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

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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° (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° (decomp.) (Found: I, 47·9. $C_7H_5O_3I$ requires I, 48·1%), and gives no colour with ferric chloride.

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