

CCCCIII.—*The Reimer-Tiemann Reaction with  
m-Bromo- and m-Iodo-phenol.*

By HERBERT HENRY HODGSON and THOMAS ALFRED JENKINSON.

MIXTURES of 4-bromo-2-hydroxy- and 2-bromo-4-hydroxy-benzaldehyde and of 4-iodo-2-hydroxy- and 2-iodo-4-hydroxy-benzaldehyde in almost equal quantities have been obtained by the Reimer-Tiemann reaction from *m*-bromo- and *m*-iodo-phenol, respectively, which in this respect behave like *m*-chlorophenol (this vol., p. 1740). The individual constitutions were determined by the methods previously adopted (*loc. cit.*).

Walther and Wetzlich (*J. pr. Chem.*, 1900, **61**, 198) describe a substance of m. p. 52° as either 2- or 3-bromo-4-methoxybenzaldehyde. The latter constitution appears to be correct, since the 2-bromo-compound is now found to melt at 77°.

EXPERIMENTAL.

*General.*—Unless otherwise stated, the methods of preparation, general properties, and crystalline form of the various products now recorded are identical with those of the chloro-analogues (*loc. cit.*). The colours produced by alcoholic alkalis on alcoholic solutions of the *p*-nitrophenylhydrazones are given immediately after the m. p.'s.

(a) *The Reaction with m-Bromophenol.*

4-Bromo-2-hydroxybenzaldehyde (yield, 14 g. from 67 g. of *m*-bromophenol), on being warmed with acetic anhydride and a little sulphuric acid, gives a mixture of mono- and tri-acetates. The *sodium*, *potassium*, and *copper* derivatives have been prepared. The oxime melts at 168° (Müller, *Ber.*, 1909, **42**, 3698, gives m. p. 151°) (Found : Br, 37.1. Calc. : Br, 37.0%). The *p*-nitrophenylhydrazone crystallises in orange-yellow micro-needles, m. p. 258° (decomp.); cherry-red (Found : Br, 23.7.  $C_{13}H_{10}O_3N_3Br$  requires Br, 23.8%). The *semicarbazone* has m. p. 212° (Found : Br, 31.2.  $C_8H_8O_2N_3Br$  requires Br, 31.0%). The *benzoate* is best prepared by gently

warming the sodium derivative (0.5 g.) with benzoyl chloride (0.3 g.), and separates from alcohol in colourless needles, m. p. 115° (Found: Br, 26.3.  $C_{14}H_9O_3Br$  requires Br, 26.2%); the pyridine method of preparation (*loc. cit.*) failed.

4-Bromo-2-methoxybenzaldehyde, obtained best from 4-amino-2-methoxybenzaldehyde (*loc. cit.*), melts at 71° (Found: Br, 37.3.  $C_8H_7O_2Br$  requires Br, 37.2%). Oxime, m. p. 132° (Found: Br, 34.8.  $C_8H_8O_2NBr$  requires Br, 34.8%). p-Nitrophenylhydrazone, bright orange needles, m. p. 215°; violet-red (Found: N, 12.1.  $C_{14}H_{12}O_3N_3Br$  requires N, 12.0%). Semicarbazone, m. p. 224° (Found: Br, 29.3.  $C_9H_{10}O_2N_3Br$  requires Br, 29.4%). 4-Bromo-2-methoxybenzoic acid, m. p. 155° (Found: Br, 34.5.  $C_8H_7O_3Br$  requires Br, 34.6%).

4-Bromo-2-hydroxybenzoic acid, colourless plates, m. p. 214° (Found: Br, 36.7.  $C_7H_5O_3Br$  requires Br, 36.9%); it gives a violet colour with ferric chloride.

2-Bromo-4-hydroxybenzaldehyde (yield 15 g.; compare isomeride above) gives copper and alkali-metal derivatives. The p-nitrophenylhydrazone forms dark red micro-needles, m. p. 274° (decomp.); cherry-red (Found: Br, 23.6.  $C_{13}H_{10}O_3N_3Br$  requires Br, 23.8%). The semicarbazone has m. p. 212° (Found: Br, 30.9.  $C_8H_8O_2N_3Br$  requires Br, 31.0%). The oxime forms colourless needles, m. p. 184° (Gattermann, *Annalen*, 1907, **357**, 335, gives m. p. 128.5°) (Found: Br, 37.0. Calc.: Br, 37.0%).

2-Chloro-4-methoxybenzaldehyde (m. p. 62.5°. Compare Tiemann, *Ber.*, 1891, **24**, 699) and 2-bromo-4-methoxybenzaldehyde, m. p. 77° (Found: Br, 37.1.  $C_8H_7O_2Br$  requires Br, 37.2%) possess hawthorn-like odours, are insoluble in water, volatile in steam, and crystallise from alcohol in long, colourless needles; the oximes both melt at 93° (Found: Br, 34.5.  $C_8H_8O_2NBr$  requires Br, 34.8%), the p-nitrophenylhydrazones, orange-red needles, melt at 249° (decomp.), violet (Found: N, 13.7. Calc.: N, 13.7%), and 250° (decomp.), reddish-violet (Found: Br, 22.8.  $C_{14}H_{12}O_3N_3Br$  requires Br, 22.8%), respectively; the semicarbazones, colourless micro-needles, melt at 240° (Found: Cl, 15.7.  $C_9H_{10}O_2N_3Cl$  requires Cl, 15.6%) and 232° (Found: Br, 29.2.  $C_9H_{10}O_2N_3Br$  requires Br, 29.4%). 2-Bromo-4-methoxybenzoic acid, m. p. 199° (Found: Br, 34.4.  $C_8H_7O_3Br$  requires Br, 34.6%), crystallises from alcohol in short needles. 2-Bromo-4-hydroxybenzoic acid was best prepared from 3-bromo-4-nitrophenol by reduction, conversion into 3-bromo-4-cyanophenol, and hydrolysis with sulphuric acid; it crystallises from water in colourless needles, m. p. 151° (Found: Br, 36.8.  $C_7H_5O_3Br$  requires Br, 36.9%), and gives a faint pink colour with ferric chloride.

(b) *The Reaction with m-Iodophenol.*

4-Iodo-2-hydroxybenzaldehyde, m. p. 87° (yield, 12 g. from 73 g. of *m*-iodophenol) is more slowly volatile in steam than its halogeno-analogues (Found: I, 51.1.  $C_7H_5O_2I$  requires I, 51.2%). The *alkali-metal*, *ammonium*, and *silver* derivatives are all yellow and readily soluble in water; the green *copper* derivative is bluer than its isomeride. *Oxime*, m. p. 171° (Found: I, 48.2.  $C_7H_6O_2NI$  requires I, 48.3%). *p-Nitrophenylhydrazone*, orange needles, m. p. 242° (decomp.); cherry-red (Found: I, 33.0.  $C_{13}H_{10}O_3N_3I$  requires I, 33.1%). *Semicarbazone*, pale yellow needles, m. p. 252° (Found: I, 41.4.  $C_8H_8O_2N_3I$  requires I, 41.6%). *Benzoate*, best prepared by the action of benzoyl chloride on the silver derivative, melts at 62° (Found: I, 36.0.  $C_{14}H_9O_3I$  requires I, 36.1%).

4-Iodo-2-methoxybenzaldehyde, m. p. 85° (Found: I, 48.1.  $C_8H_7O_2I$  requires I, 48.4%). *Oxime*, m. p. 138° (Found: I, 45.6.  $C_8H_8O_2NI$  requires I, 45.8%). *p-Nitrophenylhydrazone*, orange-red needles, m. p. 238° (decomp.); violet-red (Found: I, 31.8.  $C_{14}H_{12}O_3N_3I$  requires I, 32.0%). *Semicarbazone*, m. p. 228° (Found: I, 39.7.  $C_9H_{10}O_2N_3I$  requires I, 39.8%). 4-Iodo-2-methoxybenzoic acid, m. p. 150° (Found: I, 45.9.  $C_8H_7O_3I$  requires I, 45.7%), sublimes between 120° and 130° and when heated above the m. p. evolves iodine.

4-Iodo-2-hydroxybenzoic acid, colourless plates, m. p. 230° (decomp.) (Found: I, 47.8.  $C_7H_5O_3I$  requires I, 48.1%); it gives a reddish-violet colour with ferric chloride.

2-Iodo-4-hydroxybenzaldehyde is odourless, non-volatile in steam, and crystallises from alcohol in very pale yellow needles, m. p. 163° (Found: I, 51.0.  $C_7H_5O_2I$  requires I, 51.2%). The *alkali-metal* derivatives are yellow and the *copper* derivative is less bluish-green than its isomeride. *p-Nitrophenylhydrazone*, dark red needles, m. p. 265° (decomp.); cherry-red (Found: I, 33.0.  $C_{13}H_{10}O_3N_3I$  requires I, 33.1%). *Semicarbazone*, pale yellow plates, m. p. 232° (decomp.) (Found: I, 41.3.  $C_8H_8O_2N_3I$  requires I, 41.6%). *Oxime*, long, colourless needles, m. p. 155° (Found: I, 48.1.  $C_7H_6O_2NI$  requires I, 48.3%). *Benzoate*, m. p. 112° (Found: I, 36.1.  $C_{14}H_9O_3I$  requires I, 36.1%).

2-Iodo-4-methoxybenzaldehyde has a faint hawthorn-like odour, is volatile in steam, and crystallises from alcohol in colourless needles, m. p. 115° (Found: I, 48.5.  $C_8H_7O_2I$  requires I, 48.4%). *p-Nitrophenylhydrazone*, reddish-orange needles, m. p. 247° (decomp.); reddish-violet (Found: I, 31.8.  $C_{14}H_{12}O_3N_3I$  requires I, 32.0%). *Semicarbazone*, pale yellow needles, m. p. 211° (Found: I, 39.5.  $C_9H_{10}O_2N_3I$  requires I, 39.8%). *Oxime*, colourless needles, m. p. 101° (Found: I, 45.6.  $C_8H_8O_2NI$  requires I, 45.8%).

*2-Iodo-4-methoxybenzoic acid*, m. p.  $184^{\circ}$  (Found : I, 45.8.  $C_8H_7O_3I$  requires I, 45.7%). *2-Iodo-4-hydroxybenzoic acid* was best prepared from 2-iodo-4-nitrotoluene; it crystallises from water (charcoal) in colourless needles, m. p.  $179^{\circ}$  (decomp.) (Found : I, 47.9.  $C_7H_5O_3I$  requires I, 48.1%), and gives no colour with ferric chloride.

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

TECHNICAL COLLEGE, HUDDERSFIELD.

[Received, October 10th, 1927.]

---