CCCLXXII.—*The Nitrosation of Phenols. Part VII. Resorcinol Monomethyl Ether and* m-*Cresol.*

By Herbert Henry Hodgson and Hubert Clay.

Henrich and Rhodius (*Ber.*, 1902, **35**, 1475) described two nitrosation products from resorcinol monomethyl ether which were oriented as 2- and 4-nitroso-3-methoxyphenol, respectively. The constitution of the former depended upon its alleged reduction to 2-amino-3-methoxyphenol, but Henrich and Eisenach (*J. pr. Chem.*, 1904, **70**, 332) altered it to 6-nitroso-3-methoxyphenol, because the reduction product did not give 2-aminoresorcinol on demethylation.

It has now been shown that the nitroso-compound in question is indeed 6-nitroso-3-methoxyphenol, since the 6-nitro-3-methoxyphenol obtained from it by oxidation has been converted into 4-nitroresorcinol dimethyl ether and also synthesised from 3-chloro-4-nitroanisole.

In the nitrosation of resorcinol monomethyl ether, the attack of the kationoid reagent is almost entirely at the 6-position, only a very small amount of any other product being formed. This fact has been established by an almost quantitative oxidation of the crude nitrosation product to 6-nitro-3-methoxyphenol.

That ortho-nitrosation should take place preferentially, and also that the nitration of resorcinol monomethyl ether should yield mainly the 6-nitro-derivative, may be explained on current electronic conceptions (see, in particular, Lapworth and Robinson, *Mem. Manchester Phil. Soc.*, 1928, **72**, 473) as follows. The anionoid (electron-repelling) groups in resorcinol monomethyl ether each activate hydrogen in positions 4 and 6 in the reactive phases (I and II), and, although the frequencies of activation may reasonably be assumed to be similar, the proximity of hydrogen in the 6-position to the partly ionised hydroxyl group will secure for it a greater degree of activation than obtains at the 4-position. Further, should ionisation of the hydroxyl group be repressed by the methoxyl group, as appears probable, activation at the 4-position would be

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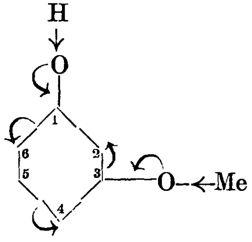

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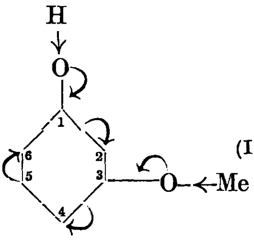
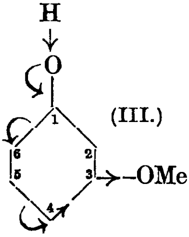


still more weakened and even made to depend mainly on the methoxyl group itself. Now, anisole cannot be nitrosated under the experimental conditions employed for resorcinol monomethyl ether; therefore, from the above electronic considerations, the 6-position in the latter compound should enjoy the preference, and this may even be augmented by the circumstance that the reagent itself in its polarised phase, $\overset{\ominus}{\mathrm{H}}\mathrm{O}\ \overset{\oplus}{\mathrm{N}}\mathrm{O}$, may tend to become attached to the charged phenolic hydroxyl group and so unduly be caused to favour nitrosation at the 6-position. The same argument holds for the case of nitration.

Alternatively, should the methoxyl group exercise an inductive electron-attraction (Ingold, *Ann. Reports*, 1928, **25**, 122), hydrogen in the 4-position would be deactivated to a certain extent (III), whereas ionisation of the phenolic group would not be repressed but rather promoted, and so hydrogen in the 6-position should again be preferentially more intensely activated.



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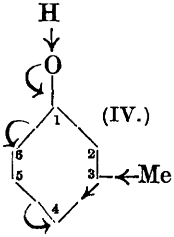

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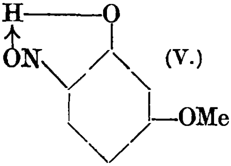

(V.)

In *m*-cresol (IV), however, the methyl group produces the general (inductive) effect of electron-repulsion, which is much stronger at the ortho- than at the para-position with respect to it (compare the nitration of toluene, where the ortho-para ratio is 58 : 38, and also the Reimer–Tiemann reaction with *m*-cresol; Hodgson and Jenkinson, this vol., p. 469) and in consequence hydrogen in the 4-position becomes more strongly activated than hydrogen in the 6-position. The only nitroso-compound produced by nitrosation of *m*-cresol is 4-nitroso-3-methylphenol (6-nitroso-*m*-cresol), in agreement with the above theoretical deduction; it is accompanied by a small amount of 6-nitro-3-methylphenol (4-nitro-*m*-cresol) (compare the nitrosation of *p*-chlorophenol, where the product is almost entirely 4-chloro-2-nitrophenol).

That 6-nitroso-3-methoxyphenol is moderately easily soluble in cold benzene, whereas, according to Henrich and Rhodius (*loc. cit.*), the 4-nitroso-isomeride is insoluble, might be anticipated from the probable co-ordination (V) of the *o*-nitroso- and the phenolic hydroxyl group (compare Sidgwick and Callow, J., 1924, **125**, 533, for similar co-ordination in *o*-chlorophenol; and Hodgson and Kershaw, this vol., p. 1555, for the stability of 3-chlorobenzoquinone-4-oxime).

EXPERIMENTAL.

The Nitrosation of Resorcinol Monomethyl Ether.—In addition to the process of Henrich and Rhodius (*loc. cit.*), the following method, which gives excellent results with phenol and its *m*-halogeno-derivatives, was used. Resorcinol monomethyl ether (5 g.), dissolved in water (450 c.c.) containing sodium hydroxide (2·5 g.) and sodium nitrite (7·5 g.), was treated below 0° during 30 minutes with dilute sulphuric acid (5 c.c. of concentrated acid in 100 c.c. of water). The mixture was kept over-night in the dark (compare Hodgson and Kershaw, *loc. cit.*), and the deposited product washed with water and dried in the dark. It appeared to be identical in composition with Henrich and Rhodius's product when examined by (1) its solubility in benzene and (2) oxidation to 6-nitro-3-methoxyphenol.

Oxidation of the Benzene-soluble Fraction with Dilute Nitric Acid.—The nitrosation product (3 g.) was suspended in water (35 c.c.) and vigorously stirred during the gradual addition of 27 c.c. of a mixture of concentrated nitric acid (3 parts) and water (1 part). The original yellow product turned light brown and nitrous fumes were evolved. After 12 hours, the mixture was steam-distilled; the 6-nitro-3-methoxyphenol (2·4 g.) that passed over crystallised from alcohol in small, pale yellow needles, m. p. and mixed m. p. 95° (Found: N, 8·4. Calc.: N, 8·3%).

Oxidation with alkaline potassium ferricyanide, although confirming the result, proved less satisfactory.

Oxidation of the Crude Nitrosation Mixture.—(a) *With nitric acid.* A fine suspension of the crude product (5 g.) in water (50 c.c.) was oxidised with dilute nitric acid (54 c.c.) as described above. The yield of steam-volatile 6-nitro-3-methoxyphenol was 3·5 g. From the results of the oxidation of the benzene-soluble product, this amount would account for almost the whole of the original crude mixture.

(b) *With hydrogen peroxide.* The crude nitrosation product (5 g.) was mixed with 30% hydrogen peroxide (15 c.c.), and a drop of 10% aqueous ferrous sulphate solution added; the mixture then became hot and turned olive-green. When the violence of the reaction had abated, 4 c.c. of 20% aqueous sodium hydroxide were added and the mixture was kept over-night, diluted with water to 150 c.c., heated to boiling, filtered, cooled, acidified, and steam-distilled, 2·9 g. of volatile 6-nitro-3-methoxyphenol being obtained

Nitration of Resorcinol Monomethyl Ether.—The ether (5 g.), dissolved in glacial acetic acid (5 g.), was nitrated below 0° by the gradual addition of nitric acid (5 g.; *d* 1·5) in glacial acetic acid (15 g.). The mixture, at first green and finally reddish-brown, was after an hour poured on ice; steam-distillation then removed 6-nitro-3-methoxyphenol, which crystallised from alcohol in small, pale yellow needles, m. p. 95° (Weselsky and Benedikt, *Sitzungsber. Akad. Wiss. Wien*, 1880, **82**, 1219, give m. p. 95°) (Found : N, 8·4. Calc. : N, 8·3%). The very small non-volatile residue of 4-nitro-3-methoxyphenol was extracted with ether and recrystallised from alcohol, giving yellow needles, m. p. 144° (Weselsky and Benedikt, *loc. cit.*, give m. p. 144°).

Proof of the Constitution of 6-*Nitro*-3-*methoxyphenol*.—(a) *Conversion into* 4-*nitroresorcinol dimethyl ether*. This was accomplished by heating the assumed 6-nitro-3-methoxyphenol (1·5 g.), dissolved in xylene (10 c.c.), with potassium carbonate (1·3 g.) and methyl sulphate (1·2 g.) at 140° for 8 hours. From the mixture, made alkaline with sodium hydroxide, steam-distillation removed 4-nitroresorcinol dimethyl ether (0·7 g.), which crystallised from alcohol in small white needles, m. p. 74° (Found : N, 7·8. Calc. : N, 7·65%), identical (mixed m. p.) with the product of the action of excess of methyl-alcoholic sodium methoxide on 1 : 3-dichloro-4-nitrobenzene (Hodgson and Handley, J., 1928, 163).

(b) *Preparation from* 3-*chloro*-4-*nitroanisole*. This substance (2·5 g.) was heated with concentrated aqueous ammonia (15 c.c.) in a sealed tube for 8 hours. The mixture was then acidified and steam-distilled to remove unchanged material (1·2 g.), and the non-volatile product was dissolved in dilute sulphuric acid and diazotised; decomposition by the standard procedure (Hodgson, E.P. 200,714) gave 6-nitro-3-methoxyphenol, which was isolated in steam.

Nitrosation of m-*Cresol*.—Obtained by the methods of Henrich and Rhodius (*loc. cit.*) and of Hodgson and Kershaw (*loc. cit.*), the nitrosation products of *m*-cresol gave in each case a small quantity of 6-nitro-3-methylphenol (4-nitro-*m*-cresol), volatile in steam, and non-volatile 4-nitroso-3-methylphenol (6-nitroso-*m*-cresol). The latter was oxidised entirely to 6-nitro-*m*-cresol, the absence of 4-nitro-*m*-cresol indicating the absence of 4-nitroso-*m*-cresol.

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