

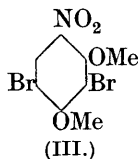
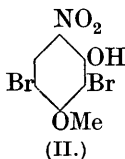
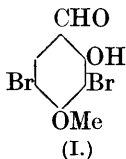
CCVI.—*Substitution in Resorcinol Derivatives. Part II. Bromo-derivatives of β -Resorcylaldehyde and their Orientation.*

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CONTINUING the investigation of 2-hydroxy-4-methoxybenzaldehyde (J., 1925, **127**, 556), which can conveniently be obtained from the roots of *Decalepis Hamiltonii*, we have studied the action of bromine under different conditions, obtaining first the *monobromo*-derivative corresponding to 5-nitro-2-hydroxy-4-methoxybenzaldehyde, and subsequently the *dibromo*-derivative in which the halogen occupies the 3:5-position. This appears to represent the limit of the bromination process. The correspondence between the nitro-compound and the monobromo-derivative was established by the

identity of the latter with the product of applying the Sandmeyer reaction to the reduced nitro-compound: but the orientation of the dibromo-derivative depends on the following principles.

When the dibromo-derivative is treated with a mixture of concentrated nitric and sulphuric acids the CHO-group is replaced by a nitro-group; the resulting substance appears to be 2:6-dibromo-4-nitroresorcinol monomethyl ether (II), because on methylation the product is identical with the 2:6-dibromo-4-nitroresorcinol dimethyl ether (III) of Jackson and Fiske (*Amer. Chem. J.*, 1903, **30**, 53). We therefore conclude that the dibromo-derivative of 2-hydroxy-4-methoxybenzaldehyde (I) is 3:5-dibromo-2-hydroxy-4-methoxybenzaldehyde.



E X P E R I M E N T A L.

5-Bromo-2-hydroxy-4-methoxybenzaldehyde.—A solution of 2-hydroxy-4-methoxybenzaldehyde (3 g.) in 15 c.c. of formic acid (d 1.20) was mixed with 15 g. of finely powdered fused sodium acetate and gradually treated with 1 c.c. of bromine (also dissolved in 15 c.c. of formic acid). After 1 hour, the thick white precipitate was collected, washed with water, and recrystallised from methyl alcohol (yield, almost quantitative). Larger quantities in only 75% yield were obtained by dissolving 30 g. of the aldehyde in glacial acetic acid and passing a stream of bromine vapour diluted with carbon dioxide through the solution. After 30 g. of bromine had been used, the pinkish solid was shaken with a little methyl alcohol; it crystallised from methyl alcohol in white needles, m. p. 120—121° (Found: Br, 34.75. $C_8H_7O_3Br$ requires Br, 34.6%). Ferric chloride gives a dark violet coloration with the product dissolved in methyl alcohol. The oxime forms colourless needles, m. p. 148—149°, and the phenylhydrazone pale yellow leaflets, m. p. 177—178°.

3:5-Dibromo-2-hydroxy-4-methoxybenzaldehyde.—A solution of 2-hydroxy-4-methoxybenzaldehyde (10 g.) in the requisite quantity of glacial acetic acid was mixed with 20 g. of fused sodium acetate and gradually treated, in a stoppered bottle containing glass beads, with the calculated quantity of bromine with frequent shaking. The reaction mixture was kept over-night and, when the yellow colour was permanent, gradually poured into well-stirred water.

The solid obtained, having been washed repeatedly with water, crystallised from ethyl alcohol in yellowish-white needles, m. p. 97—98° (Found : Br, 51.5. $C_8H_6O_3Br_2$ requires Br, 51.6%). The same compound, m. p. 96—97°, was obtained in a similar way from the monobromo-aldehyde and excess of bromine. It gives a violet coloration with methyl-alcoholic ferric chloride. The oxime is colourless and melts at 215°. The phenylhydrazone consists of colourless needles, m. p. 131—132°.

During the preparation of the dibromo-derivative of 2-hydroxy-4-methoxybenzaldehyde, if the product remains with excess of bromine during 15 days, a large quantity of a white solid is obtained which is crystallisable from hot water, is free from halogen, and gives a violet coloration with ferric chloride; it does not melt below 250°, and is perhaps the anhydro-aldehyde (Davies, J., 1923, **123**, 1575).

All attempts to prepare the tribromo-derivative resulted in the dibromo-aldehyde only, although a small quantity of tribromoresorcinol monomethyl ether was invariably obtained. The dibromo-aldehyde was heated with bromine in a sealed tube with a trace of iodine at 180°, and alternatively with aluminium, iodine, and bromine, but in both cases remained unchanged.

Preparation of the Monobromo-aldehyde from the 5-Nitro-aldehyde.—The 5-nitroaldehyde (5 g.) was mixed with 8 g. of sodium hydro-sulphite in a little water and well shaken; heat was developed and the colour changed to dark brown. After 2 hours, the reaction mixture was diazotised with the calculated quantity of sodium nitrite and sulphuric acid, treated with the requisite quantity of cuprous bromide in hydrobromic acid, and heated under reflux for 2 hours. Steam distillation gave colourless needles, m. p. 118—119° after recrystallisation from methyl alcohol and also when mixed with the monobromo-aldehyde obtained by direct bromination.

Nitration of the Dibromo-derivative.—The dibromo-aldehyde (3 g.) was dissolved in a mixture of 50 c.c. of glacial acetic acid and 5 c.c. of concentrated sulphuric acid, treated with 1 c.c. of nitric acid (*d* 1.52), and heated on a water-bath for 10 minutes: a violent action ensued and oxides of nitrogen escaped freely. When the product was allowed to cool slowly and diluted with a little water, a golden-yellow, bulky precipitate separated. This crystallised from ethyl alcohol in long, yellowish needles, m. p. 127—128°, and was identical with the product, m. p. 126—127°, obtained by partly methylating by the Purdie method 2 : 6-dibromo-4-nitroresorcinol (m. p. 148°), prepared by treating a solution of 2 : 4 : 6-tribromoresorcinol in glacial acetic acid with sodium nitrite (Dahmer, *Annalen*, 1904, **333**, 346).

2 : 6-Dibromo-4-nitroresorcinol 1-monomethyl ether, melting at 122°, has also been obtained by the nitration of 2 : 4 : 6-tribromo-resorcinol monomethyl ether with potassium nitrite and an acid (Kohn and Löff, *Monatsh.*, 1924, **45**, 589). When both substances were further methylated with methyl iodide, they gave the same dimethyl ether in colourless needles, m. p. 81°, the constitution of which is known definitely (Jackson and Fiske, *Amer. Chem. J.*, 1903, **30**, 53).

It is therefore concluded from the above that the dibromo-aldehyde is 3 : 5-dibromo-2-hydroxy-4-methoxybenzaldehyde.

The following bromo-compounds of β -resorcyaldehyde derivatives were prepared to ascertain the factors affecting the position of an entering group in trisubstituted benzene derivatives.

(I) 2 : 4-Dimethoxybenzaldehyde was brominated by treating a solution in excess of acetic acid (in presence of sodium acetate) with the calculated amount of bromine (also dissolved in acetic acid), and the product thrown into water. A white crystalline substance, m. p. 136—137°, was obtained identical with the product of methylating 5-bromo-2-hydroxy-4-methoxybenzaldehyde. The oxime formed white needles, m. p. 175—176°. Oxidation of the 5-bromo-2 : 4-dimethoxybenzaldehyde in a hot solution of magnesium sulphate by potassium permanganate gave white needles, m. p. 195—196°, identical with brominated 2 : 4-dimethoxybenzoic acid.

(II) 2-Ethoxy-4-methoxybenzaldehyde was brominated as above, yielding white needles, m. p. 126—127°, identical with the ethylated product of the monobromo-derivative of 2-hydroxy-4-methoxybenzaldehyde. The oxime formed slightly pinkish needles, m. p. 169—170°. Oxidation by potassium permanganate gave a white crystallisable substance identical with brominated 2-ethoxy-4-methoxybenzoic acid.

(III) Methyl *p*-methoxysalicylate on bromination formed a monobromo-derivative which on subsequent hydrolysis with alcoholic potash yielded a product identical with the bromo-derivative of 4-methoxysalicylic acid obtained by brominating the acid in question and whose constitution has been determined already (Fries and Saftien, *Ber.*, 1926, **59**, 1246).

In every one of these cases only the 5-bromo-derivative is obtained, the methoxy- and ethoxy-groups being powerfully para-directive.

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