

CCXLIII.—*The Action of Nitrous Acid on Resorcinol Diethyl Ether.*

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THIS reaction, due to Aronheim (*Ber.*, 1879, **12**, 30), was repeated by Kraus (*Monatsh.*, 1892, **12**, 368), who obtained a nitrosoresorcinol monoethyl ether, which Kietaihl (*Monatsh.*, 1898, **19**, 536) believed to be 4-nitroso-3-ethoxyphenol, and a very unstable substance

which was thought to be a nitrosoresorcinol diethyl ether (see, however, below).

It has now been established that the reaction does not proceed in acetic acid alone, but that in the presence of hydrochloric or sulphuric acid, 4-nitroso-3-ethoxyphenol is formed in 80–90% yield. Moreover, 4-nitrosoresorcinol diethyl ether has been synthesised and found to be stable towards aqueous 5% potassium hydroxide and the usual organic solvents, although it is rapidly converted into 4-nitroso-3-ethoxyphenol by the above mineral acids. These properties indicate that nitrous acid first reacts with resorcinol diethyl ether to form the 4-nitroso-derivative, which is then decomposed by the mineral acids as above, the last reaction probably proceeding with much greater velocity than the nitrosation, since no 4-nitrosoresorcinol diethyl ether has been isolated. If de-ethylation to resorcinol monoethyl ether preceded nitrosation, then the main reaction product should have been 6-nitroso-3-ethoxyphenol (compare Hodgson and Clay, this vol., p. 963).

That mineral acids should preferentially attack the ethoxyl substituent para to the nitroso-group is indicated by Robinson (*Chem. and Ind.*, 1925, 456), since the electron-restraining effect ($-I$, Ingold and Shaw, J., 1927, 2918) is greater at the 3- than at the 1-carbon atom, whilst the electron-releasing ($+T$) effect will more readily reach the 1-carbon atom and thereby preferentially admit of the capture of the proton by the attached oxygen of the ethoxyl group. In this way an unstable oxonium salt will be formed at the 1-ethoxyl group whose subsequent decomposition is a de-ethylation.

It is noteworthy that resorcinol dimethyl ether and also its methyl ethyl ether cannot be nitrosated under the conditions employed for the diethyl ether, thereby indicating that the ethyl group has a greater activating influence than the methyl group, and supporting the view that nitrosation precedes de-ethylation. Also, in preparing the methyl ethyl ether, it has been found better to methylate resorcinol monoethyl ether by the usual procedure with methyl sulphate in caustic alkaline solution than to ethylate the mono-methyl ether by the corresponding reagents.

EXPERIMENTAL.

Preparation of Resorcinol Diethyl Ether.—Resorcinol (110 g.; 1 mol.), dissolved in 10% aqueous sodium hydroxide (400 c.c.), was treated gradually at 60–70° with ethyl sulphate (160 g.; 10% excess over 1 mol.), and heated on the water-bath with frequent shaking for 30 minutes longer; the mixture, which was in two layers, was saturated with sodium chloride, the upper oily layer

removed, and the lower layer twice extracted with ether, the oil resulting from the evaporation of the ether being added to the main portion. The oil was steam-distilled, the distillate saturated with salt, extracted with ether, and the extract shaken with successive portions (100 c.c. and 50 c.c.) of 10% aqueous sodium hydroxide, whereby resorcinol monoethyl ether, 25 g., b. p. 246—247° (Kietailb gives b. p. 246—247°), was removed. The ethereal solution was dried with calcium chloride and distilled; yield 15 g., b. p. 234—235° (Herzig and Zeisel, *Monatsh.*, 1890, **11**, 291, give b. p. 234.4—235.2°). When 2 mols. of ethyl sulphate were employed, the alkali-insoluble oil obtained always boiled over a range, but by the above procedure both the mono- and the di-ethyl resorcinol were obtained pure.

Nitrosation of Resorcinol Diethyl Ether.—This was first carried out according to the directions of Kraus (*loc. cit.*), whereby a solution of the ether (1 part) in glacial acetic acid (10 parts) was saturated with hydrogen chloride,* cooled to 0°, and treated with a large excess of a saturated aqueous solution of sodium nitrite. A dark green solid separated, and after 30 minutes the mixture was diluted with a large excess of water, the precipitated solid filtered off, and examined as follows:

(a) *By Kraus's procedure.* The crude product (8.7 g.) was triturated with ice-cold aqueous 5% potassium hydroxide solution (100 c.c.), in which the major portion immediately dissolved; the deep reddish-brown solution was filtered after being kept for 2 hours in the ice-chest, and the buff-coloured residue (1.6 g.) was washed with cold alcohol and dried in a vacuum; m. p. 119—120° (Kraus gives m. p. 122—123°). This residue gave the characteristic blue colours described by Kraus with hydrochloric and sulphuric acids, and was readily soluble in benzene, chloroform, and ether, but possessed a higher nitrogen and lower ethoxyl content than those recorded by Kraus [Found: N, 7.8; OEt (Zeisel), 25.47. Calc. for $C_6H_3ON(OEt)_2$: N, 7.2; OEt, 46.2%]. The filtrate, on acidification, afforded 7 g. of crude 4-nitroso-3-ethoxyphenol, identified by comparison with an authentic specimen (Hodgson and Clay, *loc. cit.*) and by oxidation with alkaline potassium ferricyanide to 4-nitro-3-ethoxyphenol.

(b) *By avoiding use of alkali.* The crude product after nitrosation was repeatedly extracted with cold benzene until no more dissolved. The insoluble residue (83.1%) was identified as 4-nitroso-3-ethoxyphenol (Found: in crude product, OEt, 26.1; in product recrystal-

* The use of 5 c.c. of concentrated sulphuric acid instead of hydrogen chloride gave similar results, but the substitution of acetic acid failed to effect nitrosation.

lised from alcohol, OEt, 26.8. Calc. : OEt, 26.94%) by comparison with an authentic specimen and by oxidation to 4-nitro-3-ethoxyphenol. The soluble portion (16.9%) was identical with the alkali-insoluble product (17.2%) in (a) above.

Preparation of 4-Nitrosoresorcinol Diethyl Ether.—6-Nitro-3-ethoxyphenol (14 g.) was converted into 4-nitrosoresorcinol diethyl ether (10 g.) by Haworth and Lapworth's procedure (J., 1923, 123, 2986) (ethyl sulphate, 15 c.c. added at the rate of 1 c.c. in 10 mins.; potassium carbonate, 12 g.; xylene, 90 c.c.) and this was reduced, either by tin and hydrochloric acid or by iron powder and dilute acetic acid to the 4-amino-compound. The hydrochloride of this (1.5 g., colourless needles, m. p. 198°; Will and Pukall, *Ber.*, 1887, 20, 1119, give m. p. 198°) was dissolved in water (150 c.c.), cooled to 0°, and the solution just rendered alkaline with aqueous sodium hydroxide and then faintly acid with acetic acid. Into this solution was rapidly stirred a solution obtained by dissolving potassium persulphate (4.2 g.) in concentrated sulphuric acid (5 c.c.), keeping it ice-cold for one hour, pouring it on ice (100 g.), neutralising it with potassium carbonate, and just acidifying it with acetic acid. A pale green solid separated almost immediately, and after it had been kept for 10 mins. at 0°, it was rapidly filtered off, washed with water (during which it quickly turned blue), and immediately steam-distilled. The 4-nitrosoresorcinol diethyl ether which passed over crystallised from light petroleum in pale-green needles, m. p. 104° (Found: N, 7.3. $C_{10}H_{13}O_3N$ requires N, 7.2%), which were readily soluble in acetic acid, alcohol, and benzene, but less soluble in light petroleum, giving stable green solutions. Cold aqueous hydrochloric and sulphuric acids convert this ether into 4-nitroso-3-ethoxyphenol, whereas cold aqueous 5% potassium hydroxide is without action upon it.

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