CCCLXXVI.—*Preparation of the 5-Halogenoresorcinols.*

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The three 5-halogenoresorcinols have been prepared by converting the 3-halogeno-5-amino-anisoles (this vol., p. 2078) into the 5-halogeno-3-hydroxyanisoles and hydrolysing these.

5-*Halogeno*-3-*hydroxyanisoles*.—The 3-halogeno-5-aminoanisole (14 g.) or its sulphate (20 g.) in a mixture of sulphuric acid (15 g.) and water (150 c.c.) was diazotised at 0·5°, the excess of nitrous acid destroyed by carbamide, and the clear solution added gradually to a vigorously boiling mixture of sulphuric acid (120 g.) and water (150 c.c.) through which a current of steam was passing. The 5-halogeno-3-hydroxyanisole was only slowly volatilised. The voluminous distillate was made just alkaline, concentrated to small bulk, and acidified; the product then separated as an oil which solidified.

The 5-halogeno-3-hydroxyanisoles all reduce boiling Fehling's solution very slowly, and in aqueous solution give a faint bluish-pink coloration with ferric chloride.

5-*Chloro*-3-*hydroxyanisole* is readily soluble in water, alcohol, benzene, or glacial acetic acid, and crystallises from light petroleum or water in colourless needles, m. p. 99° (Found: Cl, 22·45. $C_7H_7O_2Cl$ requires Cl, 22·4%). 5-*Chloro*-2 : 4 : 6-*tribromo*-3-*hydroxyanisole* is obtained from glacial acetic acid in colourless needles, m. p. 110° (0·0884 g. gave 0·1574 g. of silver halides. Calc., 0·1581 g.), and 5-*bromo*-3-*hydroxyanisole* from water in colourless needles, m. p. 102° (Found: Br, 39·2. $C_7H_7O_2Br$ requires Br, 39·4%); the latter is less readily soluble in water than the chloro-analogue. 2 : 4 : 5 : 6-*Tetrabromo*-3-*hydroxyanisole* crystallises from glacial acetic acid in colourless needles, m. p. 120° (Found: Br, 72·5. $C_7H_4O_2Br_4$ requires Br, 72·7%). 5-*Iodo*-3-*hydroxyanisole* sublimes in colourless needles, m. p. 90° (Found: I, 50·7. $C_7H_7O_2I$ requires I, 50·8%). It is almost insoluble in water or light petroleum, but dissolves readily in alcohol or benzene. 2 : 4 : 6-*Tribromo*-5-*iodo*-3-*hydroxyanisole* crystallises from dilute acetic acid in colourless needles, m. p. 125° (0·0991 g. gave 0·1621 g. of silver halides. Calc., 0·1626 g.).

5-*Halogenoresorcinols*.—The 5-halogeno-3-hydroxyanisole (7 g.) was boiled under reflux for 3 hours with hydriodic acid (60 c.c.; *d* 1·6), the solution decolorised by addition of sodium thiosulphate, and the 4-halogenoresorcinol extracted with ether. The product was stirred in cold 5% aqueous sodium hydroxide (80 c.c.)

to remove sulphur and recovered by acidification and extraction with ether (yields, 5—6 g.).

The 5-halogenoresorcinols all reduce boiling Fehling's solution and give pronounced bluish-purple colorations with ferric chloride. 5-Chloro- and 5-iodo-resorcinols differ from 5-bromoresorcinol in that their monohydrates are much more stable.

5-*Chlororesorcinol*.—The crude product from the foregoing hydrolysis crystallised from benzene in colourless needles, m. p. 67°, of the monohydrate (Found : Cl, 21·5. $C_6H_5O_2Cl,H_2O$ requires Cl, 21·8%). When this was sublimed in a vacuum, microcrystalline needles of the anhydrous substance were obtained, m. p. 117° (Found : Cl, 24·4. $C_6H_5O_2Cl$ requires Cl, 24·5%). The anhydrous substance is readily soluble in all the usual solvents except light petroleum, in which it is insoluble, and rapidly absorbs water, regenerating the hydrate (Found : loss in a vacuum over concentrated sulphuric acid, 10·8. Calc. : H_2O, 11·1%). 5-*Chloro*-2 : 4 : 6-*tribromoresorcinol* crystallises from glacial acetic acid or dilute alcohol in colourless needles, m. p. 143° (0·1539 g. gave 0·2762 g. of silver halides. Calc., 0·2851 g.). The low m. p. and the poor analytical result probably indicate the presence of a hydrate. 5-*Bromoresorcinol* crystallises from benzene in colourless needles, m. p. 87° (Found : Br, 42·4. $C_6H_5O_2Br$ requires Br, 42·3%). These remain unchanged in m. p. after sublimation in a vacuum, but on recrystallisation from water large prisms of the monohydrate, m. p. about 79°, are obtained (Found : Br, 39·2. Calc. for monohydrate : Br, 38·6%). 2 : 4 : 5 : 6-Tetrabromoresorcinol crystallises from glacial acetic acid or dilute alcohol in colourless needles, m. p. 212° (Claassen, *Ber.*, 1878, **11**, 1440, gives m. p. 163°; Benedikt, *Monatsh.*, 1880, **1**, 366, gives m. p. 167°) (Found : Br, 75·0. Calc. : Br, 75·1%). 5-*Iodoresorcinol* crystallises from benzene in colourless needles, m. p. 92·3° (Found : I, 49·9. $C_6H_5O_2I,H_2O$ requires I, 50·0%). On sublimation in a vacuum, colourless needles were obtained which still retained water but melted at 105—113° (Found : I, 52·0. $C_6H_5O_2I$ requires I, 53·8%). Keeping over concentrated sulphuric acid or crystallisation from dry benzene in presence of phosphorus pentoxide failed to dehydrate the product completely. 2 : 4 : 6-*Tribromo*-5-*iodoresorcinol* separates from glacial acetic acid in colourless needles, m. p. 214° (0·0793 g. gave 0·1339 g. of silver halides. Calc., 0·1340 g.).

The authors thank Messrs. J. W. Leitch and Co. and the Nobel Industries, Limited, for gifts of chemicals used in this investigation.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August* 14*th*, 1926.]
