followed by a light brown or buff precipitate soluble in hydrochloric acid to a golden-brown solution.

3-Chloro-4-aminophenol, long, flat needles, m. p. 159·5° (Found : Cl, 24·5%) (compare D.R.-P. 143449, 1903); *hydrochloride*, plates (Found : Cl, 39·2%). *3-Bromo-4-aminophenol*, very long needles, m. p. 151° (Found : Br, 42·6%); *hydrochloride*, prisms (0·2221 g. gave 0·3285 g. of mixed silver halides. Calc., 0·3278 g.). *3-Iodo-4-aminophenol*, plates, m. p. 145·5° (Found : I, 53·8%); *hydrochloride*, plates (0·1180 g. gave 0·1650 g. of mixed silver halides. Calc., 0·1645 g.).

The 3-Halogeno-6-aminophenols.—Colour reactions. (1) Ferric chloride gives initially a bright violet colour, followed by a dark

purple precipitate the reddish-brown solution of which in concentrated hydrochloric acid becomes violet on dilution. (2) Bleaching powder solution produces a transient violet coloration, followed by a deep brown precipitate which rapidly changes to a bright red gelatinous form soluble in hydrochloric acid to an eosin-red solution unchanged on dilution. (3) Bromine water gives initially a brown coloration, followed by a light brown precipitate soluble with difficulty in hydrochloric acid to a straw-coloured solution.

3-*Chloro*-6-*aminophenol*, prisms, m. p. 154° (Found : Cl, 24·5%); *hydrochloride*, plates (Found : Cl, 39·3%). 3-*Bromo*-6-*aminophenol*, prisms, m. p. 150° (Found : Br, 42·4%); *hydrochloride*, elongated plates (0·1137 g. gave 0·1699 g. of mixed silver halides. Calc., 0·1678 g.). 3-*Iodo*-6-*aminophenol*, long needles, m. p. 141° (Found : I, 54·2%); *hydrochloride*, plates (0·1234 g. gave 0·1727 g. of mixed silver halides. Calc., 0·1720 g.).

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