

64. *Substitution in Resorcinol Derivatives. Part III. Molecular Rearrangement during Bromination.*

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It has been pointed out (J., 1925, **127**, 557) that 2-hydroxy-4-methoxybenzaldehyde on nitration yields mainly the 5-nitro-aldehyde (IV) and the quantity of solids obtained from the nitration mother-liquor was so small as to preclude a decision whether the 3-nitro-aldehyde was formed, or the aldehyde group had been replaced by the nitro-group. As a result of further study we have now isolated in very small quantities 3-nitro-2-hydroxy-4-methoxybenzaldehyde (VII) and 6-nitroresorcinol 3-methyl ether (I).

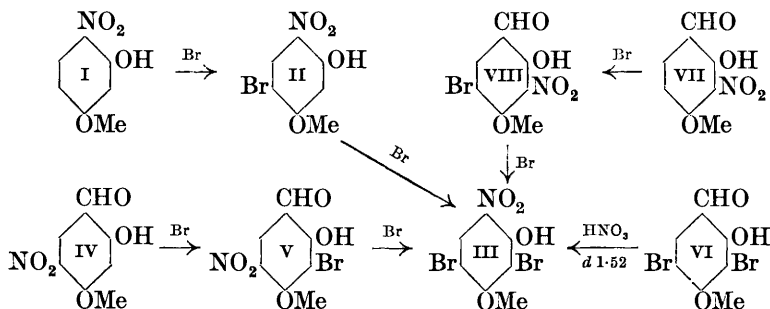
The 6-nitroresorcinol 3-methyl ether (I) thus obtained yielded on bromination the *monobromo*-derivative (II) and the *dibromo*-derivative (III). 5-Nitro-2-hydroxy-4-methoxybenzaldehyde (IV), in which the nitro-group is in a different position (J., 1925, **127**, 558), gave on bromination the *bromonitro-aldehyde* (V) and the yellow *dibromo*-derivative (III), the colour indicating an *o*-phenolic structure. 3 : 5-Dibromo-2-hydroxy-4-methoxybenzaldehyde (VI) (J., 1929, 1579) on nitration gave a yellow solid identical with (III).

The bromonitro-compounds in all three cases were proved to be identical by the undepressed melting points of mixtures of the three substances and of mixtures of their dimethyl ethers and of their ethyl ethers. The methyl ethyl ethers were found to be identical with that obtained by the nitration (Dahmer, *Annalen*, 1904, **333**, 346) and subsequent partial methylation and ethylation of tribromo-resorcinol.

Since 6-nitroresorcinol 3-methyl ether (I) and 5-nitro-2-hydroxy-4-methoxybenzaldehyde (IV) are *o*- and *p*-nitrophenols respectively, but give rise to identical *dibromo*-derivatives when treated with excess of bromine, it is suggested that an intramolecular rearrangement may have taken place during the bromination of one or other of the two nitro-compounds. The rearrangement may be due to migration of a bromine atom or of a nitro-group or to successive replacement reactions. But since 5-nitro-2-hydroxy-4-methoxybenzaldehyde yields a bromonitro-aldehyde (V) when treated with the calculated amount of bromine, and on further bromination gives a *dibromo*-compound (III) in which apparently the aldehyde group also is replaced by bromine, we are led to conclude that in the first instance the nitro-group may have wandered during bromination. There are many instances of a nitro-group being easily replaced by a bromine atom with the possible liberation of nitrous acid (Kohn

and Heller, *Monatsh.*, 1925, **46**, 91). Replacement of halogens by nitro-groups is also common; but cases of successive disubstitution of groups in a benzene nucleus during bromination are rare.

As it was likely that the bromination of 3-nitro-2-hydroxy-4-methoxybenzaldehyde (VII) would give more definite ideas regarding the molecular rearrangement, this nitro-aldehyde was brominated under different conditions; a *monobromo*- and a *dibromo*-derivative were produced. The *dibromo*-derivative was identical with (III) obtained by the bromination of 6-nitroresorcinol 3-methyl ether. It is therefore clear that both from the 5- and the 3-nitro-aldehyde the same *dibromo*-compound is obtained. The molecular rearrangement may therefore be due to a disubstitution reaction taking place as follows: (1) the first bromine atom enters position 3 or 5 according as the 5- or the 3-nitro-aldehyde is brominated; (2) the second bromine atom replaces the nitro-group, and the aldehyde group is replaced by a nitro-group by the action of the nitrous acid thus produced.



EXPERIMENTAL.

6-Nitroresorcinol 3-Methyl Ether.—The nitration mother-liquor after removal of the 5-nitro-aldehyde (J., 1925, **127**, 557) was diluted and steam-distilled. A substance which passed over crystallised from alcohol in pale yellow needles, m. p. 94–95°; it did not give an oxime or a phenylhydrazone (Found: N, 8.5. Calc. for $\text{C}_7\text{H}_7\text{O}_4\text{N}$: N, 8.3%). Its identity with 6-nitroresorcinol 3-methyl ether (Weselsky and Benedikt, *Monatsh.*, 1880, **1**, 892, 898) was confirmed by preparing its methyl ether, m. p. 74–75°. The aldehyde group of the initial 2-hydroxy-4-methoxybenzaldehyde has therefore been replaced by a nitro-group (Salway, J., 1909, **95**, 155; Harding, J., 1911, **99**, 1585).

Bromination of 6-Nitroresorcinol 3-Methyl Ether.—*Monobromo-derivative* (II). The ether (2 g.) was dissolved in glacial acetic acid and treated dropwise with a solution of bromine (2 g.) in about 10

c.c. of acetic acid. The product was diluted with water after 1 hour. The solid obtained crystallised from ethyl alcohol in stout yellow needles, m. p. 117—118° (Found : Br, 32.1. $C_7H_6O_4NBr$ requires Br, 32.2%). This *monobromo-derivative* was found to be identical with the nitro-derivative obtained by nitrating 5-bromo-2-hydroxy-4-methoxybenzaldehyde with cold fuming nitric acid; the product obtained in the latter case did not give an oxime.

Dibromo-derivative (III). The foregoing ether (2 g.), dissolved in acetic acid, was treated with about 4 g. of bromine in acetic acid and diluted with water after 4 hours. The precipitated solid (3 g.) crystallised from ethyl alcohol in golden-yellow needles, m. p. 127—128°; with methyl-alcoholic ferric chloride it gave a light red coloration (Found : Br, 48.6. Calc. for $C_7H_5O_4NBr_2$: Br, 48.9%). The compound was found to be identical with 2 : 4-dibromo-6-nitro-resorcinol 3-methyl ether (J., 1929, 1579).

Bromination of 5-Nitro-2-hydroxy-4-methoxybenzaldehyde.—5-Nitro-3-bromo-2-hydroxy-4-methoxybenzaldehyde (V). 5-Nitro-2-hydroxy-4-methoxybenzaldehyde (3 g.) was dissolved in glacial acetic acid and treated dropwise with bromine (2.5 g.) in the same solvent. The mixture was well shaken and diluted with much water after 2 hours. The solid (3.5 g.) that separated crystallised from methyl alcohol in long white needles, m. p. 129—130°; with ferric chloride in methyl alcohol it gave a dark red colour (Found : Br, 28.8. $C_8H_6O_5NBr$ requires Br, 29.0%). The yellow oxime melted at 216—217°, and the orange phenylhydrazone at 201—202°.

This monobromo-derivative on oxidation with a hot alkaline solution of potassium permanganate yielded a light yellow acid, m. p. 212—214°, identical with that obtained by the bromination of 5-nitro-2-hydroxy-4-methoxybenzoic acid (J., 1925, 127, 557), and is therefore inferred to be 3-bromo-5-nitro-2-hydroxy-4-methoxybenzaldehyde (V). On further bromination in acetic acid it yielded the dibromo-compound (III).

The 5-nitro-aldehyde (3 g.) was treated with bromine (5 g.) in acetic acid with repeated shaking, and the solution diluted with water after 12 hours. The precipitate crystallised from ethyl alcohol in golden-yellow needles, m. p. 127—128°, and was identical with (III) (Found : Br, 49.45%). It did not give an oxime. The dimethyl ether had m. p. 81—82°, and the methyl ethyl ether 73—74°. This dibromonitro-compound is identical with the nitration product of 3 : 5-dibromo-2-hydroxy-4-methoxybenzaldehyde (J., 1929, 1580).

3-Nitro-2-hydroxy-4-methoxybenzaldehyde.—2-Hydroxy-4-methoxybenzaldehyde (20 g.) was dissolved in 40 c.c. of glacial acetic acid, heated on a water-bath for 10 minutes, and then treated

with 6 c.c. of nitric acid (d 1.52); a brisk reaction took place, oxides of nitrogen being evolved. When this had ceased and the solution cooled, 5-nitro-2-hydroxy-4-methoxybenzaldehyde separated. The filtrate was carefully diluted with water; the light brown needles obtained (2 g.) crystallised from ethyl alcohol in long colourless needles, m. p. 146—147° (Found: N, 7.2. $C_8H_7O_5N$ requires N, 7.1%). In methyl-alcoholic solution the product gave a blood-red colour with ferric chloride. The oxime formed colourless needles, m. p. 191—192°, the phenylhydrazone golden-yellow leaflets, m. p. 180°. The methyl ether had m. p. 104—105°, and the ethyl ether 57—58°. The compound does not respond to the indigotin reaction, showing the absence of a nitro-group ortho to the aldehyde; the nitro-group must therefore be in position 3.

5-Bromo-3-nitro-2-hydroxy-4-methoxybenzaldehyde.—The 3-nitro-aldehyde (1 g.) was dissolved in glacial acetic acid and treated gradually with a solution of bromine (0.8 g.) in the same solvent. After 15 minutes, water precipitated a light yellow solid, which crystallised from ethyl alcohol in pale yellow needles, m. p. 126°; with ferric chloride it gave a blood-red colour (Found: Br, 29.0. $C_8H_6O_5NBr$ requires Br, 29.0%). The oxime formed light yellow needles, m. p. 153—154°, and the phenylhydrazone golden-yellow leaflets, m. p. 147—148°.

To establish the position of the bromine in the above product, 5-bromo-2-hydroxy-4-methoxybenzaldehyde was dissolved in the minimum quantity of hot glacial acetic acid and treated with the calculated quantity of nitric acid (d 1.52). After the vigorous reaction had ceased, the mixture was cooled and kept for an hour. A light yellow, crystalline solid separated; recrystallised from ethyl alcohol, it had m. p. 126—127° (Found: N, 5.1. $C_8H_6O_5NBr$ requires N, 5.1%), and was identical with the preceding bromination product (oxime, m. p. 153—154°; phenylhydrazone, m. p. 148—149°; no response in the indigotin reaction).

When the 3-nitro-aldehyde was treated with an excess of bromine in acetic acid, a golden-yellow solid separated during 4 hours. Crystallised from ethyl alcohol, it formed golden-yellow needles, m. p. 127—128°, of the compound (III) (Found: Br, 48.65%); the dimethyl ether melted at 81—82°, and the methyl ethyl ether at 74—75°.

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