CXVIII.—*The Nitrosation of Phenols. Part VIII. Resorcinol Monoethyl Ether.*

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KIETAIBL (*Monatsh.*, 1898, **19**, 536) described two *o*-nitrosoresorcinol monoethyl ethers, but was unable to settle their constitutions. It has now been shown that in his nitrosation process 6-nitroso-3-ethoxyphenol alone is produced, for the product on oxidation gives only 6-nitro-3-ethoxyphenol: this compound has also been prepared from 4-nitro-3-aminophenetole, and both specimens give 4-nitroresorcinol diethyl ether on ethylation.

Only the 3-chlorine could be replaced by ethoxyl when an excess of ethyl-alcoholic sodium ethoxide reacted with 1 : 3-dichloro-4-nitrobenzene (see Hodgson and Handley, J., 1928, 163, for the replacement of both chlorine atoms by methoxy-groups): the 4-nitro-group renders the 3-carbon more positive than the 1-carbon atom by the general effect (Allan, Oxford, Robinson, and Smith, J., 1926, 401) and consequently the anionoid reagent $(\overset{\oplus}{\mathrm{Na}}\mathrm{O}\overset{\ominus}{\mathrm{Alk}})$ first replaces the 3-chlorine by the OAlk group; but since ethoxyl is much more strongly anionoid than methoxyl, its excess of "negativity" so diminishes the general (electron-attracting) effect of the nitro-group on the 1-carbon atom that the anionoid reagent is unable under ordinary conditions to displace the chlorine atom in position 1.

The explanation of the predominant ortho-nitrosation of resorcinol monoethyl ether is similar to that for the monomethyl ether (Hodgson and Clay, J., 1929, 2775, formula I with Et in place of Me). With the assumption there made regarding the partly ionised hydroxyl group, since ethoxyl has a greater repressive effect on ionisation than methoxyl, the activation of hydrogen in the 4-position should be relatively increased; moreover, the kationoid reagent in its polarised phase, $\overset{\ominus}{\mathrm{HO}}\overset{\oplus}{\mathrm{NO}}$, will have less tendency for attachment to the less highly charged phenolic hydroxyl group. On both counts the monoethyl ether should undergo nitrosation in the 4-position : this actually takes place to the extent of 10—15%. The same argument holds for nitration and is confirmed by the experimental results.

Alternatively, should the ethoxy-group exert an inductive electron-attraction, the 4-carbon (*loc. cit.*, formula III, with Et in place of Me) would be deactivated to a less extent in the ethoxy- than in the methoxy-compound, and so be relatively more reactive.

The solubility (1·32%) of 6-nitroso-3-ethoxyphenol in benzene is appreciably less than that (2·26%) of 6-nitroso-3-methoxyphenol, showing that the co-ordination (*loc. cit.*, formula V) of the *o*-nitroso- and the hydroxyl group is relatively weakened in the former compound. It would appear, therefore, that the increased repression of ionisation (see above) exceeds the concurrent increased activation of the chelating electrons of the nitroso-group.

EXPERIMENTAL.

The Nitrosation of Resorcinol Monoethyl Ether.—The method described by Hodgson and Clay (*loc. cit.*, p. 2777) for the nitrosation of resorcinol monomethyl ether, when applied to the monoethyl ether, gave a larger yield (5·5 g.) of crude product than that (4·7 g.) obtained by Kietaibl's method (*loc. cit.*). The quantities used were : resorcinol monoethyl ether 5 g., water 250 c.c., sodium hydroxide 2·5 g., sodium nitrite 3 g., concentrated sulphuric acid 5 c.c., water 100 c.c.

Separation of the isomerides. Kietaibl's method of extraction with boiling benzene was used, the operation being continued until the solvent remained practically colourless. From the extract, only one product could be crystallised, and this had the characteristics of Kietaibl's α-*o*-nitroso-3-ethoxyphenol as described by Henrich (*J. pr. Chem.*, 1904, **70**, 313) (Found : N, 8·5. Calc. : N, 8·4%).

The residue insoluble in benzene (0·79 g.) crystallised from alcohol (charcoal) in small yellow needles, which slowly decomposed above 170° (Found : N, 8·6%).

Oxidation of the Benzene-soluble Fraction with Dilute Nitric Acid.—The substance (1 g.) was suspended in water (10 c.c.) and vigorously stirred during the gradual addition of 10 c.c. of a mixture of nitric acid (*d* 1·4 ; 3 parts) and water (1 part). After 5 hours, the mixture was diluted with water and the product was collected and distilled with steam; the 6-nitro-3-ethoxyphenol (0·9 g.) that passed over crystallised from alcohol or light petroleum in yellow needles, m. p.

and mixed m. p. with an authentic specimen (see later) 79° (Found : N, 7·8. Calc. : N, 7·65%). Weselsky and Benedikt (*Sitzungsber. Akad. Wiss. Wien*, 1880, **82**, 1219) describe a steam-volatile mononitro-derivative of resorcinol monoethyl ether as sulphur-gold needles, m. p. 79°.

Oxidation of the Benzene-insoluble Fraction with Alkaline Potassium Ferricyanide.—The substance (0·5 g.), dissolved in 10% aqueous potassium hydroxide (30 c.c.), was mixed with a saturated aqueous solution of potassium ferricyanide (10 g.) and heated on the water-bath until the colour became yellow. The solution was then filtered hot, cooled, and acidified. After some time, long greenish-yellow needles of 4-nitro-3-ethoxyphenol separated. These, after recrystallisation from dilute alcohol, melted, alone or mixed with an authentic specimen, at 131° (Found : N, 7·9. Calc. : N, 7·65%). The respective dibrominated products, separately or mixed, melted at 69° (Found : Br, 46·7, 47·0. Calc. : Br, 46·9%). Weselsky and Benedikt (*loc. cit.*) give m. p. 69° for 2 : 6-dibromo-4-nitro-3-ethoxyphenol.

Oxidation of the Crude Nitrosation Mixture.—(a) *With alkaline potassium ferricyanide.* The crude product (5 g.) was dissolved in 10% aqueous potassium hydroxide (300 c.c.) and oxidised with a saturated aqueous solution of potassium ferricyanide (100 g.) as described above. The solution was filtered hot, cooled, acidified with dilute sulphuric acid, and extracted with ether. The extracted product was steam-distilled : 6-nitro-3-ethoxyphenol (3·0 g.) passed over ; the liquor in the flask, on cooling, deposited a substance (1·5 g.) from which 4-nitro-3-ethoxyphenol (0·9 g.) was obtained by crystallisation from alcohol (charcoal). From the results of the oxidation of the benzene-soluble fraction (above), these combined amounts would account for almost the whole of the original crude mixture, to the exclusion of any other *o*-nitrosophenol such as Kietaibl's so-called β-*o*-nitroso-3-ethoxyphenol.

Under the above conditions the crude nitrosation product (3·0 g.) from resorcinol monomethyl ether yielded no 4-nitro-3-methoxyphenol, but gave 2·5 g. of the steam-volatile 6-nitro-isomeride.

(b) *With dilute nitric acid.* The crude nitrosation product (5 g.), suspended in water (60 c.c.), was oxidised as described above with 54 c.c. of dilute nitric acid. The yield of steam-volatile 6-nitro-3-ethoxyphenol was 3·6 g. The non-volatile residue consisted of tarry matter, from which a small amount of the 4-nitro-isomeride was obtained by extraction with ether.

Nitration of Resorcinol Monoethyl Ether.—The following method gives a better yield of the mononitro-derivatives than the method of Weselsky and Benedikt (*loc. cit.*). The ether (5 g.), dissolved in acetic anhydride (20 c.c.), was nitrated below 0° by the gradual addition of nitric acid (*d* 1·5 ; 2 c.c.) in acetic anhydride (8 c.c.). The mixture was kept over-night and then poured on ice. The precipitate was collected, washed, and steam-distilled; the volatile 6-nitro-3-ethoxyphenol (2·0 g.) crystallised from light petroleum in greenish-yellow needles, m. p. 79° (Weselsky and Benedikt, *loc. cit.*, give m. p. 79°) (Found : N, 7·7. Calc. : N, 7·65%). The hot filtrate from the non-volatile tarry residue was cooled and extracted with ether, 0·5 g. of 4-nitro-3-ethoxyphenol being obtained which crystallised from alcohol in pale yellow needles, m. p. 131° (Weselsky and Benedikt, *loc. cit.*, give m. p. 131°) (Found : N, 7·75. Calc. : N, 7·65%).

Proof of the Constitution of 6-*Nitro*-3-*ethoxyphenol*.—(a) *Conversion into* 4-*nitroresorcinol diethyl ether*. The potassium salt (1·3 g.), suspended in absolute alcohol, was heated under reflux with excess of ethyl iodide for 6 hours. The mixture was then made alkaline and steam-distilled; the volatile 4-nitroresorcinol diethyl ether (0·4 g.) crystallised from alcohol in almost colourless leaflets which, alone or mixed with an authentic specimen (Kauffmann and de Pay, *Ber.*, 1906, **39**, 2725), melted at 85° (Found : N, 6·9. Calc. : N, 6·6%). The liquor in the distillation flask, on acidification and steam-distillation, yielded 0·4 g. of unchanged 6-nitro-3-ethoxyphenol.

An attempt was made to obtain 4-nitroresorcinol diethyl ether by the action of excess of ethyl-alcoholic sodium ethoxide on 1 : 3-dichloro-4-nitrobenzene (compare Hodgson and Handley, *loc. cit.*). The product, however, was 3-chloro-6-nitrophenetole, which crystallised from alcohol in colourless leaflets, m. p. 63° (Blanksma, *Rec. trav. chim.*, 1904, **23**, 322, gives m. p. 63°) (Found : Cl, 17·5. Calc. : Cl, 17·6%), identical with the product obtained from 3-chloro-6-nitrophenol by ethylation (compare Haworth and Lapworth, J., 1923, **123**, 2986).

The same method, applied to 3-chloro-2-nitrophenol (13 g.), gave 3-*chloro*-2-*nitrophenetole* (12 g.), which crystallised from alcohol in colourless leaflets, m. p. 52° (Found : Cl, 17·5. $C_8H_8O_3NCl$ requires Cl, 17·6%).

(b) *Synthesis from* 3-*chloro*-4-*nitrophenetole*. The ethylation of 3-chloro-4-nitrophenol as above gave 3-*chloro*-4-*nitrophenetole*, which crystallised from alcohol in colourless micro-prisms, m. p. 39—40° (Found : Cl, 17·4%). This was converted into 4-*nitro*-3-*aminophenetole* by heating it (2 g.) with concentrated aqueous ammonia (6 c.c.) and alcohol (5 c.c.) in a sealed tube at 170—180° for 8 hours. The product (1 g.), isolated from the reaction mixture after dilution with water, crystallised from alcohol in yellow needles,

m. p. 105—106° (Found: N, 15·5. Calc.: N, 15·4%), and was identical with a specimen prepared by the method of Reverdin and Lokietek (*Bull. Soc. chim.*, 1916, **19**, 252; *Arch. Sci. phys. nat.*, 1916, **42**, 47). The 4-nitro-3-aminophenetole (1 g.) was diazotised in dilute sulphuric acid and then converted by the standard procedure (Hodgson, E. P. 200714) into 6-nitro-3-ethoxyphenol (0·3 g.).

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