CCXXVI.—*The Reimer–Tiemann Reaction with* m-*Chlorophenol.*

By Herbert Henry Hodgson and Thomas Alfred Jenkinson.

A MIXTURE of 4-chloro-2-hydroxy- and 2-chloro-4-hydroxy-benzaldehyde in almost equal quantities has been obtained from *m*-chlorophenol by the Reimer–Tiemann reaction. The constitutions of the two aldehydes were determined by converting the methyl ethers into the corresponding methoxy- and hydroxy-benzoic acids, and confirmed by preparing 4-chloro-2-methoxybenzaldehyde from 4-nitro-2-methoxytoluene and 2-chloro-4-hydroxybenzaldehyde from 2-chloro-4-nitrotoluene.

EXPERIMENTAL.

4-*Chloro*-2-*hydroxy*- *and* 2-*Chloro*-4-*hydroxy-benzaldehyde*.—An intimate mixture of slaked lime (140 g.), sodium carbonate (160 g.), *m*-chlorophenol (56 g.), water (1000 c.c.), and chloroform (104 g.) was submitted to the usual Reimer–Tiemann procedure. 4-Chloro-2-hydroxybenzaldehyde (13 g.) was removed by steam distillation, the operation being stopped when the much less volatile 2-chloro-4-hydroxybenzaldehyde began to pass over. The hot liquor in the flask was filtered from tar and, on cooling, deposited 2-chloro-4-hydroxybenzaldehyde (13 g.) in pale yellow, feathery needles.

With alcoholic potash in place of the lime–soda mixture, the reaction proceeded much more vigorously and produced more tar. Aqueous sodium and potassium hydroxides gave intermediate results.

4-*Chloro*-2-*hydroxybenzaldehyde* is very volatile in steam, being removed even from its yellow solutions in caustic alkalis. It is appreciably soluble in water and sulphurous acid, readily soluble in the usual organic solvents, and crystallises from alcohol or dilute acetic acid in long, colourless needles, m. p. 52·5° (Found: Cl, 22·6. $C_7H_5O_2Cl$ requires Cl, 22·7%). It has an odour resembling that of walnuts, gives a brown precipitate with ferric chloride, does not reduce ammoniacal silver nitrate or Fehling's solution, and is very resistant to acetylation and to oxidation by acid, neutral, or alkaline potassium permanganate. Although not readily methylated, yet it benzoylates easily under suitable conditions. In aqueous solution, it gives with copper and chromium sulphates, on careful treatment with dilute aqueous sodium hydroxide, a bright green *copper* salt and a dark green *chromium* salt. The *oxime* is fairly readily soluble in hot water, easily soluble in alkalis, alcohols, and glacial acetic acid, but less soluble in chloroform, and crystallises from alcohol in colourless needles, m. p. 155° (Found: Cl, 20·8. $C_7H_6O_2NCl$ requires Cl, 20·7%). The p-*nitrophenylhydrazone* crystallises from glacial acetic acid in orange needles, m. p. 257° (Found: Cl, 12·2. $C_{13}H_{10}O_3N_3Cl$ requires Cl, 12·2%), and gives a dark cherry-red colour with aqueous sodium hydroxide. The *semicarbazone* is readily soluble in alkalis, moderately easily soluble in alcohol, and separates from glacial acetic acid in very pale yellow clusters of micro-crystals, m. p. 212° (Found: Cl, 16·8. $C_8H_8O_2N_3Cl$ requires Cl, 16·6%). The *benzoate* is best prepared by dissolving the aldehyde (0·6 g.) in ether (2 c.c.), adding pyridine (0·1 c.c.), and then a solution of benzoyl chloride (0·5 g.) in ether (2 c.c.); after vigorous shaking, removal of the ether, and extraction of the product with warm dilute hydrochloric acid, the white, waxy residue is washed with water and crystallised from alcohol, from which it separates in long, colourless needles, m. p. 98·5° (Found: Cl, 13·5. $C_{14}H_9O_3Cl$ requires Cl, 13·6%).

4-*Chloro*-2-*methoxybenzaldehyde* is obtained in only moderate yield by direct methylation. It has a faint sweet odour, is readily soluble in the usual organic solvents, and crystallises from alcohol in colourless needles, m. p. 74° (Found: Cl, 20·9. $C_8H_7O_2Cl$ requires Cl, 20·8%).

Alternative method of preparation. 4-Nitro-2-methoxytoluene (5 g.), dissolved in alcohol (20 c.c.), was added gradually to a hot solution of sodium hydroxide (3 g.) and sulphur (2 g.) in water (30 c.c.), and the mixture was heated for an hour on the water-bath. The alcohol and 2-methoxy-*p*-toluidine were then removed in steam, and the residue (2 g.) of crude 4-amino-2-methoxybenzaldehyde was dissolved in hot dilute sulphuric acid (30%), and converted by the Sandmeyer method into 4-chloro-2-methoxybenzaldehyde; after crystallisation from alcohol, this (Found: Cl, 20·7%), alone or mixed with the substance described above, melted at 74°.

The *oxime* crystallises from hot water in long, colourless needles, m. p. 132° (Found: Cl, 19·1. $C_8H_8O_2NCl$ requires Cl, 19·1%). The p-*nitrophenylhydrazone* separates from glacial acetic acid in bright orange clusters of micro-crystals, m. p. 238° (Found: N, 13·6. $C_{14}H_{12}O_3N_3Cl$ requires N, 13·7%), and develops with alkali a less intense but more violet colour than the unmethylated *p*-nitrophenylhydrazone. The *semicarbazone* crystallises from glacial acetic acid in very pale yellow, almost colourless micro-plates, m. p. 228° (Found: Cl, 15·5. $C_9H_{10}O_2N_3Cl$ requires Cl, 15·6%). 4-*Chloro*-2-*methoxybenzoic acid*, prepared by oxidising the aldehyde with aqueous alkaline potassium permanganate, crystallises from alcohol in clusters of micro-crystals, m. p. 148° (Found: Cl, 19·1.

$C_8H_7O_3Cl$ requires Cl, 19·0%). 4-Chloro-2-hydroxybenzoic acid was obtained by boiling the preceding acid with hydriodic acid (*d* 1·7); it was slowly volatile in steam, crystallised from water in fine, colourless needles which sublimed with slight decomposition at about 209° and melted at 211° (Varnholt, *J. pr. Chem.*, 1887, **36**, 27, gives m. p. 207°) (Found: Cl, 20·4. Calc.: Cl, 20·5%), and gave a reddish-violet colour with ferric chloride.

The 2-chloro-4-hydroxybenzaldehyde obtained as described above crystallised from mineral or glacial acetic acid in colourless needles, m. p. 147—148° (Gattermann, *Annalen*, 1907, **357**, 334, gives m. p. 146·5°) (Found: Cl, 22·6%). It does not react with ammoniacal silver nitrate or Fehling's solution, and gives only a slight precipitate with ferric chloride. The *copper* and *chromium* salts are of a lighter green colour than those of the 4-chloro-isomeride. The p-*nitrophenylhydrazone* crystallises from alcohol in dark red plates and from glacial acetic acid in vermilion-red clusters of micro-crystals, m. p. 288° (decomp.) (Found: Cl, 12·1. $C_{13}H_{10}O_3N_3Cl$ requires Cl, 12·2%) and gives a bluer red with caustic alkalis than the 4-chloro-isomeride. The *semicarbazone* crystallises from alcohol in yellow clusters of micro-crystals, m. p. 214° (Found: Cl, 16·8. $C_8H_8O_2N_3Cl$ requires Cl, 16·6%), the *acetate* from dilute acetic acid in colourless needles, m. p. 51·5° (Found: Cl, 17·8. $C_9H_7O_3Cl$ requires Cl, 17·9%), and the *benzoate* from alcohol in colourless needles, m. p. 96·5° (Found: Cl, 13·6. $C_{14}H_9O_3Cl$ requires Cl, 13·6%).

2-Chloro-4-hydroxybenzaldehyde was also prepared, in almost quantitative yield, by treating 2-chloro-4-nitrotoluene with sodium hydroxide and sulphur (see above), diazotising the resulting amino-compound, and boiling the very stable diazo-compound with 40% sulphuric acid for 20 minutes.

The following derivatives were prepared in the same way as the corresponding 4-chloro-isomerides: The p-*nitrophenylhydrazone* separates from dilute acetic acid in orange-red needles, m. p. 249° (Found: N, 13·8. $C_{14}H_{12}O_3N_3Cl$ requires N, 13·7%), and gives a reddish-violet colour with aqueous-alcoholic alkali. The *semicarbazone* crystallises from alcohol in clusters of colourless micro-crystals, m. p. 240° (Found: Cl, 15·7. $C_9H_{10}O_2N_3Cl$ requires Cl, 15·6%). 2-*Chloro*-4-*hydroxybenzoic acid* crystallises from water (charcoal) in colourless needles, m. p. 159° (Found: Cl, 20·3. $C_7H_5O_3Cl$ requires Cl, 20·5%), and gives no definite colour with ferric chloride.

The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, April* 30*th*, 1927.]