CCXCV.—*Nitrosation of Phenols. Part IV. 3 : 5-Dichlorophenol.*

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THE object of this investigation was to extend the work of Hodgson and Moore (J., 1923, **123**, 2499) on the nitrosation of 3-chlorophenol to the case of 3 : 5-dichlorophenol.

Blanksma (*Rec. trav. chim.*, 1908, **27**, 25) claimed to have obtained 3 : 5-dichloro-4-nitrosophenol as a by-product in the conversion of 3 : 5-dichloroaniline to the phenol, and Willstätter and Schudel (*Ber.*, 1918, **51**, 782) stated that it was obtained by the addition of sulphuric acid to an aqueous solution of the sodium salt of 3 : 5-dichlorophenol and sodium nitrite. These products, however, gave no Liebermann nitrosoamine reaction and proved to be identical with 3 : 5-*dichloro*-4-*nitrophenol*, prepared by direct nitration of 3 : 5-dichlorophenol. Willstätter and Schudel gave no analysis for chlorine, but recorded N, 6·95%, whereas the nitro- and nitroso-compounds require N, 6·7 and 7·3%, respectively.

After numerous unsuccessful attempts, both direct and indirect, to nitrosate 3 : 5-dichlorophenol, the required substance was obtained by the oxidation of 3 : 5-*dichloro*-4-*aminoanisole* with Caro's acid and subsequent hydrolysis of the 3 : 5-*dichloro*-4-*nitrosoanisole* by concentrated sulphuric acid.

3 : 5-Dichloro-4-nitrosoanisole is colourless, and, since 4-nitrosoanisole was described by Baeyer and Knorr (*Ber.*, 1902, **35**, 3035) as bluish-green, whilst 3-chloro-4-nitrosoanisole is now shown to be deep green, the suppression of colour may be ascribed to the chlorine atom in the 5-position.

A similar explanation would apply to the colourless 3 : 5-*dichloro*-4-*nitrosophenol*, which resembles the almost colourless 3-chlorobenzoquinone-4-oxime (Hodgson and Moore, *loc. cit.*), and may better be formulated as 3 : 5-dichlorobenzoquinone-4-oxime. Kehrmann's 2 : 6-dichlorobenzoquinone-4-oxime (*Ber.*, 1888, **21**, 3318) is light yellow and decomposes at 140°, whereas its colourless 3 : 5-isomeride decomposes at 165°.

Since 3-iodophenol on nitrosation behaves differently from 3-chloro- and 3-bromo-phenols (Hodgson and Moore, 1925, **127**, 2260), the direct nitrosation of 3-chloro-5-iodophenol was attempted, but without success.

During the attempts at nitrosation, it was found that nitrous acid nitrated 3 : 5-dichlorodimethylaniline in formic acid solution (the usual procedure was fruitless); the 3 : 5-dichloro-grouping has, therefore, the same effect as in 3 : 5-dichlorophenol, which is also nitrated by nitrous acid.

EXPERIMENTAL.

The initial material, 3 : 5-dichlorophenol, was prepared from trinitrobenzene (Hodgson and Wignall, J., 1926, 2077) and also by the following modification of Willstätter and Schudel's method (*loc. cit.*) : 3 : 5-Dichloroaniline (26 g.) was dissolved in 220 c.c. of hot dilute sulphuric acid (2 : 9 by vol.), the mixture cooled, and diazotised at room temperature. Excess of nitrous acid was removed by carbamide (otherwise 3 : 5-dichloro-4-nitrophenol may be formed), and the mixture added gradually to a boiling solution of sulphuric acid (100 g.) in water (140 c.c.) through which steam was passing. The aqueous distillate was made alkaline, evaporated to very small bulk, cooled, and the 3 : 5-dichlorophenol (19·5 g.)

precipitated by careful addition of 30% sulphuric acid with vigorous stirring.

3 : 5-Dichlorophenol (16 g.) was nitrated in a solution of sodium nitrate (12 g.) in water (180 c.c.) at 90—100° by the gradual addition of 48 c.c. of dilute sulphuric acid (1 : 5) during 1 hour; the mixture was then heated on the water-bath for 2 hours and steam-distilled, 3 : 5-*dichloro*-2-*nitrophenol* (5 g.) passing over, and 3 : 5-*dichloro*-4-*nitrophenol* (6 g.) being obtained from the tarry residue by repeated extraction with hot dilute hydrochloric acid.

3 : 5-Dichloro-2-nitrophenol is moderately soluble in water and readily soluble in the usual organic solvents except light petroleum, from which it crystallises in lemon-yellow needles, m. p. 51° (Found : N, 6·5; Cl, 34·0. $C_6H_3O_3NCl_2$ requires N, 6·7; Cl, 34·1%); it does not form a hydrate (compare 3-chloro-2-nitrophenol, Hodgson and Moore, J., 1926, 155), and remains unchanged when kept for 2 hours at 110°. A solid acetate could not be obtained.

3 : 5-Dichloro-4-nitrophenol is readily soluble in the usual organic solvents except light petroleum, and crystallises from water in very pale yellow needles, m. p. 150° (Found : N, 6·7; Cl, 34·1%). The *acetate*, formed when a solution of the phenol in glacial acetic acid is warmed with acetyl chloride, crystallises from dilute alcohol in colourless needles, m. p. 99° (Found : Cl, 28·2. $C_8H_5O_4NCl_2$ requires Cl, 28·4%).

Action of Nitrous Acid on 3 : 5-*Dichlorophenol.*—This was carried out according to the directions both of Blanksma (*loc. cit.*) and of Willstätter and Schudel (*loc. cit.*). In each case a product of m. p. 150° [Found : N, (i) 6·8, (ii) 6·7; Cl, (i) 34·1, (ii) 34·2. Calc. for $C_6H_3O_3NCl_2$: N, 6·7; Cl, 34·3; calc. for $C_6H_3O_2NCl_2$: N, 7·3; Cl, 37·0%] was obtained, which was identical (mixed m. p. determination) with the 3 : 5-dichloro-4-nitrophenol above; the corresponding acetates were similarly shown to be identical.

Reduction of the 3 : 5-*Dichloro*-2- *and* -4-*nitrophenols.*—3 : 5-Dichloro-2- and -4-nitrophenols are reduced to the corresponding amino-phenols by dissolving them in 12 times their weight of water containing the theoretical amount of sodium carbonate and warming the solution on the water-bath with solid sodium hyposulphite until colourless. 3 : 5-*Dichloro*-2-*aminophenol* separates from the hot solution, but in the case of the 4-*amino*-isomeride the solution has to be cooled. 3 : 5-Dichloro-2-aminophenol is readily soluble in the usual organic solvents, except light petroleum, and crystallises from water in colourless needles, m. p. 132° (Found : Cl, 39·7. $C_6H_5ONCl_2$ requires Cl, 39·9%), which darken somewhat on keeping. Its aqueous solutions give a reddish-brown precipitate with ferric chloride. 3 : 5-Dichloro-4-aminophenol is less soluble in chloroform, carbon tetrachloride, and carbon disulphide than its 2-amino-isomeride, but more soluble in water, from which it crystallises in colourless needles, m. p. 154° (Found : Cl, 39·8%). Its aqueous solutions give a violet coloration with ferric chloride.

3 : 5-*Dichloro*-2- and -4-*nitroanisoles* are prepared by boiling for 6 hours a mixture of the appropriate nitrophenol (6 g.) with xylene (60 c.c.) and potassium carbonate (12 g.) to which methyl sulphate (12 c.c.) is gradually added. After removal of the xylene, the anisoles can be obtained pure by steam-distillation. Yield, 70% in each case. 3 : 5-Dichloro-2-nitroanisole is much more volatile in steam than its 4-nitro-isomeride, and crystallises from methyl alcohol in colourless needles, m. p. 75° (Found : Cl, 31·7. $C_7H_5O_3NCl_2$ requires Cl, 32·0%). 3 : 5-Dichloro-4-nitroanisole crystallises from methyl alcohol in colourless needles, m. p. 70° (Found : Cl, 31·9%).

3 : 5-*Dichloro*-4-*aminoanisole* is prepared by reduction of the nitro-anisole (4·2 g.) with tin (3·5 g.) and concentrated hydrochloric acid (40 c.c.), and is finally removed by steam-distillation, being much more volatile than the parent nitro-anisole. It is very soluble in methyl alcohol and carbon tetrachloride, moderately soluble in light petroleum, and only slightly soluble in water or dilute acids; it crystallises from dilute methyl alcohol in colourless needles, m. p. 71° (Found : Cl, 36·7. $C_7H_7ONCl_2$ requires Cl, 37·0%).

3 : 5-*Dichloro*-4-*nitrosoanisole* was obtained by oxidation of the amino-anisole with Caro's acid as follows : Potassium persulphate (16 g.) was stirred into concentrated sulphuric acid (32 g.), kept at room temperature for 1 hour, then poured on ice and neutralised with potassium carbonate, the final volume being about 250 c.c. The mixture was rendered faintly acidic with acetic acid, added with stirring to a cold suspension of finely-divided 3 : 5-dichloro-4-amino-anisole (2·5 g.) in 200 c.c. of water, and kept for 24 hours, the stirring being maintained for the first 6 hours; the solid product was filtered off, and unchanged amine removed from it by extraction with warm very dilute hydrochloric acid. The crude product (1·5 g.; m. p. 122°) was crystallised from carbon tetrachloride and then from methyl alcohol; colourless needles, m. p. 125° (Found : Cl, 34·23. $C_7H_5O_2NCl_2$ requires Cl, 34·46%). The nitroso-anisole turns green on melting but becomes colourless again on solidifying, and is readily soluble in chloroform and acetone, but more sparingly soluble in carbon tetrachloride, benzene, and methyl alcohol, forming green solutions; it is insoluble in light petroleum and gives the Liebermann nitrosoamine reaction.

3 : 5-*Dichloro*-4-*nitrosophenol* [-*quinone*-4-*oxime*(?)] is obtained by heating 3 : 5-dichloro-4-nitrosoanisole (1 g.) with concentrated

sulphuric acid (10 c.c.) on the water-bath for ½ hour—longer periods produce charring. An odour of quinone is noticeable during the hydrolysis. On pouring the mixture on ice, a colourless solid separates, which completely dissolves in alkalis to a green solution. The product gives the Liebermann nitrosoamine reaction, is soluble in methyl alcohol, ether, acetone, and glacial acetic acid, sparingly soluble in water, benzene, nitrobenzene, and chloroform, and insoluble in light petroleum and carbon disulphide. It separates from dilute acetic acid in colourless leaflets, which turn light brown on exposure and decompose at 165° (Found : N, 7·4; Cl, 36·9. $C_6H_3O_2NCl_2$ requires N, 7·3; Cl, 37·0%). No change appears to be effected by alkalis but decomposition takes place with boiling acids.

Among the unsuccessful attempts to prepare the foregoing nitrosophenol may be mentioned the use of : (1) Aqueous solutions of the sodium salt of 3 : 5-dichlorophenol and sodium nitrite, which gave only the 4-nitrophenol on acidification under a variety of conditions; (2) formic and acetic acid solutions; (3) amyl nitrite (compare Henrich and Rodins, *Ber.*, 1902, **35**, 4192); (4) nitrosylsulphuric acid; (5) nitrous gases and an ethereal solution of 3 : 5-dichlorophenol. The materials used as the starting-point of indirect methods included (1) 3 : 5-dichlorodimethylaniline; (2) 3 : 5-dichloro-4-aminophenol (oxidation by Caro's acid; also diazotisation, followed by oxidation with ferricyanide).

An Example of Simultaneous Reduction and Chlorination.—Reduction of 3-chloro-4-nitroanisole (6 g.) with tin (6 g.) and concentrated hydrochloric acid (50 c.c.) gave 2·5 g. of 3 : 5-dichloro-4-aminoanisole. Iron and acetic acid, or tin and dilute hydrochloric acid, however, effected normal reduction to 3-chloro-4-aminoanisole (compare Hodgson and Handley, J., 1926, 542).

3-*Chloro*-4-*nitrosoanisole* is obtained when 3-chloro-4-aminoanisole hydrochloride (3·5 g.), dissolved in water (300 c.c.), is treated with sodium hydroxide (0·7 g.) then rendered faintly acidic with acetic acid, and oxidised by potassium persulphate (20 g.) as above. The product is almost insoluble in light petroleum, but readily dissolves in the usual organic solvents, forming green solutions; from methyl alcohol it crystallises in deep green needles, m. p. 59° (Found : Cl, 20·4. $C_7H_6O_2NCl$ requires Cl, 20·7%), which give the Liebermann nitrosoamine reaction.

Action of Nitrous Acid on 3 : 5-*Dichlorodimethylaniline.*—3 : 5-Dichlorodimethylaniline was best prepared by heating 3 : 5-dichloroaniline (8 g.), methyl sulphate (12 c.c.), and methyl alcohol (15 c.c.) for 5 hours in a sealed tube at 165—170° (great pressure is developed). The viscous red product was poured into water (100 c.c.) and kept for 1 hour until solid. Yield 4 g. It crystallises from dilute methyl alcohol (charcoal) in colourless, rhombic plates, m. p. 55° (Found: Cl, 37·3. Calc.: Cl, 37·4%), which are readily soluble in the usual organic solvents.

Attempts to nitrosate this compound by the usual methods having proved fruitless, the following method was attempted: 3 : 5-Dichlorodimethylaniline (3·8 g.), dissolved in formic acid (15 c.c.), was treated at 0° with finely powdered sodium nitrite (1·4 g.). The brown needles which first formed rapidly became resinous, and, after separation, the product was extracted with a mixture of equal parts of alcohol and acetic acid and then recrystallised from methyl alcohol; golden needles, m. p. 142° (Found: Cl, 30·1.

$$C_6H_2NMe_2Cl_2{\cdot}NO_2$$

requires Cl, 30·2; $C_6H_2NMe_2Cl_2{\cdot}NO$ requires Cl, 32·4%). This product is readily soluble in acetic acid but sparingly soluble in methyl alcohol.

Nitration of 3 : 5-*Dichlorodimethylaniline.*—To 3 g. of the dichlorodimethylaniline in concentrated sulphuric acid (12 c.c.) at 0°, nitric acid (1 c.c.; 91%) was gradually added during 1 hour. The mixture was kept for a further hour at 0°, then poured on ice, and the resulting solid was filtered off, washed with cold alcohol, and crystallised from methyl alcohol; golden needles, m. p. 142° (Found: Cl, 30·3%). This product, 3 : 5-*dichloro*-4-*nitrodimethylaniline*, was identical with the preceding substance (mixed m. p. determination), thereby establishing the fact that 3 : 5-dichlorodimethylaniline is nitrated by nitrous acid in formic acid solution.

3 : 5-Dichloro-4-nitro-dimethylaniline is not decomposed on boiling with aqueous alkaline hydroxides.

The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.

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