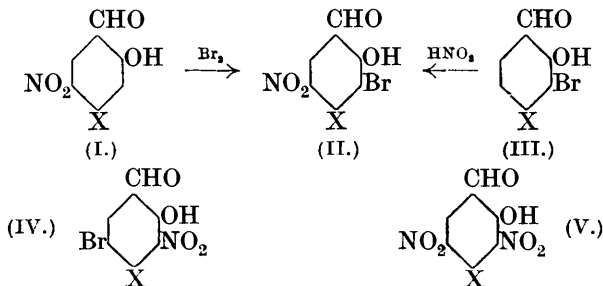


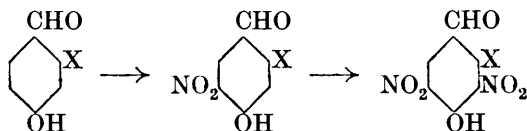
CCXCVI.—*Nitration of 4-Halogeno-2-hydroxy- and 2-Halogeno-4-hydroxy-benzaldehydes.*

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THE mononitration of the 4-halogenosalicylaldehydes, hitherto not studied, produces only one series of nitro-derivatives, although dinitration is readily accomplished. The first nitro-group appears to enter position 5, since bromination of the products (I) affords the compounds (II) obtained by nitrating the 3-bromo-4-halogenosalicylaldehydes (III). Since, however, the 4-halogenomononitro-2-hydroxybenzaldehydes were sufficiently volatile in steam to indicate that nitration might have taken place in the 3-position, the products (IV) were prepared for comparison. The sodium salts of (I) and (II) are yellow, whereas those of (IV) are bright red, indicating para- and ortho-nitrophenolic structures respectively. Dinitration of the 4-halogenosalicylaldehydes gives products which, for the same reasons, must be 3 : 5-dinitro-derivatives (V).



The 2-halogeno-4-hydroxybenzaldehydes are similarly converted into the 5-nitro- and 3:5-dinitro-compounds :



The brown colours produced by alkalis on the phenylhydrazones of certain of these substituted *m*-nitrobenzaldehydes are in accord with the observations of Chattaway and Clemo (J., 1923, 123, 3043).

EXPERIMENTAL.

Nitration of 4-Chloro-2-hydroxybenzaldehyde.—(a) *Mononitration.* 4-Chloro-2-hydroxybenzaldehyde (2 g.), dissolved in glacial acetic acid (5 c.c.), was nitrated at 18° by addition of fuming nitric acid (0.5 c.c.) during 3 minutes, and kept for 8 hours at 60° with stirring. On pouring into water, a yellow, oily liquid separated which was steam-distilled, two fractions (150 c.c. each) being collected. The first contained unchanged aldehyde (0.2 g.) with a little nitro-product. From the second fraction (0.2 g.), 4-chloro-5-nitro-2-hydroxybenzaldehyde (0.3 g.) was obtained, which crystallised from alcohol in small pale yellow needles, m. p. 116° (Found: Cl, 17.6. C₇H₄O₄NCl requires Cl, 17.6%), sparingly soluble in water and light petroleum, but readily soluble in the usual solvents; the product does not reduce ammoniacal silver nitrate or Fehling's solution or react with bromine water. The *phenylhydrazone* crystallises from alcohol in small light orange-yellow needles, m. p. 188° (decomp.) (Found: Cl, 12.0. C₁₃H₁₀O₃N₃Cl requires Cl, 12.2%), which give golden-brown solutions with caustic alkalis. The *p*-nitrophenylhydrazone crystallises from alcohol or glacial acetic acid in bright yellow micro-needles, m. p. 294° (decomp.) (Found: Cl, 10.5. C₁₃H₉O₅N₄Cl requires Cl, 10.5%), which give cherry-red colours with concentrated alkalis, turning bluer on dilution. The *semicarbazone* crystallises from dilute acetic acid in very pale yellow micro-needles, which decompose above 300° (Found: Cl, 13.5. C₈H₇O₄N₄Cl requires Cl, 13.7%).

(b) *Dinitration.* The aldehyde (0.75 g.) dissolved in glacial acetic acid (8 c.c.) is added all at once to nitric acid (8 c.c.; 91%) and, after the violent reaction has abated, the mixture is warmed at 100° for 5 minutes, kept for 15 minutes, poured into water, and steam-distilled to remove volatile mononitro-product. 4-Chloro-3:5-dinitro-2-hydroxybenzaldehyde (1 g.) crystallises from water in slender, pale golden-yellow needles, m. p. 153° (Found: Cl, 14.5.

$C_7H_3O_6N_2Cl$ requires Cl, 14.4%), which neither reduce Fehling's solution nor give a precipitate with bromine water. The *phenylhydrazone* crystallised from alcohol in light brown micro-crystals, m. p. 219° (Found : Cl, 10.3. $C_{13}H_5O_5N_4Cl$ requires Cl, 10.55%), and gives a golden-brown colour with alkalis. The *p-nitrophenylhydrazone* crystallises from dilute acetic acid in light brown micro-crystals, m. p. 286° (decomp.) (Found : Cl, 9.1. $C_{13}H_8O_7N_5Cl$ requires Cl, 9.3%), and with aqueous and alcoholic sodium hydroxide gives a cherry-red colour which turns a bluer shade on dilution. The *semicarbazone* separates from dilute acetic acid in light yellow micro-crystals, m. p. 225° (decomp.) (Found : Cl, 11.5. $C_8H_6O_6N_5Cl$ requires Cl, 11.7%).

Nitration of 2-Chloro-4-hydroxybenzaldehyde.—(a) *Mononitration.* The aldehyde (3 g.), dissolved in glacial acetic acid (15 c.c.), was nitrated by the gradual addition of nitric acid (3 g.; 63%), the mixture then being kept at 35–40° for 2 hours. The *2-chloro-5-nitro-4-hydroxybenzaldehyde* was removed by steam-distillation and crystallised from alcohol in colourless needles, m. p. 125° (Found : Cl, 17.6. $C_7H_4O_4NCl$ requires Cl, 17.6%), only slightly soluble in water and less soluble in the usual solvents than the initial aldehyde. The *phenylhydrazone* crystallised from alcohol in silky, dark purple needles, m. p. 166° (slight decomp.) (Found : Cl, 12.1%), which gave no colour with aqueous but a red with alcoholic alkalis. The *p-nitrophenylhydrazone* crystallised from glacial acetic acid in small, silky, deep orange needles, m. p. 266° (decomp.) (Found : Cl, 10.4%), which gave a violet-red colour with aqueous and alcoholic alkalis, turning bluer on dilution. The *semicarbazone* crystallised from dilute acetic acid in light orange micro-needles, m. p. 266° (decomp.) (Found : Cl, 13.6%).

(b) *Dinitration.* The aldehyde (3 g.), dissolved in glacial acetic acid (10–15 c.c.), was added gradually (10 minutes) to nitric acid (6 g.; 63%); the mixture was kept at 60° for 2 hours, poured into water, and steam-distilled. The non-volatile *2-chloro-3:5-dinitro-4-hydroxybenzaldehyde* crystallised from water in pale yellow, massive, prismatic crystals, m. p. 93° (Found : Cl, 14.3%), sparingly soluble in cold but readily soluble in hot water. The *phenylhydrazone* crystallised from alcohol in small, lustrous, brownish-purple needles, m. p. 210° (decomp.) (Found : Cl, 10.4%), which give a red colour with aqueous-alcoholic alkalis. The *p-nitrophenylhydrazone* crystallised from dilute acetic acid in reddish-brown micro-needles, m. p. 267° (decomp.) (Found : Cl, 9.1%), which gave a violet-red colour with alkalis, changing to a fine violet on dilution. The *semicarbazone* crystallised from dilute acetic acid in light brown micro-needles, m. p. 192° (decomp.) (Found : Cl, 11.5%).

Reimer-Tiemann Reaction with 3-Chloro-2-bromo- and 2:3-Dibromo-phenols.—The procedure employed was that in the authors' previous paper (J., 1927, 1740), but the yields were only moderate. 4-Chloro-3-bromo-2-hydroxybenzaldehyde forms colourless needles, m. p. 124° (0.1000 g. gave 0.1390 g. of AgX.* Calc.: 0.1407 g.), having a faint sweet odour, slowly volatile in steam, sparingly soluble in water but readily soluble in the usual organic solvents; the phenylhydrazone, colourless needles, m. p. 204° (0.1000 g. gave 0.1010 g. AgX. Calc.: 0.1018 g.), gave a pale yellow solution with aqueous-alcoholic alkalis; the p-nitrophenylhydrazone, orange micro-needles, m. p. 298° (decomp.), gave a ruby-red colour with aqueous alkalis. 3-Chloro-2-bromo-4-hydroxybenzaldehyde, colourless needles, m. p. 177° (0.1000 g. gave 0.1415 g. AgX. Calc.: 0.1407 g.), is very slowly volatile in steam and resembles its isomeride in solubilities; the p-nitrophenylhydrazone, dark crimson micro-needles, m. p. 253° (decomp.) (0.1000 g. gave 0.0900 g. AgX. Calc.: 0.0895 g.), gave a deep purplish-red colour with aqueous alkalis. 3:4-Dibromo-2-hydroxybenzaldehyde forms colourless needles, m. p. 129° (Found: Br, 56.9. C₇H₄O₂Br₂ requires Br, 57.1%), volatile in steam, and having a faint sweet odour. The p-nitrophenylhydrazone, orange micro-needles, decomp. above 220° (Found: Br, 38.3. C₁₃H₉O₃N₃Br₂ requires Br, 38.55%), gives a ruby-red colour with alkalis, becoming bluer on dilution.

2:3-Dibromo-4-hydroxybenzaldehyde, colourless needles, m. p. 192° (Found: Br, 57.0%), is only very slightly volatile in steam and odourless. The p-nitrophenylhydrazone, vermilion-red micro-needles, m. p. 254° (decomp.) (Found: Br, 38.3%), gave a deep red colour with aqueous alkalis.

Nitration of 4-Chloro-3-bromo-2-hydroxybenzaldehyde.—The aldehyde (1.5 g.), dissolved in glacial acetic acid (5 c.c.), was nitrated at 60–65° during 2 hours with nitric acid (0.5 g.; *d* 1.5). The 4-chloro-3-bromo-5-nitro-2-hydroxybenzaldehyde crystallised from alcohol in yellow prisms, m. p. 137° (Found: Cl + Br, 40.8. Calc.: 41.2%). The phenylhydrazone crystallised from alcohol in bright yellow needles, m. p. 229° (decomp.) (Found: Cl + Br, 31.3. Calc.: 31.2%), and gave brown colours with alkalis.

Bromination of 4-Chloro-5-nitro-2-hydroxybenzaldehyde.—The aldehyde (0.5 g.) in glacial acetic acid (2 c.c.) was treated with 3 c.c. of a solution of bromine (2 g.) in the same solvent (10 c.c.), the mixture warmed for 5 minutes on the water-bath, diluted with water until the slight turbidity just disappeared on heating, and allowed to cool slowly; 4-chloro-3-bromo-5-nitro-2-hydroxybenzaldehyde separated in yellow prisms, m. p. 137° (Found: Cl + Br, 40.9%),

* AgX = mixed silver halides.

unaltered when mixed with foregoing product. The yellow *sodium* salt was sparingly soluble in aqueous sodium carbonate. The *phenylhydrazone* crystallised from alcohol in bright yellow needles, m. p. 229° (decomp.) (Found: Cl + Br, 31.4%); a mixed m. p. with the corresponding product above indicated identity.

Preparation of 4-Chloro-5-bromo-2-hydroxybenzaldehyde.—To *m*-chlorophenol (23 g.), dissolved in chloroform (70 c.c.), bromine (9 c.c.) dissolved in chloroform (60 c.c.) was gradually added with shaking. After the free bromine had disappeared, the mixture was refluxed with 20% aqueous sodium hydroxide (200 c.c.) for 4 hours, the chloroform removed by means of steam, the mixture acidified, and again steam-distilled; 4-chloro-5-bromo-2-hydroxybenzaldehyde readily passed over: colourless needles, m. p. 125° (0.0838 g. gave 0.1181 g. AgX. Calc.: 0.1180 g.), from dilute acetic acid. The *phenylhydrazone* crystallised from alcohol in colourless needles, m. p. 200° (Found: Cl + Br, 35.2. Calc.: 35.5%). The *p*-nitrophenylhydrazone crystallised from glacial acetic acid in small, light brown needles, m. p. 280° (decomp.) (Found: Cl + Br, 30.9. Calc.: 31.2%), which gave a blue cherry-red colour with aqueous and alcoholic alkalis.

Nitration of 4-Chloro-5-bromo-2-hydroxybenzaldehyde.—The aldehyde (2 g.) was dissolved in warm acetic anhydride (2 c.c.) and obtained as a paste of fine crystals by chilling; it was then treated gradually with diacetylorthonitric acid (2 c.c.), maintained at 50° for 15 minutes, and kept over-night; 4-chloro-5-bromo-3-nitro-2-hydroxybenzaldehyde separated, and crystallised from alcohol in large, pale yellow prisms, m. p. 116° (Found: Cl + Br, 41.3. Calc.: 41.2%), giving a bright red *sodium* salt. The *phenylhydrazone* crystallised from alcohol in small, orange needles, m. p. 241° (decomp.) (Found: Cl + Br, 31.3%). The mixed m. p.'s with the isomerides above were depressed. Orange-red colours were given by aqueous and alcoholic alkalis.

Nitration of 2-Chloro-3-bromo-4-hydroxybenzaldehyde.—This process was carried out with quantities as for 4-chloro-3-bromo-2-hydroxybenzaldehyde, but at 30—40° for one hour. 2-Chloro-3-bromo-5-nitro-4-hydroxybenzaldehyde crystallised from glacial acetic acid in long, golden-yellow, silky needles, m. p. 140° (Found: Cl + Br, 40.9%). Bromination as above of the mononitration product of 2-chloro-4-hydroxybenzaldehyde gave an identical product, m. p. and mixed m. p. 140°. The identical *phenylhydrazones* crystallised from alcohol in very deep purple plates, m. p. 205° (decomp.) (Found: Cl + Br, 30.9, 31.0. Calc.: 31.2%), and gave brownish-red colours with aqueous and alcoholic alkalis.

Nitration of 4-Bromo-2-hydroxybenzaldehyde.—(a) *Mononitration.*

The aldehyde (3 g.) was nitrated as for the 2-chloro-4-hydroxy-compound, 6 g. of nitric acid being used. The product, *4-bromo-5-nitro-2-hydroxybenzaldehyde*, was entirely volatile in steam and crystallised from alcohol in very pale yellow rosettes, m. p. 128° (Found : Br, 32·3. $C_7H_4O_4NBr$ requires Br, 32·5%), which were slightly soluble in cold, but readily soluble in hot water and in the usual solvents. The *phenylhydrazone* crystallised from alcohol in small, orange needles, m. p. 189° (Found : Br, 23·6. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%), its yellow solution being deepened by alkalis. The *p-nitrophenylhydrazone*, yellow micro-needles, m. p. 301° (decomp.) (Found : Br, 21·2. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%), gave a cherry-red colour with alkalis, turning bluer on dilution. The *semicarbazone*, pale yellow micro-needles, decomposed above 210° (Found : Br, 26·2. $C_8H_7O_4N_4Br$ requires Br, 26·4%).

(b) *Dinitration*. The aldehyde (2 g.), dissolved in glacial acetic acid (5 c.c.), was nitrated at 0° with fuming nitric acid (3 c.c.), and heated at 100° for 10 minutes; *4-bromo-3 : 5-dinitro-2-hydroxybenzaldehyde* was separated from volatile products by steam-distillation and then crystallised from alcohol in colourless plates and from dilute acetic acid in colourless needles, m. p. 143° (Found : Br, 27·3. $C_7H_3O_6N_2Br$ requires Br, 27·5%). The *phenylhydrazone* crystallised from alcohol in small orange needles, m. p. 209° (decomp.) (Found : Br, 20·8. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%), and its yellow solution was turned brown by caustic alkalis. The *p-nitrophenylhydrazone*, light orange micro-needles, m. p. 250° (decomp.) (Found : Br, 18·6. $C_{13}H_8O_7N_5Br$ requires Br, 18·77%), gave a deep red colour in concentrated solution with caustic alkalis, which became bluer on dilution. The *semicarbazone*, light yellow micro-needles, had m. p. 224° (decomp.) (Found : Br, 22·7. $C_8H_6O_6N_5Br$ requires Br, 23·0%).

Nitration of 2-Bromo-4-hydroxybenzaldehyde.—(a) *Mononitration*. Quantities and procedure as for the previous isomeride. *2-Bromo-5-nitro-4-hydroxybenzaldehyde* was much more slowly volatile in steam than the chloro-analogue and also more soluble in water; it crystallised from alcohol in pale yellow needles, m. p. 131° (Found : Br, 32·7. $C_7H_4O_4NBr$ requires Br, 32·5%), gave an orange-red *silver* salt and a bright green *copper* salt. The *phenylhydrazone*, fine, silky, purple needles, had m. p. 181° (decomp.) (Found : Br, 23·5. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%), and gave a reddish-brown colour with aqueous alkalis. The *p-nitrophenylhydrazone*, orange micro-needles, m. p. 265° (decomp.) (Found : Br, 20·8%), gave violet-red colours with alkalis, turning bluer on dilution. The *semicarbazone*, light orange micro-needles, had m. p. 267° (decomp.) (Found : Br, 26·1%).

(b) *Dinitration*. The aldehyde (2 g.), dissolved in glacial acetic acid

(15 c.c.), was nitrated with 63% nitric acid (3 g.) in the cold and then kept at 50° for 3 hours; 2-bromo-3 : 5-dinitro-4-hydroxybenzaldehyde was non-volatile in steam and crystallised from water in massive pale yellow prisms, m. p. 110° (Found: Br, 27.4%), slightly soluble in water; it gave a deep golden-brown colour with ferric chloride, but did not reduce ammoniacal silver nitrate or Fehling's solution. The brown, flocculent *silver salt* was soluble in water. The *phenylhydrazone* crystallised from alcohol in dark purple plates, m. p. 186° (decomp.) (Found: Br, 20.8%), the golden-brown solution being changed to reddish-brown by caustic alkalis. The *p-nitrophenylhydrazone*, brown micro-needles, m. p. 248° (decomp.) (Found: Br, 18.9%), gave violet-red colours with caustic alkalis, turning bluer on dilution. The *semicarbazone*, orange micro-needles, had m. p. 188° (decomp.) (Found: Br, 22.9%).

Nitration of 2 : 3-dibromo-4-hydroxybenzaldehyde gave 2 : 3-di-bromo-5-nitro-4-hydroxybenzaldehyde, m. p. 155° (Found: Br, 49.0. $C_7H_3O_4NBr_2$ requires Br, 49.2%), identical with the brominated product from the mono-nitrated 2-bromo-4-hydroxybenzaldehyde, m. p. and mixed m. p. 155°, the procedures being as for the chloro-analogues. Their identical *phenylhydrazones* crystallised from alcohol in deep purple parallelepipeds, m. p. 204° (decomp.) (Found: Br, 38.3, 38.6. $C_{13}H_9O_3N_3Br_2$ requires Br, 38.5%), and gave brownish-red colours with aqueous and alcoholic alkalis.

Nitration of 3 : 4-dibromo-2-hydroxybenzaldehyde gave 3 : 4-di-bromo-5-nitro-2-hydroxybenzaldehyde, which crystallised from alcohol in pale yellow needles, m. p. 114° (Found: Br, 48.8%), and did not depress the m. p. of the product obtained by the bromination of the mononitrated 4-bromo-2-hydroxybenzaldehyde (above).

4 : 5-Dibromo-2-hydroxybenzaldehyde, colourless needles, m. p. 132° (Found: Br, 57.2%), was prepared in the same way as 4-chloro-5-bromo-2-hydroxybenzaldehyde (*loc. cit.*). It gives a yellow *silver salt*. The *p-nitrophenylhydrazone* crystallised from glacial acetic acid in deep orange-brown micro-needles, m. p. 266° (decomp.) (Found: Br, 38.4%), and gave deep bluish-red colours with alkalis. 4 : 5-Dibromo-3-nitro-2-hydroxybenzaldehyde crystallised from alcohol in pale yellow prisms, m. p. 118° (Found: Br, 49.1%). The *silver salt* is deep orange. The *phenylhydrazone* crystallised from alcohol in orange needles, m. p. 236° (decomp.) (Found: Br, 38.4%), and gave a deep red colour with aqueous caustic alkalis.

Nitration of 4-Iodo-2-hydroxybenzaldehyde.—(a) *Mononitration.* The aldehyde (2 g.), dissolved in glacial acetic acid (6 c.c.), was treated with fuming nitric acid (3 g.), kept for 2½ hours, and then heated at 45° for 5 minutes; the mixture was diluted with water, nearly neutralised by alkali, and steam-distilled.

4-Iodo-5-nitro-2-hydroxybenzaldehyde (1.5 g.), which passed over, crystallised from alcohol in small golden-yellow needles, m. p. 118° (Found : I, 42.9. $C_7H_4O_4NI$ requires I, 43.3%). The yellow *silver* salt was only sparingly soluble in water. The *phenylhydrazone*, small, old-gold needles, had m. p. 177° (decomp.) (Found : I, 33.0. $C_{13}H_{10}O_3N_3I$ requires I, 33.2%) and gave a brown colour with alkalis. The *p-nitrophenylhydrazone*, bright yellow micro-needles, m. p. 297° (decomp.) (Found : I, 29.3. $C_{13}H_9O_5N_4I$ requires I, 29.7%), gave violet-red colours with alkalis, turning bluer on dilution. The *semicarbazone*, pale yellow micro-needles, decomposed at 230—240° (Found : I, 35.9. $C_8H_7O_4N_4I$ requires I, 36.2%).

3-Bromo-4-iodo-5-nitro-2-hydroxybenzaldehyde crystallised from alcohol in small pale yellow needles, m. p. 145° (Found : Br + I, 55.9. $C_7H_3O_4NBrI$ requires Br + I, 55.6%).

(b) *Dinitration*. In the above process the residue (0.5 g.) after steam-distillation was 4-iodo-3 : 5-dinitro-2-hydroxybenzaldehyde, which crystallised from alcohol in small, brown needles, m. p. 160° (Found : I, 37.8. $C_7H_3O_6N_2I$ requires I, 37.6%). The *silver* salt was light orange. The *phenylhydrazone*, small, light brown needles, had m. p. 229° (decomp.) (Found : I, 30.0. $C_{13}H_9O_5N_4I$ requires I, 29.7%) and gave brown colours with alkalis. The *p-nitrophenylhydrazone*, brownish-orange micro-needles, m. p. 257° (decomp.) (Found : I, 26.4. $C_{13}H_8O_7N_3I$ requires I, 26.8%), gave deep violet-red colours with alkalis. The *semicarbazone*, light brownish-yellow micro-needles, decomposed when heated (Found : I, 31.8. $C_8H_6O_6N_5I$ requires I, 32.15%).

5-Bromo-4-iodo-2-hydroxybenzaldehyde is slowly volatile in steam and crystallises from alcohol in very pale yellow needles, m. p. 117° (0.1100 g. gave 0.1428 g. AgX. Calc. : 0.1422 g.), and its rather insoluble *sodium* salt in golden spangles. It gives a yellow *silver* salt. The *phenylhydrazone* crystallises in slender, pale yellow needles, m. p. 151°, and the *p-nitrophenylhydrazone* in orange micro-needles, m. p. 266° (decomp.), which give deep bluish-red colours with aqueous alkalis.

5-Bromo-4-iodo-3-nitro-2-hydroxybenzaldehyde crystallises from alcohol in small, golden-yellow prisms, m. p. 153° (0.1042 g. gave 0.1180 g. AgX. Calc. : 0.1185 g.), and gives an orange *silver* salt. The *phenylhydrazone* crystallises from alcohol in deep orange needles, m. p. 245° (decomp.) (0.1000 g. gave 0.0922 g. AgX. Calc. : 0.0915 g.), and gives a deep red colour with aqueous caustic alkalis.

Nitration of 2-Iodo-4-hydroxybenzaldehyde.—(a) *Mononitration*. A method giving better results than the foregoing was to nitrate the aldehyde (4.5 g.), dissolved in acetic anhydride (12 c.c.), with diacetylorthonitric acid (4 c.c.) added in two portions, the temperature

not being allowed to exceed 40—50°. After being kept for 15 minutes at 50°, the mixture was diluted and steam-distilled; 2-iodo-5-nitro-4-hydroxybenzaldehyde, which passed over, crystallised from alcohol in small, colourless prisms, m. p. 162° (Found : I, 43·5. $C_7H_4O_4NI$ requires I, 43·3%). The orange *silver* salt was sparingly soluble in water. The *phenylhydrazone*, very dark purple needles, had m. p. 204° (decomp.) (Found : I, 33·3%) and gave golden-brown solutions with alcoholic alkalis. The *p-nitrophenylhydrazone*, reddish-brown micro-needles, m. p. 273° (Found : I, 29·8%), gave violet-red colours with alkalis. The *semicarbazone*, light brown micro-needles, had m. p. 211° (decomp.) (Found : I, 36·6%).

3-Bromo-2-iodo-5-nitro-4-hydroxybenzaldehyde crystallises from dilute acetic acid in pale yellow needles, m. p. 178° (Found : Br + I, 55·8%). An authentic specimen had m. p. 178°.

(b) *Dinitration*. Procedure as for the analogues. 2-Iodo-3:5-dinitro-4-hydroxybenzaldehyde crystallised in massive yellow prisms, m. p. 162° (Found : I, 37·5%). The colours of the *silver* and *copper* salts were canary-yellow and bright green, respectively. The *phenylhydrazone*, deep brownish-purple needles, had m. p. 197° (decomp.) (Found : I, 30·0%), and gave a reddish-brown solution with alkalis. The *p-nitrophenylhydrazone*, dark-red micro-needles, m. p. 240° (decomp.) (Found : I, 27·2%), gave a reddish-violet colour with aqueous sodium hydroxide, which changed to reddish-pink on heating. The *semicarbazone*, orange micro-needles, had m. p. 205° (decomp.) (Found : I, 32·4%).

3-Bromo-2-iodo-4-hydroxybenzaldehyde crystallises from alcohol in pale yellow prisms, m. p. 204° (Found : AgX, 129·7. $C_7H_4O_2BrI$ requires AgX, 129·4%).

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

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[Received, June 16th, 1928.]