

XIII.—*2-Hydroxy-4-methoxy- and 4-Hydroxy-2-methoxy-benzaldehydes.*

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By the action of hydrogen cyanide (9 mols.) on *m*-methoxyphenol in presence of hydrogen chloride and aluminium chloride, with benzene as solvent, Gattermann and Berchermann (*Ber.*, 1898, **31**, 1767) obtained only 4-hydroxy-2-methoxybenzaldehyde, but Ott

and Nauen (*Ber.*, 1922, 55, 928) showed that 2-hydroxy-4-methoxybenzaldehyde was also formed.

The two aldehydes have now been obtained in good yield as follows. A solution of *m*-methoxyphenol (20 g.; 1 mol.) in 70 c.c. of absolute ether was after addition of hydrogen cyanide (20 g.; 3 mols.) saturated with dry hydrogen chloride and kept in a refrigerator for not more than 24 hours. (If kept for a longer time, the yellow crystalline mass becomes deep crimson owing to the conversion of 4-hydroxy-2-methoxybenzaldehyde into a red tar by the action of the hydrogen chloride.) The ether was decanted, the aldimine hydrochlorides were washed with dry ether and dissolved in 2 litres of cold water, the solution was heated to boiling, and the 2-hydroxy-4-methoxybenzaldehyde removed in a current of steam. It crystallised from the distillate in long white needles, m. p. 41—42°, and more was obtained by salting-out and extraction with ether (total yield, 9.5 g.). The residue after steam-distillation slowly deposited 4-hydroxy-2-methoxybenzaldehyde in straw-coloured needles, and salting-out and extraction with ether gave a further quantity (total yield, 10 g.). After crystallisation from hot water (charcoal) this aldehyde had m. p. 153°. A small quantity of the mixed aldimines may be obtained from the original ethereal mother-liquor and washings.

4-Hydroxy-2-methoxybenzaldehyde forms a *phenylhydrazone*, yellow needles, m. p. 158°, from dilute acetic acid (Found: N, 12.0. $C_{14}H_{14}O_2N_2$ requires N, 11.6%), a *p-nitrophenylhydrazone*, dark red, rhombic plates, m. p. 255° (decomp.), from glacial acetic acid or alcohol (Found: N, 14.7. $C_{14}H_{13}O_2N_2^s$ requires N, 14.6%), and a *semioxamazone*, short white plates, m. p. 242°, from glacial acetic acid (Found: N, 17.1. $C_{10}H_{11}O_4N_3$ requires N, 17.8%).

2-Hydroxy-4-methoxybenzaldehyde yields a *p-nitrophenylhydrazone*, bright red needles, m. p. 226.5°, from acetic acid (Found: N, 15.5. $C_{14}H_{13}O_4N_3$ requires N, 14.6%), a *semioxamazone*, pale lemon-yellow plates, m. p. 247°, from 50% acetic acid (Found: N, 17.9. $C_{10}H_{11}O_4N_3$ requires N, 17.8%), and a *semicarbazone*, short white rods, m. p. 230°, from glacial acetic acid (Found: N, 19.9. $C_9H_{11}O_3N_3$ requires N, 20.1%).

An investigation of the formation of pyrylium compounds from aldehydes will be published shortly.

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